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NOTES ON SOME FATTY OILS.*

By So Uchida.

PARA RUBBER TREE SEED OIL.

The oil is obtained from the seed of *Hevea braziliensis*. One liter of seed obtained from Singapore weighed on an average 364.1 grams. The kernel, which constitutes about 51.0 per cent. of the seed, contains 52.19 per cent. of oil and 6.01 per cent. of water. When the kernel was pressed with a screw press, it furnished the following result: Kernel, 1,825 grams. First oil (cold drawn), 554 grams. Second oil (hot drawn), 46 grams. Total amount of oil, 600 grams. Percentage of oil obtained to the kernel, 32.88 per cent. The yield of oil obtained by pressing is poor.

The oil is a pale yellow liquid having an odor resembling that of linseed oil. In the winter months, it deposits a considerable amount of "stearine." With one drop of concentrated sulphuric acid, the oil assumes a reddish brown color and after stirring it turns to brown. With nitric acid of specific gravity 1.3, it assumes a yellow color. When the oil is heated in a thin layer at 100° C. for 6 hours it dries to a soft film; on continuing the heating for 7 hours more the film remains soft. In the elaidin test no solidification is observed even after 48 hours' standing. The oil needs hardly any rectification, but to decolorize it completely it is best to filter it over 10 per cent. of its weight of Kambara earth or to shake it first with dilute sulphuric acid, followed by filtration over 5 per cent. of its weight of Kambara earth. It is a drying oil but exhibits weak drying power and in its general properties it resembles Inukaya seed oil. It can be used for the manufacture of paints, varnishes, boiled oil, and oilcloth, as well as for soap-making.

The physical and chemical constants of this and the other oils are given in the tables which follow.

SHIROMOJI SEED OIL.

The oil is obtained from the seed of *Lindera triloba* BL., a plant belonging to the family of *Lauracea*. One liter of seeds obtained from Nagano prefecture weighed on an average 378.9

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* *J. S. C. I.* Nov. 15, 1916, pp. 1089–93.

grams. The yellow kernel, which is found in the grayish brown husk, constitutes about 68.1 per cent. of the seed and contains 57.69 per cent. of oil and 3.34 per cent. of water. When the powdered kernel was pressed in a screw press, the following result was obtained: Kernel, 3,505 grams. First oil (cold drawn), 1,034 grams. Second oil (hot drawn), 329 grams. Third oil (hot drawn), 223 grams. Total amount of oil 1,586 grams. Percentage of oil obtained from the kernel, 45.26 per cent. Thus one hectoliter of the seed will yield 10.9 kilos. of oil by pressing.

The oil is a pale yellow liquid at the ordinary temperature but solidifies in winter months to a hard white mass. It is odorless and has a pleasant taste. When one drop of concentrated sulphuric acid is added it assumes an orange color. On being shaken with nitric acid of specific gravity 1.3, it assumes a yellow color. It yields no solid product in the elaidin test. The oil is non-drying and has the highest saponification value of all known natural oils. Its high saponification value as well as its low Hehner value indicates the presence of a considerable amount of lower fatty acids, while its low iodine value indicates that the oil is low in unsaturated fatty acids. The content of volatile fatty acids is small as judged from its low Reichert-Meissl value. The oil probably consists chiefly of laurin (saponification value 263.8). The cold-drawn oil is pale yellow, but the hot-drawn oil is somewhat darker. It can best be decolorized by filtering over 10 per cent. of its weight of natural absorbent earth or by shaking it first with dilute sulphuric acid, followed by filtration over 5 per cent. of its weight of natural absorbent earth. The oil is best suited for soap-making.

CALLOPHYLLUM OIL.

Callophyllum oil is obtained from the seed of *Callophyllum inophyllum* L., a tree indigenous to Eastern Africa and Southern Asia. In Japan it grows in Formosa, in the Loochoo Islands, and in the Ogasawara Islands. The green nut is 2.5 to 3.0 cm. in diameter and becomes yellow on ripening. The round, pale yellow kernel which is found in a hard, thick wall is about 1.3 cm. in diameter and constitutes about 33 per cent. of the seed. One liter of the air-dried seed obtained from the Ogasawara Islands weighed on an average 400 grams.

The kernel, separated from the husk, was dried in the sun, crushed, steamed, and pressed with a screw press, when it gave the following result: Kernel, 955 grams. First oil (hot drawn), 264 grams. Second oil (hot drawn), 44 grams. Third oil (hot drawn), 15 grams. Total, 323 grams. Percentage of oil pressed from the kernel, 33.83 per cent. Hence one hectoliter of the seed will yield 4,444 grams of oil.

The oil thus obtained is a dark green, viscous liquid having a peculiar odor and contains a quantity of resin. In winter months it deposits "stearine" and becomes semi-solid. With one drop of concentrated sulphuric acid, the oil becomes reddish brown. On being shaken with nitric acid of specific gravity 1.3, the oil assumes a brownish-red color. In the elaidin test, it becomes a buttery mass after 2 hours. The dark green color can be removed by shaking with dilute sulphuric acid but not with dilute sodium carbonate solution. It can be used for soap-making and also as an illuminant, but is unfit for edible purposes owing to its poisonous nature, especially when not rectified. It is a semi-drying oil and its high acid value is chiefly due to the presence of a considerable amount of resin.

The physical and chemical constants of the oil from Ogasawara Islands are given in the tables.

HERNANDIA SEED OIL.

The oil is obtained from the seed of *Hernandia peltata* Meisn., a tree indigenous to Eastern Africa and Southern Asia. The nut is round and green, but when it ripens a part of it becomes reddish. The flesh of the nut is thin, while the kernel wall is thick; the kernel constitutes about 57 per cent. of the seed. A sample of oil was forwarded in 1914 from the Office of the Ogasawara Islands. The yield of oil by pressing was reported to be as follows, the press used being a primitive one: Kernel, 26,250 grams. First oil (hot drawn), 6,832 grams. Second oil (hot drawn), 2,063 grams. Total amount of oil, 8,895 grams. Percentage of oil obtained from the kernel, 33.89 per cent.

The oil is a reddish brown liquid and has a characteristic odor. It deposits "stearine" in winter months. With one drop of concentrated sulphuric acid, it becomes reddish brown. With nitric acid of specific gravity 1.4, it assumes a red color. When it is heated in a thin layer at 100° C. for 6 hours it dries to a soft film, which remains soft and brittle after heating for a further 7 hours. The oil can best be rectified by shaking with dilute sulphuric acid or by treating with 4 per cent. of its weight of 50 per cent. solution of caustic alkali. It is a drying oil but its drying properties are rather weak, and the amount of free acid is considerable, as the acid value indicates. It can be used for the manufacture of soaps, boiled oil, and rubber substitute, and also for illuminating purposes.

HAKUUNBOKU SEED OIL.

The oil is obtained from the seed of *Styrax obassia* S et Z. The seed, which ripens in September, is much like an acorn in shape and is about 1 cm. long. One liter of the seed (without cups) weighs 500 grams on an average. The pale yellow kernel, found in the brown hard husk, constitutes about 48.6 per cent. of the seed, and contains 43.71 per cent. of oil and 5.45 per cent. of water. The seed separated from the husks was crushed and expressed first cold and then hot, when it furnished the following figures: Kernel, 1,518 grams. First oil (cold drawn), 434 grams. Second oil (hot drawn), 29 grams. Total oil, 463 grams. Percentage of oil on kernel, 30.51 per cent. Thus, one hectoliter of the seed will yield 7,491 grams of oil.

The cold drawn oil is a pale brownish yellow liquid and remains liquid even in winter months, but the second hot expressed oil is darker in color and deposits "stearine" on long standing at the ordinary temperature. With one drop of concentrated sulphuric acid, the oil becomes brownish red and on stirring becomes brown. When shaken with nitric acid of specific gravity 1.3, it turns greenish red. In the elaidin test, no solidification is observed after 5 hours; at the end of 72 hours only a small deposit of buttery consistency is deposited. When heated at 100° C. in a thin layer for 14 hours, it becomes more viscous but does not dry. It can be rectified by filtering over 10 per cent. of its weight of natural absorbent earth or by treating with 2 per cent. of its weight of caustic alkali as a 50 per cent. solution. It is a semidrying oil and its high Reichert-Meissl value indicates the presence of a considerable amount of volatile fatty acids such as butyric acid. In general properties it closely resembles Yego (*Styrax japonica*) seed oil.

AKEBIA SEED OIL.

The oil is obtained from the seed of *Akebia quinata*, Dcne., a climbing shrub indigenous to Japan. The fruit, which is the same size and shape as an European pear, is at first green but becomes partly reddish on ripening. It contain numerous black seeds 0.5 cm. long. One liter of the air-dried seed weighs 600 grams on the average. The seed being small it was very difficult to separate the kernel from its shell, so the whole seed was crushed and subsequently pressed with a screw press first cold and then hot. The result was as follows: Seed, 5,388 grams. First oil (cold drawn), 721 grams. Second and third oils (hot drawn), 232 grams. Total 953 grams. Percentage of oil obtained to the seed, 17.69 per cent. Hence one hectoliter of the seed will yield about 10,609 grams of oil.

The oil is a pale yellowish brown liquid having a characteristic odor and deposits a considerable amount of "stearine" in winter months; the second and the third oils almost solidify at 12-13° C. With one drop of concentrated sulphuric acid the oil assumes a greenish yellow color, and on stirring a cochineal red color. On being shaken with nitric acid, specific gravity 1.3, it assumes a yellow color with reddish tints. In the elaidin test, it gives a very soft buttery mass after five hours, the consistency remaining the same even after 72 hours.

This oil is non-drying and its most prominent characteristic is its extraordinary high Reichert-Meissl value—the highest of any vegetable fatty oil. It also has a high acid value. Thus it contains a considerable amount of lower volatile fatty acids such as butyric acid. The oil can be decolorized by filtering over 10 per cent. of its weight of Kambara earth or by shaking with dilute sulphuric acid. It can be utilized for the preparation of soap and Turkey red oil as well as for edible and burning purposes.

KUROMIJI SEED OIL.

The oil is obtained from the seed of *Lindera serica* BL, a small tree belonging to the family of *Lauracea*. The seed is round, 0.5-

0.7 cm. in diameter, and one liter of the seed weighs about 492 grams on an average. The yellow kernel, which is found in a black brown husk, constitutes about 63.3 per cent. of the seed and contains 69.60 per cent. of oil and 3.25 per cent. of water. The kernel roughly separated from the husks—the complete separation is very difficult—was crushed, then steamed and subsequently pressed with a screw press while still warm; 905 grams of kernels yielded 340 grams of first oil (hot drawn), 165 grams of second oil (hot drawn), and 20 grams of third oil (hot drawn). Total amount of oil, 525 grams. Percentage, 58.02 per cent. One hectoliter of seed will thus yield about 18,045 grams of oil.

The oil is a yellowish brown liquid having an aromatic odor, and does not solidify even in winter. When one drop of concentrated sulphuric acid is added to 20 drops of oil placed on a white porcelain plate, it assumes an orange-brown color. With nitric of specific gravity 1.3, the oil becomes yellowish red. In the elaidin test it remains liquid even after 48 hours' standing; only a small deposit of buttery consistency was found. It is non-drying and its high saponification value as well as its low Hehner value indicates the presence of a considerable quantity of the lower fatty acids, while its low iodine value indicates that the content of unsaturated fatty acids is low. Again the content of volatile acids is low as indicated by its low Reichert-Meissl value. Complete decoloration of the oil is difficult, but when it is treated with 1 per cent. of caustic alkali as a 50 per cent. solution and then filtered over 10 per cent. of its weight of Kambara earth, it is fairly well decolorized. The oil can best find application in soap-making.

ABURACHAN SEED OIL.

The oil is obtained from the seed of *Lindera praecox,* a tree belonging to the family of *Lauracea,* growing in Shikoku, Kyushu, and Honshu, Japan. The seed is round, 1.0-1.3 cm. in diameter, and contains a pale yellow kernel in a reddish brown husk. One liter of the air-dried seed obtained from Nagano prefecture weighs on an average 432.3 grams. The kernel, constituting 80.7 per cent. of the seed, contains 29.44 per cent. of oil and 7.35 per cent. of water. The oil was prepared by steaming and pressing the powdered kernel. The result was as follows: Kernel, 6,348 grams. First oil (hot drawn), 790 grams. Second oil (hot drawn), 161 grams. Third oil (hot drawn), 150 grams. Fourth oil (hot drawn), 52 grams. Total, 1,153 grams = 18.17 per cent. of the kernel. Hence one hectoliter of the seed will yield about 6,341 grams of oil by pressing.

The oil is a dark brown liquid possessing a somewhat aromatic odor. It solidifies in winter. When one drop of concentrated sulphuric acid is added to 20 drops of oil a brownish red liquid is produced. With nitric acid, specific gravity 1.3, it becomes red. In the elaidin test, it remains liquid even after 72 hours, at the end of which time only a minute quantity of buttery consistency is formed. This oil is non-drying and its saponification value exceeds that of cocoanut oil, indicating the presence of a large amount of lower fatty acids. The amount of volatile fatty acids is small as shown by its low Reichert-Meissl value.

The oil can best be purified by filtering over 10 per cent. of its weight of Kambara earth or by shaking with dilute sulphuric acid.

The physical and chemical constants of the hot drawn oil from Shinano province seeds are given in the tables.

MAGNOLIA FRUIT OIL.

The oil is obtained from the fruit of *Magnolia hypoleuca* S. et Z., a large tree growing in Shikoku, Kyushu, and Honshu, Japan. The fruit is red, ellipsoidal, and 1.0-1.3 cm. long. The pale yellow flesh is thick and rich in oil. The black kernel is 0.7-0.9 cm. long and has very thick and hard walls. One liter of the fruit weighs 637 grams on an average. The flesh and the kernel (kernel wall and kernel) are in the ratio of 45 : 55. The kernel separated from its wall contains 59.60 per cent. of oil and 4.69 per cent. of water. The fruit of *Magnolia hypoleuca,* without separating its seed and flesh, was crushed and pressed with a screw press, when 4,055 grams of the fruit yielded 1,270 grams of first oil (cold drawn), 217 grams of second oil (hot drawn), and 74 grams of third oil (hot drawn); total 1,561 grams = 31.51 per cent. One hectoliter of the seed will thus yield about 20.6 kilos. of oil.

The oil thus obtained is dark brown with purple tints, and is very difficult to decolorize. It is viscous and deposits a considerable amount of "stearine" even at the ordinary temperature on long standing. Twenty drops of the oil placed on a white porcelain plate and treated with one drop of concentrated sulphuric acid, assumes a greenish yellow color which on stirring turns to greenish brown. On shaking with nitric acid of specific gravity 1.3 it becomes a reddish brown color. In the elaidin test it deposits a considerable amount of a buttery mass after 5 hours' standing, and after 48 hours the whole mass becomes soft and of buttery consistency. When heated to 100° C. in a thin layer for 14 hours it becomes more viscous but does not dry. It is semi-drying and its somewhat high acid value indicates the presence of free acid in considerable quantity. The oil can be used for soap-making and also as a burning oil.

MAGNOLIA FLESH OIL.

The flesh of the magnolia fruit was separated and pressed with a screw press. 1,480 grams yielded 394 grams of first oil (cold drawn); 129 grams of second and third oil (hot drawn). Total, 523 grams = 35.34 per cent.

The oil is dark brown and deposits a large amount of "stearine" in winter months and becomes viscous. The color can easily be removed by treating first with 2 per cent. of caustic alkali as 50 per cent. solution, followed by the filtration over 10 per cent. of Kambara earth.

The oil gives a green coloration with concentrated sulphuric acid and a yellow color with nitric acid of specific gravity 1.3. In the elaidin test it becomes turbid after 5 hours and then separates into two layers, liquid and solid; finally at the end of 72 hours the whole mass becomes buttery. When heated in a thin layer at 100° C. for 14 hours it shows no tendency to dry. It contains a considerable amount of free acid, and can be used as the raw material for soap and rubber substitute, but as it is very difficult to separate the flesh and the kernel, it is not likely to be of any technical importance.

MAGNOLIA SEED OIL.

As the wall of the kernel is very thick and hard, the seed was crushed whole, sifted with a winnowing basket to separate any coarse wall pieces, and subsequently steamed and pressed with a screw press. The yield of the oil was very poor as it was absorbed by the pieces of kernel wall. 3,180 grams of seed yielded 246 grams of oil or 7.74 per cent.

The oil is a dark brown liquid and is exceedingly difficult to decolorize. It does not solidify even in winter months. Treated with nitric acid it becomes reddish brown. In the elaidin test, no solidification is observed after two hours; at the end of 72 hours a small deposit of buttery consistency is formed. When it is spread in a thin layer and heated at 100° C., it dries after 11 hours. It is a non-drying oil but exhibits weak drying properties. It can be used for the manufacture of soap and boiled oil, but as it is not profitable to press the oil separately from the flesh and the seed it is not likely to acquire any technical importance.

TEA SEED OIL.

This oil is obtained from the seed of the ordinary tea plant, *Thea chinensis*, a shrub largely cultivated in the provinces of Musashi, Suruga, Ise, Yamashiro, and Omi for the manufacture of tea; it also grows wild extensively in Shikoku and Kyushu. In some parts of these districts, the tea plant grows abundantly as undergrowth of the forest. The seed is round, about 1 cm. in diameter, and contains a yellowish white kernel in a blackish brown husk. One liter of the air-dried seed of wild tea plant obtained from Tosa province weighed 380 grams on the average. The kernel, which constitutes 65.3 per cent. of the seed, contains 27.62 per cent. of oil and 10.25 per cent. of water. The kernel was ground to a coarse meal, then steamed and subsequently pressed while still warm with a screw press. 3,384 grams of the kernels yielded 498 grams of first oil (hot drawn), 102 grams of second oil (hot drawn), and 14 grams of third oil (hot drawn). Total, 612 grams, or 18.09 per cent. of the weight of the kernel. One hectoliter of the seed will hence yield about 4,488 grams of oil by pressing.

The oil is a pale brown liquid having a peculiar odor, and deposits a large amount of "stearine" in winter. With concentrated sulphuric acid an indigo blue coloration is produced which becomes greenish brown on stirring. On shaking with nitric acid, specific gravity 1.3, a pale blue color is produced. In the elaidin

PHYSICAL AND CHEMICAL CONSTANTS OF OILS.

Kind of oil (from seeds, except as noted.)	Specific gravity, 15° C.	Refractive index, 27° C.	Butyro-refractometer reading, 27° C.	Acid value	Saponification value	Iodine value, Hübl's method	Ester value	Reichert-Meissl value	Hehner value
Para rubber tree..	0.9239	1.4720[5]	69.5[5]	4.21	191.9	130.80	187.7	0.30	95.37
Shiromoji	0.9361	1.4732[4]	40.2[4]	0.63	282.0	11.68	281.4	2.03	85.72
Callophyllum	0.9452	1.4792[2]	81.6[2]	45.95	194.1	95.49	148.1	0.38	93.61
Hernandia	0.9380	1.4773[3]	78.3[3]	7.39	195.7	126.10	188.3	1.77	93.17
Hakuunboku	0.9610	1.4892	99.5	1.73	181.8	115.40	180.1	16.45	92.94
Akebia	0.9340	1.4614[3]	53.2[3]	25.45	246.4	78.38	221.0	39.76	85.80
Kuromoji	0.9401[1]	1.4680	63.2	18.78	255.6	65.29	236.8	2.53	86.22
Aburachan	0.9348	1.4550	43.6	2.60	273.6	20.53	271.0	1.39	89.21
Magnolia	0.9288	1.4754	75.0	6.69	207.4	124.50	250.7	0.17	96.54
Magnolia (fruit)..	0.9315	1.4739[2]	72.5[2]	13.43	224.4	109.20	211.0	4.93	93.11
Magnolia (flesh)..	0.9239	1.4693	65.3	13.59	205.0	89.53	101.4	4.67	91.83
Tea plant	0.9126[1]	1.4669[6]	61.6[6]	4.12	193.8	86.20	189.7	0.10	95.67

[1] at 30° C. [2] at 26.8° C. [3] at 27.2° C. [4] at 27.3° C. [5] at 27.5° C. [6] at 27.6° C.

CONSTANTS OF MIXED INSOLUBLE FATTY ACIDS.

Kind of oil	Color	Physical State	Melting point degrees C.	Solidifying point degrees C.	Neutralization value	Mean molecular wt.	Iodine value (Hübl)
Para rubber tree	yellow	semi-solid		27	185.0	303.3	116.5
Shiromoji ...	red-brown	liquid		14	287.1	105.4	12.19
Callophyllum	greenish brown	semi-solid	37	28-29	190.1	295.1	95.4
Hernandia...	dark green	liquid		12-13[2]	185.7	302.1	130.0
Hakuunboku	yellowish	liquid		13.5-14[2]	166.1	337.8	114.7
Akebia	pale greenish	solid	38 39	31	191.7	292.7	77.78
Kuromoji	dark brown	liquid		9.5	262.0	214.1	37.0
Aburachan...	red-brown	liquid		13	277.2	202.4	18.28
Magnolia	brownish black	liquid		17-17.5[2]	193.7	289.6	125.5
Magnolia (fruit). ...	dark brown	solid	35-35.5	28-28.5	201.9	277.9	99.66
Magnolia (flesh)	pale brown	solid	36.5	32-32.5	205.1	273.5	86.16
Tea plant	pale green	solid		25.5	190.5	294.5	80.79

[1] Deposits a large amount of a white substance at the ordinary temperature.
[2] Begins to become turbid.

test it became turbid and very viscous after 5 hours, owing to the production of solid matter, and after standing for 24 hours the whole mass assumed a buttery consistency.

This oil is non-drying and in its general properties resembles Sazanqua (*Thea sazanqua*) seed oil. The best way to rectify the oil is to filter it over 10 per cent. of its weight of Kambara earth, or it may first be shaken with dilute sulphuric acid and then filtered over 5 per cent. of its weight of Kambara earth. It can be used for soap-making and also for lubricating and burning.

The constants of the pressed oil from Tosa province seed are given in the table.

THE ANALYSIS OF LIMED PELT.*

By Hugh Garner Bennett, M. Sc.

The methods for the analysis of pelt, described below, are to some extent adopted from those methods previously described for the analysis of lime liquors (*Collegium*, London Ed., 1915, pp. 258, 313 and 329; this JOURNAL, March, 1916, pp. 98-130). The substances which are to be estimated, are much the same, the difference being that in the case of pelt they are enclosed by the fibrous structure of the hide or diffused through the fibers themselves being reversibly adsorbed or, in some cases possibly, feebly combined with the hide substance. This fact creates the analytical difficulty of reaching the particular ingredient it is desired to estimate. There are three ways by which this difficulty may be overcome. The pelt may be dissolved, be burnt off, or the substances may be allowed to diffuse out of the pelt under favorable conditions. Each of these methods is employed in the processes herein described.

1. *The Estimation of Total Alkalinity.*—This determination, as in the case of lime liquors (*Collegium*, Lond. Ed., 1915, p. 260; this JOURNAL, 1916, p. 98), includes the hydrates and sulphydrates of lime and soda, ammonia and organic bases. These are extracted from the pelt by diffusion into a boric acid solution, and are then titrated with standard acid and methyl orange, which is unaffected by the boric acid and hydrogen sulphide. Ex-

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* *Collegium*, London Ed., 1916, pp. 85-89.

cess of boric acid is employed and the alkaline swelling is thus quickly reduced. The boric acid will not cause any acid swelling. Both these facts tend to hasten the operation. The pelt itself, after weighing out, is cut up with a sharp knife into fine shavings. This is important, for the finer the shavings the quicker the extraction. The extraction is best conducted in an ordinary "shake bottle," as used in tannin analysis, and the pelt shavings are churned slowly in the boric acid solution. The diffusion is also hastened by titrating the liquor at intervals with the standard acid. The alkali which has been extracted is thus neutralized. It will be found advantageous to commence the process towards the close of the day and to leave the pelt in the boric acid solution overnight, starting the titration and churning on the following morning. The acid is, of course, sufficiently antiseptic to prevent any decomposition, and is not strong enough to cause any appreciable error through the hydrolysis of the nitrogenous matter.

About 10 grams of pelt are weighed out, cut up on a porcelain tile with a sharp knife and washed into a "shake bottle" with 50 cc. of a 3 per cent. boric acid solution. The bottle is closed with a rubber bung, placed in the churn and left overnight. Next morning the liquor is titrated with N/10 hydrochloric acid and methyl orange, and churned again for one hour. The titration is repeated at intervals of about one hour until the methyl orange is permanently reddened.

The rate of neutralization is best illustrated by an example:

1st titration	....	12.4 cc.	N/10 HCl.
2nd "	one hour	2.4	"
3rd "	two hours	0.6	"
4th "	three "	0.4	"
5th "	four "	0.3	"
6th "	five "	0.2	"
7th "	six "	0.1	"
Total alkalinity	....	16.4	"

When no sulphides have been used in depilation, methyl red may replace methyl orange.

2. *The Estimation of Ammonia.*—Practically all limed pelts contain some ammonia, originally coming from the hides as nitrogenous matter and afterwards reabsorbed in its alkaline

capacity. This ammonia is extracted from the hide in the estimation of total alkalinity, as described above, and is best estimated by using this boric acid extract. After titrating the total alkali, the neutralized liquor is transferred to the Kjeldahl apparatus, a few pieces of granulated zinc and about 20 grams caustic soda are added and the ammonia distilled off and collected in 50 cc. of a 3 per cent. boric acid solution (see *Collegium*, Lond. Ed. 1915, p. 264; this JOURNAL, 1916, p. 103). In this distillation some care is needed to prevent the liquor frothing over. The contents of the receiver are then titrated with N/10 HCl and methyl orange.

3. *The Estimation of Sulphide.*—When sulphide limes have been used a certain amount of the SH^1 ion is absorbed by the pelt. This may be estimated by dissolving the pelt in hydrochloric acid, distilling off the hydrogen sulphide and estimating it by Mohr's residual method (see *Collegium*, Lond. Ed. 1915, p. 315; this JOURNAL, 1916, p. 113.) About 10 cc. N/1 NaOH are run through the trap in the receiver of the distillation apparatus. About 50 grams of pelt are added to 300 cc. 10 per cent. hydrochloric acid in the distilling flask, which is immediately connected up with the apparatus. The whole is then allowed to stand overnight in the cold. Next day the liquor in the distilling flask is warmed up nearly to boiling point and maintained at that temperature for about half an hour without boiling. By that time the pelt has thoroughly disintegrated and all except portions of the grain is completely dissolved. The liquor is then boiled vigorously for 20 minutes. The sulphide in the receiver is precipitated with N/10 sodium arsenite, and the excess arsenite determined by titration with iodine, exactly as in the case of lime liquors.

4. *The Estimation of Soda.*—When any form of soda has been employed in the limes, soda is also a normal constituent of the pelt. It is best estimated by an adaption of Procter's method for the estimation of soda in lime liquors, *viz.*, ignition, carbonation of the residue to render the lime insoluble, solution of the soda in water, and titration with standard acid. The oxalate suggested by the writer as more convenient for lime liquors is not so suitable for pelt. For pelt the most convenient procedure is as follows:

From 10 to 15 grams pelt are weighed into a platinum dish and heated strongly at once by a "Fletcher" burner. It is better not to dry the pelt at all before ignition, for if this be done there is such a voluminous swelling of the melted and half-charred pelt. If the ignition be as quick as possible this difficulty is hardly experienced. When the ignition is well advanced the flame should be removed and the residue crushed down with a smooth glass rod. The ignition is then completed and the residue moistened with a strong solution of ammonium carbonate, to carbonate any caustic alkali. The excess of ammonium carbonate is driven off by 15 minutes heating by a rose burner, the dish being placed on a silica (or pipe clay) triangle, which itself rests upon a wire gauze. The carbonation is repeated to constant weight. Usually only two weighings are necessary. Distilled water is added to the dish, which is warmed up to boiling point for some time. The contents are then emptied on to a filter and washed well with hot distilled water. The filtrate, containing the sodium carbonate, is then titrated with N/10 hydrochloric acid and methyl orange.

5. *The Estimation of Lime.*—For the estimation of lime in pelt, previous workers have suggested methods which will be referred to below. The lime in pelt may occur in three different forms, *viz.*, caustic lime (either in *or* between the fibers), lime salts of weak acids derived from the hide, and lime salts of strong inorganic acids which have been present in the lime liquors and have diffused into the swollen hide.

(*a*) TOTAL LIME.—This determination includes all the three forms just mentioned, and is quite well made by the method suggested by Procter (*L. I. L. B.* p. 101). This consists of igniting the pelt, dissolving the inorganic residue in hydrochloric acid and precipitating the lime as oxalate, which precipitate, after washing well, may be dissolved in warm dilute sulphuric acid and titrated with N/10 permanganate.

This is practically identical with the Procter method for determining total lime in lime liquors (*L. I. L. B.* p. 86; see also *Collegium*, Lond. Ed., 1915, pp. 179 & 318.) Where nothing but lime is used in the liquors, *i. e.*, no soda, no calcium chloride, etc., fairly accurate results may be obtained by simply weighing the ash of the skin. This course was adopted by Wood (Bating, Puering and Drenching of Skins, p. 39.)

(*b*) ALKALINE LIME.—This term may be applied to that lime which is *not* combined with strong acids. This includes the caustic lime, any carbonate or oxalate of lime and the lime salts of the weak organic acids derived from the hides or skins, *e. g.*, lime soaps, calcium caproate, calcium salts of amino acids, etc. These portions of the total lime may be estimated indirectly by the determination of soda, as above, and subsequently the "lime and soda" together by a method given by Procter for "total lime," (*L. I. L. B.*, p. 101, and *L. C. P. B.*, p. 44). This consists of igniting the pelt, dissolving the inorganic residue with excess of standard hydrochloric acid and titrating the excess with phenolphthalein and caustic soda. The writer has found it better to titrate the excess of acid with methyl orange and N/10 sodium carbonate, for unless the residue be very strongly ignited, calcium carbonate is liable to be left and the carbon dioxide causes error in the phenolphthalein end point. From 5 to 8 grams of pelt may be taken and 20 cc. N/10 hydrochloric acid will be sufficient to ensure a reasonable excess. The residue should be warmed with the 20 cc. N/10 acid until dissolved. An alternative plan is to dissolve the residue in 50 cc. boiling 3 per cent. boric acid, and titrate the lime and soda direct with N/10 HCl. This is, however, somewhat slower, as ignited calcium carbonate is not readily soluble in boric acid. This determination of "lime and soda," minus the "soda" as determined separately, gives the amount of lime present as alkali, mild or caustic.

(*c*) CAUSTIC LIME.—There is no method as yet which will satisfactorily determine the caustic lime in pelt. Payne's method is to titrate fine shavings of pelt in a stoppered bottle with standard acid and phenolphthalein until the pink color is permanently discharged. This method is scarcely accurate, even for ordinary lime liquors, for the ammonia is also partly estimated. In the case of sulphide limes and when caustic soda is employed, the matter is further complicated. In pelt obtained from such liquors, caustic soda will be estimated in addition to lime and ammonia. If the determination of soda be used as a correction it is necessary to determine what proportion of the total soda is present as the hydrate. The presence of any sulphydrates also increases the errors, for sulphureted hydrogen affects phenolphthalein and yet in such a prolonged process as this titration, some of the gas is sure to be lost. Unless the NH_4, the Na and the SH^1 ions are a negligible quantity, little accuracy is to be expected on these lines. In cases where the limes are fresh throughout and contain no sulphide or soda, the method gives approximate results, but is insufferably tedious to execute, as the diffusion of lime is very slow It may be hastened a little by churning, as suggested in Part 1, for total alkali. When the amount of acid required is known approximately the greater part may be added at the commencement of the operation. This also hastens the end point a little. At best the end point is doubtful.

6. *The Estimation of Hide Substance.*—This may be done by Kjeldahl's method; about 1 gram of pelt of a suitable quantity. It may be remarked that if permanganate be used to complete the digestion, it yields a yellow not a colorless liquid. If it be used a second time, however, the liquid becomes quite colorless. It should be noted also, perhaps, that by Kjeldahl's method the total nitrogen is estimated, and that to estimate hide substance accurately it is necessary to correct for the nitrogen present as ammonia, as determined in Part II. above. It will be sometimes found that the correction is negligible.

7. *The Estimation of Salt.*—Chlorides in pelt are generally due to common salt used in salting the hides, but may be present also owing to the nature of the water employed in the wet work, or possibly because of the use of calcium chloride in liming. The best method for estimating chlorides in pelt is a modification of that suggested by the writer for lime liquors (*Collegium,* Lond. Ed., 1915, p. 334). In the case of pelt the process is as follows:

From 10 to 20 grams of pelt are allowed to stand overnight in a beaker flask containing 100 cc. 10 per cent. nitric acid. Next morning the flask and contents are heated on the steam bath for 1-2 hours until the pelt is thoroughly disintegrated and almost completely dissolved. The liquor is then transferred to a 200 cc. graduated flask and re-heated on the steam bath. While hot 25 cc. N/10 silver nitrate are pipetted into it, and the digestion continued until the precipitate settles. The liquid is then cooled to 15° C., made up to mark, mixed and filtered. One hundred cc. of the filtrate are titrated with N/10 KCNS and the ferric indicator. If *n* cc. are required, the N/10 silver nitrate used up for precipitating chlorides is then, of course $(25 - 2n)$ cc. The nitric acid serves not only to dissolve the pelt, but also to oxidize both organic and inorganic matters.

GENERAL PRECAUTIONS.

Limed pelt rapidly desiccates in the laboratory atmosphere, and the caustic alkali quickly carbonates. The pelt should be blotted gently to remove surface moisture, and the quantities required for each of the above operations should be weighed out at once, before any of these operations are continued. It is essential that all apparatus required should be quite ready before the sample is brought to the laboratory. It will usually be found most convenient to calculate the various alkalinities first into cc. N/10 acid per 10 grams pelt. This facilitates the grouping of hydrate and sulphydrate ions (see *Collegium*, Lond. Ed., 1915, pp. 319 and 320; this JOURNAL, 1916, pp. 118-119), and the calculation of "organic bases" by subtracting the lime, soda and ammonia, from the total alkalinity.

TANNERS' INSTITUTE.

Fifth Annual Report, School Year 1915-16.

(The report is published in pamphlet form, embracing twenty pages of text and three full-page illustrations. The following is an abstract of the text of the report.)

Tanners' Institute comprises a co-operative arrangement between the National Association of Tanners and Pratt Institute, Brooklyn, N. Y., by which two lines of activity are conducted: first, the training of young men for responsible positions in connection with the manufacture of leather, and second, the investigation, both practical and scientific, of processes and problems of leather manufacture. The courses corresponding to these two aims are a one-year course in tanning and a one-year course in applied leather chemistry. The former is intended for young men who desire to become tannery foremen. While previous experience in a tannery is not made an essential for admission to this course, such experience is highly advisable, and a considerable proportion of the students who have taken these courses have been employed in tannery work before coming to the Institute. The applied leather chemistry course is open only to graduates of technical schools and others who have already obtained an extensive general knowledge of chemistry, and who wish specialized training with the view of becoming leather chemists. Each of the courses is arranged to occupy the entire time of a student for one school year.

Experimental investigation of problems in the manufacture of leather has been carried on under the direction of the staff of the Institute, and the results of this work have been published by the National Association of Tanners. (Reports given by Dr. Allen Rogers at meetings of the A. L. C. A., and abstracts of students' work have appeared from time to time in this Journal.) The salaries of instructors and the overhead expense of conducting the Tanners' Institute, including plant and equipment, are paid by Pratt Institute, the tuition fees of students of the courses providing but a small part of the funds necessary to conduct them. The Tanners' Institute Fund has provided about $5,000 each year, which has been expended in providing free scholarships for students requiring financial assistance, in observation trips of students to distant tanning establishments, in lectures by specialists and in conducting the investigations before referred to.

Perhaps the most important single event of the year was the installation of a new school tannery. (See the account given in this JOURNAL last year. A full-page cut, showing students at work installing machinery, is shown on page 662, vol. 10.) The number of students completing the courses and receiving certificates this fifth year was 23, 18 in tanning and 5 in leather chemistry. Of the 18 in the tanning class, 15 had had experience in tannery work. The 5 graduates in leather chemistry were from five different schools, as follows: Pratt Institute, Lowell Textile School, Massachusetts Institute of Technology, Technical College of Sydney, New South Wales, and the New Jersey College of Pharmacy. A list of the graduates of both courses is given, with statement of present positions. All but two are employed, and the employment of all but one of these is in some way connected with leather.

The number of scholarships in force during the year was five, four of $300.00 each in the tanning course, and one of $400.00 in the applied leather chemistry course. A friend of the Institute, whose name is withheld at his request, has for several years directed the award of prizes at his expense to the students doing the most meritorious work. These were awarded as follows: Tanning Course, first prize, Erwin A. Seidel; second prize, Seymour R. Gross. Applied Leather Chemistry Course, first prize, Alfred J. E. Schmidt. Each prize included a gold medal in the form of a watch fob and a sum of money; $25.00 for a first, and $20.00 for a second prize.

The observation trips were two in number. In the first a group of tanneries readily accessible from New York City were visited, and in the second a group in eastern Massachusetts. Dr. Rogers also took the students in the course in Applied Leather Chemistry to the meeting of the A. L. C. A. at Atlantic City, May 22-25. (A brief abstract of the Massachusetts tour was published in the JOURNAL for May last, p. 225.)

At the Shoe and Leather Fair at Boston, the Institute was represented by an exhibit of the products of the school tannery and by a model tannery chemical laboratory in operation. The samples of leather shown included sole, pigskin, calfskin, cabretta, goat, etc. A large number of visitors expressed interest in the work of the Tanners' Institute, and were supplied with information concerning the work done at the School.

The following lectures were given in the course of the year:

The Manufacture of Sole Leather by the Acid Hemlock Process.
  Stephen Frisard, of the Vacuum Oil Co., New York, N. Y.
Tannery ·Cost Accounting.
  O. H. Cushwa, of the J. H. Ladew Co., Newark, N. J.
The Bating of Hides and Skins.
  Carl Muckenheim, of Röhm & Haas, Philadelphia, Pa.
The Chemistry of Colloids, twelve lectures.
  Dr. Arthur W. Thomas, of Columbia University.

The following investigations were prosecuted during the year:

Further study of color tests of tanning materials and their weight giving qualities, by Dr. Rogers and assistants.
Study of waste rocker liquors, by John J. Craven.
Analytical data on free sulphuric acid, by Alfred J. E. Schmidt.
Further study of spewing problems, by Frank S. Hunt.

Added equipment includes a setting-out machine, presented by Percival Foerderer, a glazing jack, a splitting machine, two paddles and numerous vats for soaking and tanning. A few machines are still needed to make the installation complete, and it is hoped that interested friends may be disposed to help in filling out these deficiencies.

The Advisory Committee consists of three members of the National Association of Tanners and three members of the American Leather Chemists' Association. The chairman is George H. Raymond, of Hans Rees' Son, New York City; the other tanner members being Morris S. Barnet of the Barnet Leather Co., New York City, and Henry W. Healy of the Central Leather Co., New York City. The representatives of the A. L. C. A. are H. C. Reed, W. H. Teas and Dr. L. E. Levi. This Committee held two meetings at the School in the course of the year. They inspected the work of the school, awarded scholarships, examined plans for investigations, for inspection tours and for the exhibit at Boston, and reviewed the progress of plans for the establishment of a Research Laboratory, beside adopting a budget for the following year for the expenditure of the Tanners' Institute Fund.

Acknowledgement is made for many gifts to the Institute, including cash contributions, tanning materials and equipment, periodicals, publicity, space at the Boston Fair, etc.

A list of the entering classes is given, seventeen in the Tanning Course and three in the course in Applied Leather Chemistry. Seven states are represented, and there is one student from the Philippine Islands.

REPORT OF THE HIDE POWDER COMMITTEE ON METHODS OF TESTING HIDE POWDERS.*

By H. G. Bennett, Hon. Sec.

The Hide Powder Committee is composed of the following:

Representatives of Public Chemists, J. G. Parker and H. Brumwell.

Representatives of Extract Manufacturers, R. R. Howroyd and T. Carter.

Representatives of Tanners' Chemists, H. E. Holmes and H. G. Bennett, Hon. Sec.

The previous reports of this Committee have dealt only with the results of their tests of the official hide powders. The present report deals with their experience in the actual working of the tests.

The results of the earliest tests of the Committee (before the report of the B_1 hide powder) showed surprising discordance between the various members of the Committee, exhibiting clearly the desirability of a greater uniformity in the methods of testing. It was also evident that the results of some tests had their influence upon other tests; *e. g.*, discordant results in non-tannins per cent. and in acidity could be explained by the fact that the various observers had previously obtained different results in the moisture determination. It seemed desirable, therefore, that there should be definite stages in the testing as well as uniform methods for the actual tests. The testing of a hide powder has therefore been divided into three stages, *viz.*, (1) the determination of the moisture content; (2) the determination of acidity and soluble matter, and the blank test, and (3) comparative non-tannin determinations with the official hide powder and its proposed successor.

For these tests 1 lb. hide powder is employed, which is divided into six equal portions of nearly 75 grams, each member of the Committee receiving one portion, which is sufficient to allow moisture, acidity, and soluble matter determinations, a blank test and tests of two extracts, all determinations except that of soluble matter being done in duplicate. Each portion is quickly weighed out into an air-tight tin, in which it is despatched.

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* *Collegium*, London Ed., 1916, pp. 155-60.

1. The Determination of Moisture.

Unexpected difficulty has been experienced in obtaining concordance in this fundamental determination. Any method of drying a definite weight of powder to constant weight seemed sufficient, but the results of the various Committee members showed divergencies of up to 3 per cent. in the moisture content. At first it was thought that this might be accounted for by the heterogeneity of the hide powder, but it subsequently appeared that the chief reason was that dry hide powder is an extremely hygroscopic substance, retaining its last traces of moisture tenaciously and reabsorbing moisture with avidity. Mr. Brumwell, who, in his earliest experiments dried and weighed the powder in open basins, found that the weight of the dry hide powder increased rapidly during the actual weighing. This was confirmed by other workers, and it became evident that the dry hide powder must be protected at this stage even from the atmosphere of the balance case. From the commencement of the Committee's work Mr. Holmes had realized this possible source of error, and had invariably dried the powder in a weighing bottle, stoppered during weighing. This course has been adopted with advantage by the rest of the Committee. Mr. Brumwell working with the same hide powder, found the following results:

Open platinum basins	(1)	12.07% moisture
	(2)	12.17% "
Official method (below) (involving weighing bottle)		12.47% "

Mr. Carter suggested that the weighing bottle or other vessel might vary in weight whilst it was being filled with hide powder and re-weighed. As a precaution he allowed the tared vessel (W_1) to stand 5 minutes in the balance case, and re-weighed it (W_2). This precaution has also been adopted by the Committee. Mr. Holmes, in examining this matter obtained the following results:

Official method	(1)	11.69% moisture
	(2)	11.63% "
Official method without this precaution		11.44% "

The writer has found that $W_1 = W_2$. It is possible that this matter is influenced by (1) the humidity of the atmosphere, and (2) the efficacy of desiccating agents in the balance case. So far as could be noted, the actual temperature of drying is not an influence of major importance; workers whose ovens were usually slightly higher in temperature often reported lower results. The Committee, for uniformity, recommend the ordinary steam oven. It is noticed that the vacuum steam oven often gives slightly higher results. In the ordinary steam oven the determining factor is probably the rate at which the air is renewed.

It was pointed out by the writer that there is no value in determining the percentage of moisture to the second decimal place, partly because the error of method makes the figure of no significance, and partly because a difference of 0.05 per cent. (the greatest error in rounding off) makes a difference of only 0.004 grams of hide powder in the quantity to take per analysis. For similar reasons it was suggested that in calculating the amount of hide powder to take for each analysis, *i. e.*, the quantity of powder equivalent to 6.5 grams dry hide powder, the result should be expressed to the nearest decigram. It was also suggested that to eliminate differences due to the heterogeneity of the hide powder, each member of the Committee should make a duplicate experiment, taking his hide powder from a different part of the bulk sample.

Taking all these points into consideration, the Committee have adopted the following procedure as the standard method for estimating moisture in hide powder.

Official Method.

A stoppered weighing bottle 1¼ in. in diameter is heated for 15 minutes at 100° C. in the steam oven with the stopper out, cooled in a desiccator for 20 minutes with the stopper in, and then weighed; (W_1). After allowing it to stand for 5 minutes in the balance case, it is reweighed; (W_2). It is then immediately filled with hide powder, about 2 grams being added, the packing being as loose as possible. The stopper is at once replaced and the bottle and contents weighed; (W_3). The bottle and contents, with the stopper out, are then dried for 3 hours at 100° C., preferably in a steam oven. The stopper is then replaced, and the bottle and contents cooled in a desiccator for 30 minutes and again weighed. The drying is continued for another hour, to see if the weight is constant, and if not, continued still longer until a constant weight is obtained; (W_4). The percentage of moisture in the powder will then of course be $\frac{100\{(W_3-W_2)-(W_4-W_1)\}}{W_3-W_2}$ A duplicate experiment should be done also, taking the hide powder from a different part of the bulk sample. This result should be reported separately.

Each member of the Committee reports his results by this method to the Secretary, and the average is taken of the mean results of each worker. This Committee average is taken as the official result for moisture in the hide powder, and on this basis the amount of hide powder is calculated equivalent to 6.5 grams dry hide powder, which quantity, rounded to the nearest decigram, is accepted as the amount of hide powder to be used in all subsequent work.

The adoption of this standard method has resulted in considerable improvement in the concordance of results by the various members of the Committee. This improvement is best illustrated by the following figures, which show the differences between the highest and lowest percentages of moisture reported on each of the American hide powders tested.

Hide powder	Greatest difference in results
2123	2.5
2124	2.4
B_1	2.3
B_2	1.8
B_3	0.6

II. ACIDITY, SOLUBLE MATTER AND BLANK TEST.

In all these determinations the quantity (R) corresponding to 6.5 grams dry powder, is taken as the unit to test.

(*a*) ACIDITY. The Committee considered two methods for this determination; the 'cold' method (*Collegium,* 1907, 153) and the 'boiling' method (*Collegium,* 1909, 118). It was found that these did not always yield the same results. Mr. Holmes obtained the following figures with one powder:

Cold method—2.9 cc. N/10 NaOH.
Boiling " —3.6 cc. " "

It was thought that there was a possible source of error in hydrolysis in the case of the boiling method, so that for the sake of uniformity the Committee adopted the cold method.

Official Method.

The quantity (R) of the air dry hide powder which, according to the Committee's average, corresponds to 6.5 grams dry hide powder is digested for about 10 minutes in an ordinary shake bottle with 100 cc. distilled water, shaking the mixture occasionally by hand. After adding 1 cc. of a 1 per cent. alcoholic solution of phenolphthalein, the mixture is titrated with N/10 NaOH until a permanent pink color is obtained. Results are stated in cc. N/10 NaOH required. A duplicate experiment should be made also, taking the hide powder from a different part of the bulk sample. This result should be reported separately. The average is taken of the mean results obtained by each member of the Committee, and this average constitutes the official result of the Committee's test. On the basis of this average any necessary correction of acidity is made.

The I. A. L. T. C. regulations stipulate that the acidity of the hide powder before chroming shall be between 2.5 and 5.0 cc. N/10 NaOH per unit. Any hide powders whose acidity lies outside these limits must be brought within them by the addition of the requisite amounts of N/10 NaOH or N/10 HCl. The Hide Powder Committee, while of course loyally adhering to these rules have adopted the principle of minimum interference, *viz.*, that sufficient only of these reagents should be used to bring the hide powder *just* within the regulations. Thus, if a hide powder have an acidity of 5.8, its acidity is brought down to 5.0 *only*, by adding 0.8 cc. N/10 NaOH per unit; and if a hide powder have an acidity of 2.0 it is to be brought up to 2.5 *only*, by the addition of 0.5 cc. N/10 per unit before chroming. If a hide powder have an acidity between 2.5 and 5.0 per unit, no additions of either hydrochloric acid or caustic soda must be made. In the case of recent official hide powders no such corrections have been necessary.

The writer has obtained results which indicate not only that all acidity before chroming is superfluous, as all materials are quite well detannized without it, but also that such acidity is a source of difficulty in washing the hide powder, and a source of error in the method of analysis, as it tends to produce the absorption of soluble non-tanning matters by the hide powder (*See J. S.*

C. I., 1914, Dec. 31). He is very strongly of the opinion that all acidity before chroming should be reduced to zero immediately before chroming, by the addition of the requisite quantity of N/10 caustic soda. A slight change in the I. A. L. T. C. regulations would be necessary for this to be adopted.

(*b*) SOLUBLE MATTER. This determination presents no difficulty in manipulation, but results differ appreciably. It is probable that this is the best test of the homogeneity of the hide powder. The test has importance also as a check upon badly manufactured hide powders. A large amount of soluble matter involves greater difficulty in obtaining a satisfactory blank test, as well as more washing of the hide powder in ordinary practice. The Committee have operated as follows:

Official Method.

The quantity (R) of hide powder used for such analysis, is placed in an ordinary shake bottle with (126.5—R) cc. of distilled water, and churned slowly for one hour. It is then filtered through linen, and through filter paper, with the assistance of about 1 gram of kaolin, and 60 cc. filtrate are evaporated to dryness and dried to constant weight. The weight of the residue multiplied by two gives the "soluble matter in 6.5 grams dry hide powder." A duplicate experiment is in this case unnecessary.

To illustrate how 1-lb. hide powder may vary in this respect, the following results, obtained recently by the Committee, in testing B_3 hide powder, may be given:

H. Brumwell	0.0443
R. R. Howroyd	0.0600
H. E. Holmes	0.0480
H. G. Bennett	0.0347
	0.0468 average

(*c*) BLANK TEST.

Official Method.

This should be carried out in exactly the same way as in an official detannization, but 100 cc. of distilled water is employed instead of 100 cc. tan infusion. Two tests should be carried out, side by side, like duplicate analyses, *i. e.*, the hide powder should be chromed, washed and squeezed in one whole, but separated for the two shakes: 60 cc. is evaporated in each case, and the residues added together and reported as one result—"Residue of blank test per 6.5 grams dry hide powder."

A certain proportion of the residue of a blank test will undoubtedly be nitrogenous, and some of this may be precipitated by the tannin in an ordinary detannization. Hence the error indicated by a blank test is probably less than is apparent.

III. Comparative Non-Tannin Determinations.

The quantity (R) of hide powder necessary for each analysis having been determined as above, (Part I), and also any correction necessary for acidity, (Part II), comparative determinations of soluble non-tannin matters are carried out by the official method of analysis. The proposed new hide powder is tested alongside the hide powder which is then the official hide powder, in order to see how the non-tannin results will vary with the change in hide powder. Usually each member has tested materials in which he has been chiefly interested, the difference between the two hide powders with any one worker, being more important than the concordance possible between different workers on one extract. These tests have a certain commercial importance, as some dislike a change of hide powder during the execution of a contract. With the last three official powders, however, there could be little objection to this, as all workers obtained much the same results with new and old powders. The chief importance of this test is that it is a safeguard against the introduction of hide powders which have the property of absorbing large quantities of soluble non-tannin matters in addition to the tannin, thus giving erroneously high figures in the tannin results, and a fictitious value to materials thus tested.

In conclusion, the Hon. Sec. would like very cordially to acknowledge the willing co-operation of every member of the Committee towards the purposes in view, the keen interest displayed in the improvement of the procedure of testing, and the usually prompt attention to the matters in hand.

ABSTRACTS.

The Alkaloids of Quebracho Bark; Aspidospermine. A. J. EWINS. *Journal Chemical Society,* 1915, p. 2738; through *Collegium,* London ed. Finely ground quebracho bark is extracted with hot alcohol. The soluble matter, after removal of the solvent, is further completely extracted with 20 per cent. acetic acid. Dilution of the resulting solution and addition of excess normal lead acetate gave a precipitate. This was separated by filtration, the excess lead removed from the filtrate as sulphide and the solution made alkaline with ammonia. The crude alkaloid bases present are precipitated, any remaining unprecipitated being extracted with chloroform. Solution in alcohol and partial crystallization led to the separation of aspidospermine. This was further purified by crystallization from methyl alcohol and sublimation in a vacuum. Other bases, at least two in number, present in the mother liquor have not as yet been successfully separated. Aspidospermine on hydrolysis with dilute mineral acids (10 per cent. HCl) gives rise to a new base deacetylaspidospermine, which can be distilled under greatly reduced pressure and is very soluble in light petroleum. Advantage was taken of these properties to separate a further amount of aspidospermine from the mother liquor previously mentioned. The yield of aspidospermine varied with different barks from 0.2 to 0.06 per cent., while the amount of total alkaloid varies from 1.4 per cent. for young bark to 0.3 per cent. for old bark. The properties and constitution of aspidospermine are detailed; the formula attributed being $C_{22}H_{30}O_2N_2$. Perkin's modification of Zeisel's method establishes the presence of one methoxy group, the absence of the N-methyl being shown by treatment with HI at 330° C. The latter treatment led to the isolation of a new base aspidosine—$C_{19}H_{26}ON_2$—prepared from the primary product of the reaction between aspidospermine and HI—$C_{19}H_{26}ON_2.HI$—by the action of ammonia. This base differed in composition from aspidospermine by the complex C_3H_4O of which the hydrolysis of one methoxyl group accounts for CH_2. The residual C_2H_2O pointed to the presence in aspidospermine of an acetyl group attached to an N atom. This was confirmed as follows: 10 per cent. dilute HCl at 100° converts aspidospermine into deacetylaspidospermine—$C_{20}H_{28}ON_2$—this latter compound being converted into a characteristic sparingly soluble dihydriodide—$C_{20}H_{28}ON_2.2HI$—by the action of hydriodic acid. Deacetylaspidospermine gives rise to a benzoyl derivative with benzoic anhydride, and forms an addition product with 2 molecules of methyl iodide. The relationship between aspidospermine and deacetylaspidospermine is shown by the preparation of the former from the latter by the introduction of an acetyl group by acetylation. Deacetylaspidospermine reacts with nitrous acid and, under suitable conditions, yields a crystalline derivative, which appears to be a nitronitroso derivative—$C_{20}H_{26}O_4N_4$—and probably contains in the molecule a reduced quinoline nucleus. Deacetylaspidospermine thus appears to be a secondary tertiary base. Boiling hydriodic acid converts this substance into aspidosine. Aspidospermine, on oxidation with chromic acid gave rise to a compound which has not been properly investigated owing to want of material, the probable formula being $C_{16}H_{24}O_2N_2$. The alkaloid quebrachine which, according to its discoverer Hesse, only occurs in certain bark specimens, was never found to be present in the sample of quebracho bark used in the present investigation; and the author has so far not been able to confirm the existence of the other bases isolated by Hesse suggesting that the method of extraction of the alkaloids used (warm dilute H_2SO_4) would hydrolyze aspidospermine, giving rise to a new base, the properties of which make it appear possible that the new bases described by Hesse may have been impure forms of this substance.

E. W. M.

Tannin Content of Some Queensland Barks. J. C. BRUNNICH and A. T. JEFFERIS.. *Queensland Agr. Jour.*, through *J. S. C. I.* Barks containing more than 20 per cent. of tannin include an undetermined species of acacia known as "black wattle," *Acacia implexa* and the inside bark of *Eucalyptus Cloeziana.* Barks containing from 10 to 20 per cent. include *Acacia harpophylla,* 16 per cent., *Eucalyptus microcorys*, 17.7 per cent., *Eucalyptus haemostoma*, 12 per cent., and *E. Cloeziana*, entire bark, 12 per cent.

Chemical and Microscopical Examination of Leather. E. SEEL and A. SANDER. *Zeitschrift für angewandte Chemie,* 1916, pp. 325-6 and 333-4, through *J. S. C. I.*, Oct. 16, 1916. Most of the reactions which have been proposed for the detection of neradol in leather are either not sufficiently sensitive or are interfered with by the presence of other tanning materials. The authors have found the following reactions satisfactory for the detection of neradol D. Boil 20 grams of the leather, in small pieces, with 200 cc. of water for 15 to 30 minutes. Treat 100 cc. of the hot, filtered solution with a mixture of equal parts of 40 per cent. formaldehyde, concentrated HCl and water (Stiasny, *J. S. C. I.*, 1906, p. 275), and boil for 30 minutes under a reflux condenser. After cooling, this solution is filtered and concentrated, preferably after a preliminary purification by dialysis; or the leather infusion may be treated with lime water or neutralized with ammonia and treated with a calcium salt, and then filtered and concentrated. (*a*) Hydroxyazo reaction. Five cc. of the concentrated solution is treated with excess of alkali, cooled with ice, mixed with about half its volume of alcohol, and 3 or 4 drops of a solution of diazotized *p*-aminophenol added. A blue coloration indicates the presence of neradol D. If the blue color does not appear immediately, the solution is acidified with HCl, shaken vigorously with ether, the ethereal solution separated and added to water, and then NaOH added, when a dark bluish-green color appears at the surface of contact of the two layers if neradol D be present. (b) Indo-phenol reaction. Five cc. of the concentrated aqueous extract of the leather is treated with a drop of solution of the hydrochloride of dimethyl-*p*-phenylenediamine (obtained by reduction of methyl orange), the mixture is made alkaline with caustic soda and treated with one or two drops of a 5 per cent. solution of potassium ferricyanide. A blue coloration indicates the presence of neradol D. The test is rendered more delicate if alcohol be introduced to form an upper layer before adding the ferricyanide. In this case a blue ring forms slowly at the surface of contact and gradually extends into the alcohol layer. Neradol ND (prepared by condensation of naphthalene-β-sulphonic acid and formaldehyde), not being a phenolic compound, does not give either of the above reactions directly, but responds to both after oxidation with sodium hypochlorite solution.

For staining sections of leather for microscopical examination, in order to ascertain whether the skin has been tanned completely through, the best results were obtained with malachite green, brilliant green, methyl green, Bismarck brown, and rhodamine, all of which dye the leather while leaving the skin unaffected. By dyeing first with a basic dyestuff, washing with water and alcohol, and then again dyeing with an acid dyestuff, the untanned skin and the leather may be stained different colors. Effective results were obtained with brilliant green and eosin, and with rhodamine and patent blue.

Swelling of Hides in Presence of Hydrogen Ions. G. POVARNIN. *J. Russ. Phys.-Chem. Soc.*, 1915, 47, 2064-2073, through *J. S. C. I.* The work of other investigators, notably Paessler and Appelius (*J. S. C. I.*, 1902, 1461), in this direction is discussed. The velocity with which hide substance swells in pure water is expressed by the equation, $\log.[M/(M-Q)] = 0.4343 k_1 t$ (1), where M represents the maximum swelling, Q the swelling after the time, *t*, and k_1 is a constant. The swelling in presence of acids depends on the following considerations: (*a*) The velocity of swelling is directly proportional to the velocity of the acid ions in penetrating the membrane (hide), and this velocity is proportional to $\sqrt{t}$, as was shown by Morse and Pierce (*Z. physik. Chem.*, 1903, 45, 589) for gelatine; in absence of acid, the rate of swelling is proportional to the velocity with which the ions of water pass through the membrane, that is, to *t*. (*b*) The rate of swelling is inversely proportional to the quantity of hide substance dissolving at the surface of contact of hide and liquid and, since this quantity is directly proportional to the time, the rate of swelling is inversely proportional to *t*. (*c*) The maximum swelling, M, for a given acid is equal to some constant maximum, M_0, multiplied by k_0, which is a coefficient varying with the nature of the acid; it may be assumed that k_1 of equation (1) is in general equal to some magnitude, $k/2$. (*d*) The rate of swelling is proportional to the index of basicity, *n*, of the acid, if the acid is completely dissociated, and in general it should be proportional to the number of free hydrogen ions in the solution of the given acid. From these theoretical foundations, the equation, $\log. [M/(M-Q)] = 0.4343.n.k._1\ t$, is derived. Paessler and Appelius's results for five acids at concentrations of 0.1-0.6 per cent. are expressed satisfactorily by this equation, $0.4343k$ having the value 0.274, while n is equal to 1, or with strongly dissociated dibasic acids, 2; M is a variable magnitude, depending on the character and concentration of the acid' T. H. P.

Leather from Shark Skins. *Commerce Reports*, Dec. 8, 1916. The condition of the leather market makes desirable the utilization of all available supplies of suitable animal skins. The Bureau of Fisheries of the Department of Commerce has taken up the possible value of shark skins in making various kinds of leather. Such skins, as is well known, have for many years had a limited demand in the United States as coverings for minor articles of ornament and utility, but their use as leather has been very restricted. An acceptable leather has been prepared from shark skins in several foreign countries, and there is no apparent reason why the skins of certain sharks caught on our own coasts or in foreign waters may not be converted into serviceable leather by American tanners. Shark skins are very tough and durable, and some of them show a beautiful surface pattern which persists in the tanning process. Leather made from the skins of the larger sharks has very considerable body, and such sharks will be in greatest demand if the experiments of the Bureau of Fisheries prove as successful as anticipated, although the skins of minor sharks and the grayfish also are being handled. Arrangements have been made for securing from Florida fishermen a supply of very large shark skins; and further specimens are expected from other sources, especially from a number of lightships off the South Atlantic and Gulf coasts. The Bureau of Lighthouses is co-operating in this matter and will authorize the men on southern lightships to catch sharks and preserve their skins. The Bureau of Fisheries is supplying fishing tackle. The skins will be sent to tanners for treatment in various ways, and it is hoped that such raw material will prove so useful that fishermen on all parts of our coast may hereafter find a market for the skins of all kinds of sharks now incidentally caught in line and net fishing. The Bureau of Fisheries solicits correspondence with tanners, leather dealers, and manufacturers who may desire to co-operate with it in exploiting this waste product.

Specific Color Reaction of Marine Animal Oils and Their Hydrogenated Products. M. TORTELLI and E. JAFFE. *Annali Chim. Applic.*, 1914, pp. 80-98; *Analyst*, Jan., 1915. Marine animal oils contain a chromogenic substance which reacts with bromine to form a compound which imparts a bright green coloration to a chloroform solution of the oil. One cc. of the sample is shaken with 6 cc. of chloroform and 1 cc. of glacial acetic acid in a test tube and the homogeneous solution is treated with 40 drops of 10 per cent. solution of bromine in chloroform, vigorously shaken and allowed to stand. In the presence of marine animal oil a fugitive rose coloration, changing to bright green, will be obtained, and will persist for an hour. Vegetable oils under the same conditions will usually remain colorless or assume a yellow tint, which does not alter within an hour. In the case of hemp-seed oil, however, the chloroform solution becomes green on the first addition of bromine and then changes to yellow. Certain animal oils, including neats-foot, give a slight rose coloration, changing to yellow within an hour, but in no instance can the reaction be confused with that given by marine animal oils. Hydrogenated fish and marine animal oils give a rose coloration, changing within a minute to pale green, and after another minute to emerald green, whereas hydrogenated vegetable oils at first remain unaffected or assume a light yellow tint, which becomes yellow or brown after an hour, while hydrogenated terrestrial animal oils immediately assume a yellow or light brown tint, changing to deep brown after an hour. As little as 5 per cent. of hydrogenated marine animal oil may thus be detected in vegetable lard substitutes, etc. Ordinary butter gives a yellowish tint, appearing slightly green by reflected light, but not such as could be confused with the distinctive reaction of the marine animal oils.

PATENTS.

Composition for Treating Hides. U. S. Patent 1,205,694. JOHN H. YOCUM, East Orange, N. J. The composition consists of common salt intimately mixed with approximately 3% of normal sodium sulphite.

Machine for Rolling Leather. U. S. Patent 1,207,109. WILLIAM W. WHITING, Nashua, N. H.

Leather-Dressing Machine. U. S. Patent 1,208,116. OTTO F. FEIX, West Hoboken, N. J.

Tanning Material. British Patent 11,509. H. WADE, London, for Robeson Process Co., New York. Lime is removed from sulphite lyes by first concentrating the lye, then adding strong sulphuric acid in insufficient quantity to precipitate the lime completely, and then adding enough of a bisulphate to finish the precipitation. The liquor should be acid to litmus, but not to Congo red. The sugars contained in the lye may be removed by fermentation. (This is apparently the same process as that patented in the U. S. in 1915 by H. H. Hurt, and described at length in this JOURNAL, Vol. X, pp. 481-4.)

Tanning Material. British Patent 11,024. M. B. LARSON, Molson, Washington, U. S. A. The material patented is a mixture of gambier and salt, in the proportion of 5 to 1, to which, after mixing, is added Epsom salts in quantity equal to the common salt used.

Leather Substitute. British Patent 101,557. A. L. BURLIN, Salford, Lancashire. Boots, leggings, head coverings, cycle or riding saddles, traveling trunks, or hand-bags are made of very thin, soft, pliable, aluminium sheet, oiled, varnished, or painted on one side and having a layer of woven woolly felt or skin fabric or of powdered cork made to adhere to the other side. The outside of the sheet may be coated similarly to the inside. The material may be used generally as a substitute for leather.

Artificial Leather, Fur Felt, Paper, Etc. British Patent 101,536. T. SCHMID and J. FOLZER, Horn, Switzerland. Artificial leather, felt, and paper products are made from a felted unbleached fibrous web which is fed by a feed table to pressure rolls, one of which is roughened, and the other provided with a rubber coating, the lower one dipping in a trough containing a cellulose solution with which the web is impregnated. The web, preferably in a stretched condition, is then passed through a trough containing a liquid for hardening the dissolved cellulose, squeezed by rolls and wound on a spindle. The material thus produced may afterwards be water-proofed, or water-proofing material may be added to the cellulose solution. By the use of long staple fibrous material and one of the rolls roughened in strips only, the surface fibers of the finished product may be released by scratching and brushing, thereby producing an imitation fur. A tough parchment-like Japanese paper is obtained if a proportion of bleached cotton is added to the fibrous web or if the web is entirely composed of bleached material, and the bleached material may be water-proofed prior to passing through the cellulose solution. The bleached products may be passed through a cold sulphuric acid bath of 50°-66° Bé. and then washed and passed through a bath of soda or potash lye, preferably under tension or rolling pressure. The cellulose solution may be applied by the upper roll or by means of a sprayer pipe. Artificial pores may be produced in the product by needle rolls.

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CORRECTION.

In the January number, the election of Messrs. J. Houston Duffy, Alfred J. E. Schmidt, and Reigen Matsuo was announced. They were elected *active* members, not associate, as indicated.

CHANGES OF ADDRESS.

William Pollard, to Andrews, Cherokee County, N. C.
Adolf Schubert, to 33 Emerson Ave., Glendale, L. I., N. Y.
Leon W. Morrow, to South St. Paul, Minn.

BOUND VOLUMES.

Copies of Vol. II are now ready, bound in half leather and cloth, uniform with previous volumes. These will be furnished to members in exchange for sets of unbound numbers at $1.50, delivered, if the unbound numbers are sent to the manager at Ridgway, carriage paid. If sets are incomplete, add 25 cents for each missing number. The increase in exchange price is rendered necessary by the increased cost of binding. Copies of all other volumes are also in stock and may be had on the same terms. In ordering, please state whether cloth or half leather binding is desired.

ALUM TANNAGE.

By Ed. Nihoul.

One of the inconveniences of using leather tanned with alum is its sensitiveness to the action of water. Professor Procter well explains the cause of this fact (*The Making of Leather,* 1914, p. 83) by the dissolving action of the water on the salt accompanying the alum: "If the salt is removed by washing, the acid swells the pelt, as in pickled skin, a portion of the basic alumina salt returns to the normal condition and washes out; the tannage goes back and the leather dries hard." It seems, in effect, that the form in which the basic salt of aluminum is fixed by the hide lends itself to dissociation by the action of the water, with re-formation of the normal salt which easily washes out, and the formation at the same time, in varying quantity, of another salt of aluminum, more basic and therefore less hydrolyzable, which is probably independent of the hide substance.

It is well known, however, that alum leather "washes out" with more difficulty when it has been kept longer, and that this leather improves with age. It may be asked whether this result would

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* *Collegium,* London Edition, 1916, pp. 178-90. Translated for the Journal of the A. L. C. A.

not be arrived at more quickly if the hide were kept in the tanning solution, or the fibers kept in contact with this solution, longer than is now done. It may also be questioned whether it would not be well to check the hydrolysis of the compounds with which the hide fibers are impregnated by protecting the fibers from the action of water by processes which have lately been suggested for fibers of a vegetable nature. For this purpose it may not be without interest to examine the chemical side of alum tannage, particularly for those members of our association (I. A. L. T. C.) who are not chemists by profession.

Hydrolyzing Action of Water on Salts.—It is supposed that in dilute solutions the solvent frequently separates the molecules of the dissolved substance into very active groups called ions. H_2SO_4 will exist in such a case in the form of ions of H_2 and ions of SO_4 and KOH in the form of ions of K and ions of OH. These uncombined groups naturally show more chemical activity than the more complex chemical groups H_2O, SO_3, K_2O. A dissolved substance is the more active in proportion as it is more completely dissociated by water, that is to say, it is more active in proportion as there are more free ions.

Consider for example a normal solution of hydrochloric acid, that is to say, a solution having a number of grams of acid per liter equal to the molecular weight of the acid, (36.45), and a normal solution of hydrofluoric acid, (20 grams per liter). Studies of the osmotic pressure and electric conductivity of these solutions show that the hydrochloric acid is dissociated to the extent of 80 per cent. of the acid present, only 20 per cent. remaining in the combined condition, while the hydrofluoric acid is only dissociated to the extent of 3 per cent. under the same conditions. The theoretical conclusion from these facts is that hydrochloric acid is *stronger* than hydrofluoric, although fluorine may be classed as having greater chemical activity than chlorine. In fact, hydrochloric acid attacks fluorides with the disengagement of hydrofluoric acid.

The *strength* of an acid or base is therefore measured by the number of free ions in equal volumes of normal solutions. On the other hand, dissociation is a direct function of the dilution. A tenth-normal solution of hydrochloric acid is dissociated to the extent of 93 per cent., and a similar solution of hydrofluoric acid to the extent of 13 per cent. A tenth-normal solution of acetic acid is dissociated to the extent of 1.3 per cent. It is boric acid which is at the bottom of the list, with a dissociation of only 0.013 per cent. Analogous differences are observed among the bases. A tenth-normal solution of caustic soda is dissociated to the extent of 90 per cent., while the corresponding figure for a solution of ammonia of the same normality is but 1.3 per cent. Acid solutions are characterized by ions of hydrogen, while solutions of bases have ions of hydroxyl, OH. Hydrogen ions redden a solution of litmus, while hydroxyl ions turn such a solution blue.

In the case of the compounds of acids and bases, otherwise called salts, there may be three conditions. If the base and the acid are of equal strength, they will be equally dissociated, as in the case of potassium sulphate, but if the strengths of acid and base are unequal, the result will be quite different. Since water itself has both H and OH ions, the saline solution may be regarded as due to the uniting in proper proportions, of an acid and a basic solution. If the H ions predominate, the solution will have an acid reaction, reddening litmus. This is the case with the mineral salts of aluminum, for instance, alum, which is merely an association of $Al_2(SO_4)_3$ with K_2SO_4. On the contrary, if the base is stronger than the acid, OH ions predominate, and the solution shows a basic or alkaline reaction; it turns litmus blue. These phenomena are in reality a consequence of the fixation of a molecule of water upon the saline substance in solution, which reconstitutes, at least potentially, the base and the acid which have given it birth. It is to these phenomena of hydrolysis that we must attribute the formation of basic salts. The sulphate of aluminum in the alum dissociates itself more or less fully after dilution into sulphuric acid on the one hand and aluminum hydroxide on the other. The latter remains in colloidal solution in the form of a *hydrosol*. (See *Collegium*, London Ed., 1915, p. 174.)

Transformation of Hydrosols into Hydrogels.—When a colloidal solution flocculates, that is to say when its particles agglomerate to such an extent that they can no longer remain insensible to the action of gravity, being insoluble, it isolates itself from the solvent in the form of a hydrogel. This phenomenon may be produced in different ways.

I. A simple method, but not of general application, is to bring the liquid to boiling. This is the method commonly used in chemical analysis to make precipitates which will not form in the cold, or to obtain quantitative precipitation. Sometimes the base set at liberty is capable of combining with a part of the non-dissociated salt, forming compounds whose basicity is limited by the amount of acid liberated at the same time. The base can be isolated by eliminating the acid in question either by the use of alkali or by evaporation if the acid is volatile. If for instance we evaporate a solution of aluminum chloride, the acid of which is easily carried over by steam, the residue from the evaporation will be only aluminum hydroxide, insoluble in water. This phenomenon depends on temperature. To secure such a result with magnesium chloride, it is necessary to exceed the boiling temperature, and the residue is the oxychloride of magnesium.

In alum tannage it is hardly possible to admit the application of heat, for the purpose of transforming hydrosols to hydrogels, for alum leather as at present understood does not bear the action of hot water. Chrome leather, on the contrary, if it is thoroughly tanned, may be submitted to the action of boiling water without losing its tanning material or its suppleness. In fact, this test is even used as a criterion of the quality of chrome tannage. One may compare this difference in the behavior of alum and chrome leathers with the fact that chromic hydrosol held in solution by the presence of a caustic alkali is almost completely transformed by boiling into a hydrogel, in the presence of a sufficient quantity of water, while under the same conditions the aluminum hydrosol remains unaffected, being more sensitive to the deflocculating action of the OH ions. It is probable that this difference is due to the nature of the metals themselves, for we may compare the fact that strongly calcined chromium hydroxide resists the action of strong acids, which is not the case to the same extent with aluminum hydroxide.

II. In colloidal solutions, the constituents are grouped in complex molecular agglomerations called micelles.[1] These micelles are carriers of electric charges like ions, and it is the repulsive actions of these charges which maintain them in suspension. If an electric current is passed through the apparent solution, the micelles of the same sign are carried toward one pole, and presently the volume of the agglomerating particles becomes sufficient for them

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[1] This term seems equivalent to Zsigmondy's "amicrons." Tr.

to obey the pull of gravity, and the solution flocculates and precipitates. This process would under present conditions be rather costly for use in tannage.

III. A third method in use for producing flocculation is to add saline substances to the colloidal solutions, especially strongly ionized salts, like the chlorides. Whatever may be the base combined with chlorine, whether a feeble one like ammonia or a powerful one like soda, these compounds are ionized in tenth-normal solution to the extent of from 92 to 93 per cent. The electric charges of the ions behave in a manner analogous to an electric current. or at least they produce the same results in saturating the charges of the micelles. All electrolytes produce more or less completely the same result, and flocculation takes place not at electrodes but throughout the mass, and the hydrogel is precipitated.

This phenomenon has been known a long while both in chemical and industrial practice. In mineral analysis it frequently happens that difficulties present in the separation of the heavy metals as sulphides, especially mercury. At the end of the washing particularly, a part of the compound passes through the filter with a disconcerting persistence, in a colloidal condition. In order to obtain rapid and easy filtration it is sufficient to add to the liquid containing the sulphide in suspension a little ammonium chloride and stir it thoroughly, or else to add the same salt to the wash water. Another example is the filtration of the mixed basic acetates of iron and aluminum, in which case it is advisable to moisten the filter beforehand with a concentrated solution of ammonium acetate. Another instance is found in soap manufacture. In order to separate the soap from the water and glycerine in the early stage of the manufacture, salt is stirred into the pasty mass, in which the soap is in a colloidal form. The soap agglomerates and floats to the surface. In alum tannage, an analogous fact is observed. The presence of salt in sufficient quantity not only results in checking the swelling of the pelt, but also transforms the hydrosol into hydrogel.

Change of Allotropic State of Hydrogels.—A property which characterizes the hydrogels is their sensitiveness to the action of reagents. They exist as very fine, amorphous particles, and are therefore in a state of aggregation which renders them particularly easy of attack by reagents. This is especially true when they are freshly precipitated. Silica is a typical example. SiO_2 in the crystalline state resists nearly all agents, physical or chemical. In the hydrogel state it reacts greedily not only with alkaline bases, but with lime and with hydrofluoric acid. The reaction takes place in the cold, and with the disengagement of a very perceptible amount of heat. Al_2O_3 crystallized in the natural form, (corundum), or made in the electric furnace, has properties similar to quartz, while the hydroxide of aluminum, like those of iron and chromium, reacts instantly with acids, even very dilute, by reason, it is true, not only of its state of subdivision, but also perhaps of its water of constitution.

After the hydrogels have been precipitated for a time, these reactions become more difficult, and at the same time the product changes its physical properties. Generally the density increases, and at the end of a long enough time, the particles are sometimes found to have oriented themselves, abandoned the amorphous state and become crystalline. Two physical agents, heat and pressure, are able to hasten the process.

I. *Heat.*—Professor Spring has shown that bismuth sulphide, which, left to itself, takes the crystalline form in the course of some years, crystallizes in three days when the temperature is raised to 265° C. It is well known that precipitates such as sulphate of barium, which pass easily through a filter, have only to be boiled, and that the hydroxides of iron and aluminum filter much more rapidly and cleanly if they are kept for a time in the liquid at the boiling temperature. Finally, it is well known that clay, which owes its plasticity to the hydrogels of aluminum, loses this property when it has been heated above a certain limit.

Similar results may be obtained more slowly by the use of temperatures which are but little above the ordinary living temperatures. The case of ammonio-magnesium phosphate may be cited. It may be obtained directly in the crystalline form and filtered in a brief time when the precipitation has been made at the boiling temperature, but in order to obtain a quantitative precipitation in a form which can be filtered and washed, the precipitate, obtained in the cold, is allowed to stand a day or two in the liquid from which it has been precipitated. Harvey recommends the same method in the determination of phosphates by the ammonium molybdate method. (*Collegium*, London Ed., 1916, p. 151.)

II. *Pressure*.—It is natural that pressure should cause the particles to come closer together and agglomerate. It tends therefore to increase the density of the substances pressed, and to make them pass into a differeut allotropic state. The action of pressure is well-known in the transformations of carbon into its different varieties. It is by causing the crystallization of carbon under considerable pressure that Moissan has produced the artificial diamond. It is also due to pressure that artificial graphite is formed during the solidification of metals or molten carbides in which amorphous carbon has been dissolved. Pressure not only results in increasing the density of carbon when it is thus obtained in the forms of diamond and graphite, but also increases their resistance to physical and chemical agents, since diamond and graphite are harder and more difficult to burn than amorphous carbon. The influence of pressure is responsible for a great number of similar transformations. The researches of Spring have shown that the majority of these reactions which cannot be brought about by the elevation of temperature are capable of being produced in the cold by means of pressure.

We may regard as a somewhat parallel class of phenomena those pointed out by Professor Procter in his recent researches on the physiological effects caused by osmotic pressure in the interior of the tissues. These phenomena are in many cases brought about by chemical reactions which persist after the death of the tissue, and we may suppose that similar transformations take place in the hide impregnated with salts of aluminum and common salt. From this point of view it is not difficult to account for the improvement of alum leather with age.

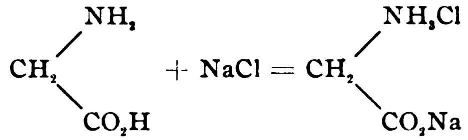
In this connection it may be interesting to recall a fact perhaps not very closely related, that hydroxide of aluminum simply by lying in a solution of an electrolyte, such for instance as ammonium chloride, (this salt seems especially well adapted to occasion the phenomenon), may be made immune from attack by bases, and even by acids if they are cold and dilute. Acids will not dissolve without residue aluminum hydroxide thus transformed without a certain concentration and the application of heat. This same transformation is brought about in aluminum hydroxide by preserving it in the dry in the absence of any electrolyte, but it is much slower, not being manifest under 3 or 4 months. The electrolyte, ammonium chloride in particular, acts as an accelerator. The considerable ionic pressure in the liquid medium and its superficial surface tension influence the phenomenon, which is a question of catalysis. It is probable that in all cases catalysis as well as the other phenomena mentioned above is concerned in fixing alumina in alum leather.

Amphoteric Character of Alumina and the Deflocculation of Aluminic Hydrogels.—It is generally admitted that alumina may react as a base and as an anhydride, and possesses the special character of behaving in the presence of strong bases like an acid. Doubts have been raised recently in regard to the acid character of alumina. At the last congress of applied chemistry, Mahin described some experiments which seemed to show that the colloidal character of $Al_2(OH)_6$ is a factor more important to consider with regard to the solubility of this hydroxide in bases than the amphoteric character of the hydroxide. In fact it is even doubtful whether alumina is amphoteric at all. In every case the solutions of alkaline aluminates precipitate crystalline alumina on contact with a trace of carbon dioxide, and the precipitation once begun continues even in the absence of carbon dioxide. The phenomenon is hastened by agitation, as if we had to do here with a supersaturated solution.

The deflocculating action of OH ions on the aluminic colloids (kaolin, clays, etc.,) has been well known for a long time in the ceramic industry, but the alkalies, whether cold and dilute or hot and concentrated are not able to restore plasticity to clay which has been heated above 400° C. Also in the experiments of Mahin, excess of caustic alkali had no action on the allotropic modification of alumina which appears in the medium on contact with traces of carbon dioxide.

However long alumina may have been in the state of a hydrogel, alkali restores it to the state of a hydrosol, and this explains the fact that washing alum leather with an alkali, however weak and however dilute, instead of rendering the product more basic and therefore more insoluble by neutralizing the combined acid, has a much greater detannizing effect than washing it with water. The case is exactly the same with chrome leather. The slightest excess of alkali gives also to this leather the aspect after drying, of a detannized material. The deflocculating action of OH ions may be avoided in neutralizing chrome leather by using for the purpose, compounds whose ionization is slight. Borax has been highly recommended, but the mixture recommended by Stiasny seems preferable on all accounts; (ammonium sulphate and sodium carbonate in equi-molecular mixture). This mixture furnishes by double decomposition ammonium carbonate, a compound made up of a feeble base and a feeble acid.

Chemical Action of Salts on the Proteids.—Having studied the possible action of alum on the hide fibers, it may perhaps be worth while to see how proteids in general behave toward saline substances. Salts are retained with great energy by albuminoid substances. Is this phenomenon physical or chemical? The presence of the groups NH_2 and CO_2H in their constitution seems to demonstrate the possibility of a double chemical combination analogous to that of glycocoll with sodium chloride:



$$CH_2\begin{cases} NH_2 \\ CO_2H \end{cases} + NaCl = CH_2\begin{cases} NH_2Cl \\ CO_2Na \end{cases}$$

Wurtz, who first prepared albumin in a pure state, showed that it was not possible to separate from the albumin by means of dialysis the salts it had absorbed. He showed further that if the albumin is subjected to dialysis while in the alkaline state it becomes acid, and that if it be again rendered alkaline and again subjected to the same process, it again becomes acid. Albumin seems to let go of alkalies easily, but to hold fast acids and salts. There is no doubt that this smaller affinity for alkalies is shared in by gelatine and hide, and that bases such as alumina, less strong than the alkalies, have even less affinity for hide.

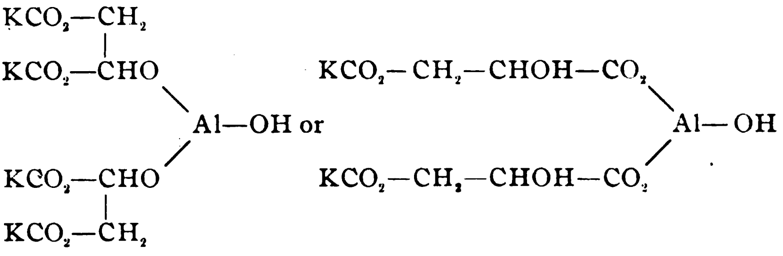
Suppose a salt such as the sulphate of aluminum in alum to be partially hydrolyzed by water: the free acid is eagerly taken up by the hide tissue, while the released alumina, which is in the state of a hydrosol in the liquid, enters into combination with a non-hydrolyzed portion of the salt to form a basic salt. The hydrolysis of the neutral salt continues until the hide has absorbed all the acid which it is capable of fixing. It is very probable that if we had to do here with a salt of neutral instead of acid reaction, the alumina in such a hydrosol would not be absorbed by the hide, or only absorbed in very small amounts. Washing with water would suffice to eliminate it. If the basic salt formed under these conditions is in the form of a hydrosol, the effect will be the same as if it had never entered into combination with the hide. If it is in the form of a hydrogel, the process will be, perhaps, a little longer. The water will at once eliminate the unhydrolyzed salt, some more neutral salt will then be formed at the expense of some basic salt and of the acid which impregnates the fibers, and so on, until finally the greater part of the material will be eliminated; but if the hydrogel, whether it be isolated or combined with the hide, undergoes an allotropic modification, complete washing out will not be possible, for the basic salts or even the base itself, which are formed, may become less and less soluble as the neutral salt passes into solution.

Discussion of the Principal Combinations Possible Between Compounds of Aluminum and Hide.—I. Suppose first the case of uncombined alumina: it is in solution in the form of a hydrosol and may therefore penetrate the hide. Two cases present themselves. (1) The alumina may combine with the hide. At first glance this seems improbable, in view of the hydrolysis phenomena described in the previous paragraph, of the relatively much less basic character of alumina compared to the alkalies, and the state of aggregation in which it is found. It may be granted that alumina might react with the COOH group of the hide substance just as it does with the same group of acetic acid. In this case the reaction may evidently be hindered not only by the high molecular weight of the hide substance, but also by its insolubility. It would seem that such a process could hardly be more rapid than tannage with vegetable tannins, but practice shows the contrary.

2. In certain special cases it has been shown that freshly precipitated alumina can combine rapidly with certain organic substances of quite complex formulas. This is notably true of coloring matters. The resultant substances, called lakes, have not well-defined composition, and are characterized by their insolubility in water. In many cases the lakes resist the action of soaps, and of liquid acids and alkalies. It is true that these reactions are not peculiar to alumina. Many metallic oxides and even some compounds of the fatty acids may behave in a similar fash-

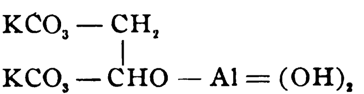
ion. On the other hand, the lakes resist washing out, while the compounds of aluminum fixed on alum-tanned leather do not.

In the case of certain oxygenated organic compounds, the reactions are better defined. To these we may compare hide-substance, which really contains more oxygen than nitrogen. (The formula given for gelatine by Professor Procter is $C_{35}H_{57}O_{13}N_{11}$.) In every case it has been shown that the aluminum is present in these compounds in the form of a complex ion, and they therefore do not react in the same manner as the ordinary salts of aluminum. Well-known among these are the combinations with the oxyacids and their salts, with the aldols, polyatomic alcohols, etc. These substances react with alumina to give rise to basic salts, sometimes of very high molecular weight, and the reaction takes place not only with the hydrosol but also with the hydrogel. Let us suppose the simple case of malate of potassium. Two alternatives may present themselves: *a*, there is a great excess of malate; we obtain one of the two following compounds, according as we suppose the intervention of the OH or the COOH groups of the malic acid:



The complex anion containing aluminum is therefore monovalent.

b, there is a less excess of malate, or the solution is more dilute; we then obtain:



$$\begin{array}{l} KCO_3-CH_2 \\ \qquad\ \ | \\ KCO_3-CHO-Al=(OH)_2 \end{array}$$

$$\text{or } KCO_3-CH_2-CHOH-CO_2Al=(OH)_2.$$

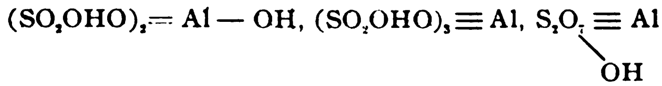
The aluminic ion is in this case bivalent and the compound is more basic. The compounds formed in the first alternative are soluble in water, although basic. As to the second alternative, it is necessary to recall that aqueous solutions containing either electrolytes or even semi-electrolytes undergo with ease what is called step by step (From *échelonée*) dissociation, resulting, in the presence of sufficient water, in isolating the groups $Al(OH)_3$ or $Al_2(OH)_6$. These remain under the form of hydrosols. They are, in this condition, soluble in water, but their flocculation may be effected.

These reactions are not peculiar to aluminum, and several substances resist precipitation by the action of malates and tartrates. Some similar reactions are notable in the case of ferric salts. For instance, the solubility of the basic malates, tartrates and citrates of iron prevents the precipitation of iron in the form of basic acetate, when the corresponding alkaline salt is added to the solution containing iron.

In the case where similar combinations involve fibers of animal origin, soluble products tend to be produced, easily washed out. These products are capable in certain cases of being converted into hydrogels by the action of saline substances. When, however, the alumina is washed out of freshly tanned alum leather, it is difficult to detect any solution of the hide fiber. It is therefore probable either that the compounds are destroyed by acid at the moment of release from the hide fiber, or else that these combinations do not exist. In the latter case it would be necessary to admit that in the sort of combinations which aluminum is able to make with oxygen-containing substances, there are more OH groups than COOH groups participating in the reaction. However, the polyatomic alcohols (glycerine, mannite, erythrite, etc.,) react in analogous fashion, and the crystalline hydrate which results from evaporation of the chloride even dissolves in ethyl alcohol. It has not, on the other hand, been demonstrated that hide substance possesses OH groups in its constitution, although, according to the theory of Löw, it possesses its oxygen in another form than as COOH groups, notably in the form of aldehyde groups.

In all probability, alumina does not enter directly into combination with hide substance, but combines by preference with a part of the non-hydrolyzed neutral salt to produce basic salts. If we consider the alum alone, the salt formed is basic sulphate of aluminum. If we consider the mixture of alum or sulphate of aluminum and sodium chloride, the salt formed may be a chlorobasic compound.

II. Suppose instead of uncombined alumina, we have the basic sulphate of aluminum. All production of basic sulphate implies the simultaneous liberation of a quantity of sulphuric acid equivalent to the quantity of base fixed by the neutral salt. Now it is quite certain that in the process of the establishment of equilibrium between this acid and the neutral salt, a part of the salt passes into the state of acid sulphate, in such fashion that the solution contains, beside H_2SO_4 and $Al_2(SO_4)_3$, other compounds, such as



$$(SO_2OHO)_2 = Al - OH,\ (SO_2OHO)_3 \equiv Al,\ S_2O_7 \equiv Al \diagdown OH$$

etc., which all retain one or many quite active acid groups, and which all contain aluminum. At first sight we might expect that these would be able to react with the hide fiber in the same manner as the acids themselves, in such a way that the formation of basic salts would be accompanied by a fixation of alumina on the fibers. One might conclude that, once these groups were fixed on the hide fiber, the aluminic hydrosol or even the sols and basic gels would be in a condition to react more or less rapidly or more or less slowly according to circumstances, to give rise to basic compounds of which the hide substance itself would be a part.

To this hypothesis the objection may be made that the compounds of alumina and ammonia do not exist in a stable state, being hydrolyzed by water. For example, if ammonium chloride be added to a solution of alumina in an alkali, (the solution commonly spoken of as "alkaline aluminate"), the alumina is precipitated. We have also seen that the solubility of alumina in solutions of caustic alkali is not due to a combination, but to the deflocculating action of the OH ions. In the presence of ammonium chloride in sufficient quantity, the OH ions of the fixed alkali disappear, and potassium chloride and ammonia are formed. The ammonia if feebly ionized, and the small number of OH ions liberated is not sufficient to deflocculate the alumina, which passes from the state of a hydrosol to that of a hydrogel. The objection is thus not sustained. Besides, there are double salts, notably ammonium alum, into which aluminum and ammonia enter, which are perfectly stable.

The combinations in question, if combinations they are, are hydrolyzable at the beginning, and do not gain stability with age except in the presence of salt. It is important also to note that leather tanned with alum or with sulphate of aluminum alone remains rigid and imperfectly tanned. It is appropriate therefore to examine in what manner sodium chloride may benefit alum tannage.

III. Suppose the case of normal tannage, in which sulphate of aluminum is mixed with sodium chloride. Between these two salts there is established as soon as they are placed in solution the following chemical equilibrium:

$$Al_2(SO_4)3 + 6NaCl \rightleftarrows Al_2Cl_6 + 3Na_2SO_4.$$

Since aluminum chloride has, like the sulphate, an acid reaction, hydrochloric acid is liberated in the solution, and since, other things being equal, this acid is ionized to a greater degree than sulphuric (92 per cent. against 62 per cent.), it will be absorbed more rapidly and in greater quantity by the hide. The result is that the above reaction has a tendency to proceed from left to right, especially if the salt is present in sufficient quantity in proportion to the sulphate of aluminum.

The employment of this mixture has the following effects: First, to make the hide absorb a greater quantity of acid and consequently to increase the internal pressure. There are reasons for believing that this increase of pressure increases the activity of chemical reactions if any are in process; second, to liberate a greater quantity of aluminic hydrosol, and consequently to increase the quantity of basic salts formed, or else to give rise to salts of a more basic character, and at any rate to cause their more rapid formation; third, since there is more acid liberated, to form at first a greater quantity of acid salt, which is apparently absorbed by the fibers, assuring a more perfect tannage; fourth, to leave in the tissues a notable quantity of aluminum chloride.

The first three points favor the tannage; it remains to examine the fourth point. In the anhydrous state, aluminum chloride is strongly hygroscopic, but it is capable of forming with water a compound of the formula $Al_2Cl_6.12H_2O$, which does not have this inconvenience to the same extent. There is also a double chloride of aluminum and sodium, whose constitution is similar to cryolite, and whose formula is $Al_2Cl_6.6NaCl$. Aluminum chloride is capable, like the sulphate, of forming a basic salt, the oxychloride, $AlOCl$.

Another interesting point to notice is the fact that aluminum chloride is an agent of condensation of the first rank. Many chemists have employed it in the preparation of ketones. Friedel and Kraft have employed it in the synthesis of aromatic compounds. Stoklasa and Gabriel Bertrant have shown the catalyzing power of aluminum sulphate in the nutrition of plants. This property is without doubt the cause of the action of aluminum salts in connection with vegetable tannage.

Finally, Mentchutkin has shown that aluminum chloride is capable of reacting with many organic substances particularly those of the cyclic series, to form addition products having well-defined formulas. Kallukow has recently studied the analogous combinations between aluminum bromide and the aromatic amines. A great number of molecules of organic substances are capable of uniting with one molecule of aluminum bromide. The same observation has been made by Mentchutkin in the case of the chloride, the number of molecules combining being a function of the temperature. It must be remarked that a property common to all these compounds is their inability to withstand the action of water.

IV. It remains to examine the possible case of a physical union between alumina and hide substance. The phenomena of adsorption seem to play the principal role in the assimilation of sulphur by the hide in two-bath chrome tannage and in the Jettmar process. We shall examine in a future note how far similar phenomena may be produced in the tannage with alum and aluminum sulphate.

The insistent fact is that alum leather does not resist the action of water, and we may hope to minimize this defect in one of two ways, either by rendering the aluminum compounds involved more insoluble or by enveloping the fibers with a substance resistant to washing. The second method is the only one which has had any success so far, and this has been by the use of fats, which have the effect of filling the tissue and preserving its suppleness. We may note in this connection, without attaching more importance than it deserves, the method recently devised by Agostini for dyeing threads and tissues. He introduces into the material by the aid of an oil the substances necessary to form an insoluble soap, in an uncombined state. The constituents do not combine until in the process of drying, the temperature reaches a certain point, and then by their union they form a substance of considerable adhesive power, at the same time fixing on the fiber the foreign substances with which they have been mixed. The products so far obtained have been completely insoluble and resistant to water and washing.

THE TREATMENT OF ANTHRAX.

By Charles R. Oberfell.

On account of the general lack of information on methods of treatment for Anthrax the COUNCIL of the A. L. C. A. thought it advisable that as much information as possible on this subject be collected and subsequently published in this JOURNAL. The data here presented are incomplete and this is due partially to the fact that most of the medical men who were asked to contribute failed to respond. Since the collection of this material was begun, the National Association of Tanners has issued a pamphlet on the treatment of Anthrax which is quite complete and this has been quoted freely.

Anthrax is an acute infectious disease caused by the *bacillus anthracis.* It is a wide-spread affection in animals, particularly in sheep and cattle; in man it occurs sporadically and usually as the result of incidental inoculation with the spores. The organism is rod-shaped, nonmotile, and shows spore formation. The bacillus is easily destroyed but the spore is particularly resistant, and may live for years in the soil.

The disease does not occur spontaneously in man but always results from infection through the skin or intestines or rarely through the lungs. At the point of infection there develops an abscess or carbuncle. This infection spreads like any other form of sepsis or blood-poisoning. A characteristic of the disease is the lack of pain and the fact that the patient retains his mind clearly to the end.

Statistics indicate that about 90 per cent. of the cases of anthrax result in a cure. It is also true that on account of its rarity the average physician has never dealt with a case and is unable to make a positive diagnosis. A more general dissemination of knowledge of the symptoms and of successful methods of treatment will probably increase the percentage of cures.

Anthrax is an infectious disease that cannot be epidemic and is probably the rarest of occupational diseases.

Symptoms and Diagnosis.

1. "(Also called—*English:* Mycosis Intestinalis; splenic fever; woolsorter's disease; malignant pustule; anthracaemia. *French:* Charbon; sang-de-rate; mal-de-rate; fievre charboneuse; charbon bacteridien; anthrax. *German:* Milzbrand.)

External anthrax, the most common form, is the result of direct injury and infection on those portions of the body habitually exposed, *i. e.*, face, neck and arms. It appears usually in one spot only. The time from the injury until the symptoms are noticed may be from 1 to 3 days.

At the point of infection, a small red pimple first appears, *always* accompanied by itching and burning, followed (perhaps the second day) by a small flat water blister, which may be surrounded by redness and swelling. Call a physician. The point to remember is, that no matter how great the swelling, there is little or no pain, even on pressure.

The general symptoms vary, and bear no relation to the extent of the local injury—a small injury may cause death in 4 days—a large injury may end in complete recovery.

In severe cases, the symptoms showing general infection may come on in 24 hours, in other cases a few days to a week. The higher the fever, the better the prognosis. There may be no fever, but even a sub-normal temperature."

2. "The skin lesion appears first as a dark spot ⅛ in. in diameter, surrounded by a pinkish areola 1 in. in diameter. The skin at the point of the lesion is *not swollen* or elevated and there is *no pain* for the first few hours. Later there is a stinging, burning sensation as if the patient had been bitten by an insect. The

character of the lesion does not materially change as the disease progresses, but the surrounding tissues become enormously swollen and very painful. A smear should always be taken from a needle-point puncture of the blackened center of the lesion and examined under the microscope for the presence of the anthrax bacillus. If this is found the diagnosis is proven."

Dr. Wakeman in commenting further says that his success in the treatment of anthrax is due to two things: Early diagnosis and early excision.

Treatment.

3. "Early diagnosis is most important. Have all pimples and abrasions or injuries to face, head and neck examined under the microscope at once. If you wish to be very scientific or sure of diagnosis, inoculate a white rat or guinea pig.

Operation: First cover lesion with collodion, cleanse the surrounding skin with 10 per cent. carbolic acid, followed by alcohol. Use a cautery (preferred) or the knife, making the line of incision at least ½ in. from border of lesion and cut deep under lesion. Swab wound with pure carbolic acid, followed immediately with full strength alcohol. Place an alcohol sponge in wound for a few minutes, apply a moist bichloride dressing to wound. *Remember,* cut early—cut wide—cut deep.

Serum treatment is of great benefit used jointly with the incision method. Mulford's (Philadelphia) Anti-Anthrax Human Serum is injected as per instructions. Always have fresh supply at hand. Mulford will exchange fresh for old without charge."

4. "Immediately a diagnosis is made an incision of the lesion is performed. The incision is made wide, at least ½ in. beyond the border of redness and carried completely through the skin, care being taken not to infect the instruments. The wound is left open to granulate. Simple dressings are applied. The patient is allowed to return home after 3 days, provided the case is operated within 12 to 18 hours after the appearance of the lesion."

5. "I have in the last 8 years attended over 42 cases of anthrax affecting the cutaneous and cellular tissues. The part is thoroughly but gently washed with 1 : 2,000 mercuric chloride solution, dried well, then swabbed with 10 per cent. tincture of

iodine and some alkali applied. This is repeated daily for several days until the slough has come away. It takes about 2 or 3 weeks for an ulcer to heal, which it does with very little scar as compared with the tissues involved. No systematic treatment is necessary other than cleaning out the bowels, though some require strychnin and alcoholic stimulants. If the trachea becomes much involved, nothing will prevent death by suffocation. It has been my experience that if the vesicles are kept unruptured it is better for the patient. The fatal cases I have seen were those in which the vesicles had been ruptured."

Treatment of Tannery Sores.

6. "Any bruise, pimple or other breaking of the skin at any point should have the immediate attention of the tannery physician. 'An ounce of prevention is worth a pound of cure.'"

(*a*) A wash for disinfecting any suspicious sore, cut or bruise on hands, face or body where exposed to suspected hides.

Make a solution of bichloride of mercury 1 to 10,000 (with water), add to this solution common salt to point of saturation. Make saturated solution of camphor in absolute alcohol (called spirits of camphor). Pour bichloride of mercury and salt solution into the spirits of camphor up to the point of precipitation, keeping the solution clear by adding additional spirits of camphor if precipitation is reached. Use the above combined solution as a wash; and in case where infection is feared, bind with adhesive plaster absorbent cotton saturated in the solution over the wound. When cotton is dry throw away and renew. Wash wound with alcohol before renewing.

(*b*) Poultice to use on sore where anthrax has developed.

Take a dish of common salt and wet the same with spirits of camphor until about the consistency of mush. Apply directly to the sore, plaster approximately 1 in. thick of this material, binding the same on with suitable bandages. Change every hour, night and day, until the swelling is materially reduced and the temperature restored to normal. After each application wash thoroughly with alcohol before renewing.

In case of anthrax, in addition to the above poultice, give internally Lachesis Trigonocephalus in 30th potency, 4 grains every

3 hours. This can be obtained of Boericke and Tafel, Philadelphia.

The following is merely of interest in relation to this subject:

A Missionary's Observation.

7. "China missionaries often come in contact with a fatal form of anthrax. It comes sporadically as a malignant pustule on or about the lip and requires usually less than a week to cause death. Heretofore our American physicians in China have said there was nothing to do for it but cut it all out in the initial stages. As it is difficult to get this accomplished, few, if any, are saved. In a case in which I saw a patient die with it, after the third or fourth day, not only the face and head but also the whole body was swollen, and death occurred shortly afterward.

In 1915 there occurred in the city and district of Haichow, China, an epidemic of rinderpest. The medical missionary, Dr. S. L. Morgan, was called in by the officials to fight it He discovered from some source that when the rinderpest attacked people, it could be treated with powdered ipecac as a poultice. He tried it and found it eminently successful. On hearing him relate his experience, I asked if he thought the ipecac would cure this other form of anthrax. He thought so. I therefore made a practice of carrying the ipecac in my first-aid package. Some weeks afterward, being in a distant town, a man came to me with this fatal anthrax, appealing for help. I poulticed him two days successively. The pustule immediately stopped growing, and became soft. On leaving I gave him an extra dose of the ipecac in case of need. The man himself was entirely cured, and, as I afterward learned, the extra dose cured another man. So far as I know this is the first time that fatal anthrax has been treated with ipecac, and it is the only cure I have ever heard of."

1. From Pamphlet issued by the National Association of Tanners.
2. Dr. B. R. Wakeman, Sanitary Supervisor N. Y. State Dept. of Health.
3. Pamphlet of National Association of Tanners.
4. Dr. B. R. Wakeman, Sanitary Supervisor N. Y. State Department of Health.
5. Dr. John Palmer, Jr., Wilmington, Del., J. Am. Med. Soc., Vol. LXV, No. 19, p. 1670.
6. Pamphlet N. A. T.
7. J. Am. Med. Soc., LXVII, No. 13, p. 969.

Philadelphia, Pa., Dec. 26, 1916.

THE STERILIZATION OF TANNERY WASTES.*

By D. D. Jackson and A. M. Buswell.

The treatment of tannery effluents has up to the present time been limited to the removal of putrescent matter and suspended solids. The aim has been simply to prevent a nuisance. With the exception of a few investigations[1] made abroad there has been little recognition of the possibility of the spread of anthrax from tannery wastes.

Anthrax, or charbon, may be defined as an infectious disease which is caused by specific bacteria known as anthrax bacilli, and which is more or less restricted by conditions of soil and moisture to definite geographical localities. While it is chiefly limited to cattle and sheep, it may be transmitted to goats, horses, cats, certain kind of game, and even to man. Smaller animals, such as mice, rabbits, and guinea pigs speedily succumb to inoculation. Dogs and hogs are slightly susceptible, while fowls are practically immune. The variety of domesticated animals which it may attack makes it a question of great economic importance.

Anthrax is a disease that is widely spread throughout the world, and in the United States is coming to be recognized as a matter worthy of extensive scientific investigation. In certain sections it is more frequent than in others. It appears to be particularly prevalent in the Southern States, and since no determined effort has been made towards its suppression it seems to be on the increase, its presence now being recorded in localities where it has never before been known.

The anthrax bacillus belongs to the group of spore-bearing bacteria, *i. e.*, it may produce small oval bodies known as spores, which are highly resistant to heat and to the action of chemical disinfectants. In the disinfection of water supplies and domestic sewage, we have as yet considered only the destruction of the non-spore bearing group of intestinal bacteria. The problem of tannery waste disinfection is essentially a new one in that it is necessary to kill or attenuate these resistant bacterial spores.

The importance of the problem may readily be seen from the following statistics: In Germany there were in the period 1900-

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* Read before the Sanitary Engineering Section, American Association for the advancement of Science, New York Meeting, Dec. 26-30, 1916.

1908, 1,042 cases of anthrax in man and 49,458 in animals. In England there were 162 human cases and 26 deaths from 1910 to 1912. In France during the same period there were 134 cases. In Russia, 1904-1909 there was an average of 16,000 cases per year. In the United States from 20 to 25 human deaths from anthrax have been reported yearly.

Anthrax among cattle has not been unusual in New York State, and for many years certain foci of the disease have been recognized. In 1912-13, there were 27 cattle outbreaks in 15 counties with 116 deaths; in 1913-14 there were 35 outbreaks in 16 counties with 83 deaths—a total of 62 outbreaks in 2 years in 21 counties, with 189 deaths. Only 10 counties in the 1913 list responsible for 22 outbreaks and 80 deaths appear in the 1914 list with 29 outbreaks and 60 deaths.

About 2 years ago an epidemic of anthrax was said to have been caused by the infection of meadows by the waste from a tannery. The authors were requested to investigate the subject and devise means for treating the effluent from the tannery which would prevent the possibility of any further spread of infectious matter.

The investigation showed that anthrax was at times present in the factory effluent. Accordingly laboratory experiments were carried out with various disinfectants to determine what was the most effective and least expensive method of treating the sewage.

It was found that both sulphur dioxide, and bleaching powder with and without the addition of acid were not effective in practicable concentrations in killing anthrax spores. Chlorine gas when dissolved in water, however, was found to be a very effective agent. Less than 5 parts per million of chlorine will kill. anthrax spores when suspended in distilled water, 15 parts per million will kill anthrax spores when suspended in the average effluent from contact beds and 50 parts per million will kill anthrax spores when suspended in tannery effluent which has settled for 20 minutes. In the above cases a time of ½ to 2 hours was allowed for the disinfecting action to take place. Tannery effluent from which the coarser particles of hair and fleshings had been removed by a ¾ mm. Reinsch Wurl screen was next tried as a medium for the suspension of spores. When as large a number as 30,000 per cc. of anthrax spores were suspended in this medium, and treated with 50 parts per 1,000,000 of chlorine the spores were not all killed. The surviving spores appear, however, to be completely attenuated. One cc. portions of several disinfected test flasks which showed 20-60 colonies per cc., when plated on agar were injected into guinea pigs. In all cases the pigs inoculated with this disinfected effluent survived.

This question of attenuation is of great importance. As in the case of the treatment of drinking water supplies, disinfection may not necessarily imply absolute sterilization, but a treatment which renders the effluent non-infectious.

In order to remove the coarse suspended matter, two Reinsch Wurl screens were then installed to screen the effluent from the tannery, which amounted to 500,000 gallons per day. These screens remove from 4 to 6 barrels per day of matted hair, fleshings, and small pieces of hide. In other words, the most likely carriers of anthrax spores, the matted hair and fleshings, are removed by the screens. The screened sewage is treated with 50 parts per 1,000,000 of liquid chlorine by means of Wallace & Tiernan's chlorine regulating apparatus.

This complete installation has been in operation for 10 months and during that period raw and treated sewage have been under constant test for anthrax. At no time since the installation was complete, was anthrax found in the treated sewage. On four occasions during this period anthrax was found in the raw sewage but not in the treated. On one of these occasions a duplicate set of samples was sent to the Department of Agriculture at Washington. This set also showed anthrax in the raw but not in the treated effluent.

Naturally the strength of the factory effluent or its absorption of chlorine should be tested in each individual case to insure efficient results.

Our work is nearly completed on an economical and efficient method for the disinfection of hides by means of chlorine solution, an account of which will be reported later.

As far as tannery effluents go, however, we feel justified in concluding as a result of this extensive series of experiments carried out in the laboratory, and corroborated by actual practical tests on a large scale, that for average conditions fine screening followed by chlorine treatment to the extent of 50 parts per 1,000,000 is effective for preventing the spread of anthrax from this source.

[1] Josef Wintersberger. Beitrag zur Frage der Disinfection Milzbrandsporenhaltiger Gerbereiweichwässer. Wiener Tierarztliche Monatsschrift. 2, 8, p. 353, (Aug. 1915.)

Gärtner und Dammann. Gutachten des Reichsgesundheitsrates über das Auftreten des Milzbrandes unter dem Rindvieh des Schmeiegebietes (Regierungsbezirkes Hohenzollern) und über den Zusammenhang dieses Auftretens mit der Verunreinigung des Schmeiebaches durch Abwasser von den Gerbereien in der Stadt Ebingen. (Arbeiten aus dem Kaiserlichen Gesundheitsamte 1907, Band VIII.)

Pfeiler. Zum Vorkommen des Milzbrandes in Gerbereien. (Zeitschrift für Hygiene der Haustiere, Band V.)

Quirlsfeld. Dampfgerbereibetrieb und Milzbrandgefahr. (Der Amtsartz 1910, Nr. VI.)

Schnürer. Zum Nachweis von Milzbrandkeimen in der Aussenwelt. (Tierärtzliches Zentralblatt 1912.)

Schultz. Modifizierte Chlorbestimmung für die Abwasserdesinfektion mit Chlorkalk. (Zeitschrift für angewandte Chemie 1903.)

A ROUGH METHOD FOR TANNIN ESTIMATION.

By Lloyd Balderston.

Many samples of crude materials are sent to this laboratory, and not a few have been sent on suspicion of being tanning materials which on careful examination were quite freed from that suspicion.

The method which is herewith described may serve to weed out from the things an explorer has under his eye those that are certainly not valuable on account of tannin content.

The plan is simply to apply the gelatine-salt test under standardized conditions and note at what dilution it fails. Weigh 5 grams of the finely pulverized material, place in 250 cc. of water, bring to a boil and keep boiling 10 minutes. Make up the quantity to 500 cc. If the liquid does not settle in a few minutes so as to be nearly clear on top, stir in a few grams of kaolin and filter a little of the infusion. Let fall a single drop of the infusion into a test tube in which from 3 to 5 cc. of 1 per cent. gelatin, 10 per cent. salt solution has been mixed with an equal volume of water. If a distinct turbidity shows when the first drop strikes, the original material contained 10 per cent. or more of tannin. If 2 or 3 drops are required to give any turbidity, the quantity of tannin in the original material is between 5 and 10 per cent., and if several drops give no turbidity, it is less than 5 per cent. If the turbidity produced by the first drop is dense, dilute a portion of the infusion with an equal quantity of water and repeat the experiment. By using increasing dilutions, and figuring back to the original infusion, the order of magnitude of the tannin content of rich materials can be estimated.

These notes are offered simply as a method for eliminating materials which have not enough tannin in them to be worth considering. The outfit demanded is not extensive. A "hand balance" costing $2.00 with weights answers for the weighing. The boiling may be done in a copper, aluminum or enameled vessel, and the 500 cc. mark may be made with sufficient accuracy on such a vessel. A 5 cc. pipette and some test tubes, a funnel and some filters and one or two measuring cylinders are all that is necessary, beside the gelatine-salt solution. The making of this solution presents no difficulties. Any good gelatine and clean salt will do, but the solution must be faintly acid.

If it is not so on being made up, a drop or two of acetic or hydrochloric acid will probably make 200 cc. of solution acid to litmus.

Elk Tanning Co. Laboratory,
Ridgway, Pa.

ABSTRACTS.

The Identification of Acids. E. EMMET REID, *Jour. Amer. Chem. Soc.*; Jan., 1917, pp. 124-36. Paranitrobenzyl bromide, prepared by heating paranitrotoluene with bromine in a sealed tube, reacts readily with sodium acetate to form paranitrobenzyl acetate, which is not very soluble in alcohol and has a sharp melting point, 78° C. These facts, discovered by Wachendorf in 1877, are the starting point of Reid's work. He found that many organic acids give compounds with *p*-nitrobenzyl which crystallize from dilute alcohol and have well defined and well scattered melting points. Among the acids investigated are acetic, formic, oxalic, tartaric and citric. The best method so far found for preparing the reagent is to heat *p*-nitrotoluene for an hour to 125°-130° C. with half the calculated amount of bromine, then open the tube and allow the hydrobromic acid to escape, introduce the remainder of the bromine and heat for several hours. The product is dissolved out of the tube with hot alcohol, from which nearly all separates on cooling. The solid thus obtained, which should be nearly white, is dissolved in about ten times its weight of boiling 95 per cent. alcohol, and half as much water as alcohol added. The hot solution is filtered quickly through a hot filter, after adding a very little powdered animal charcoal. The *p*-nitrobenzyl bromide is deposited in fine pure white needles whose melting point is 99° C. The procedure is as follows: The proper quantity of the sodium salt of an organic acid to react with 1 gram of the reagent is dissolved in 5 cc. of water in an Erlenmeyer flask. To this solution 10 cc. of 95 per cent. alcohol and 1 gram of the reagent are added, the flask connected to a reflux condenser and kept gently boiling for 2 hours. The ester will in general separate out on cooling, but if it does not, addition of successive small portions of water after reheating will eventually result in crystallization. The yields, melting points and approximate solubilities of sixteen products are given. The melting point of the oxalate is 204° C., of the tartrate 163° and of the citrate 102°.

The Identification and Estimation of Lactic Acid in Biological Products. I. K. PHELPS and H. E. PALMER. *Jour. Amer. Chem. Soc.*, Jan., 1917, pp. 136-149. Lactic acid was separated from formic and acetic acids by fractional distillation of the mixed ethyl esters, and from butyric and propionic acids by difference in solubility of the quinine compounds in carbon tetrachloride. The lactic acid is converted to gaunidine lactate by the double decomposition of guanidine sulphate and barium lactate. The resulting barium sulphate is filtered off, the filtrate dried and treated with absolute alcohol, which dissolves the guanidine lactate, leaving the excess of guanidine sulphate insoluble in absolute alcohol. The guanidine lactate is recovered by evaporation of the filtrate and weighed.

Forest Problems and Economic Development in South America. RAPHAEL ZON. *Proc. of the Society of Amer. Foresters*, Oct., 1916. The problem of how to grow and care for the valuable trees of South America is practically untouched. The fear is gaining ground that if the present methods of cutting quebracho continue, without measures being taken for its re-growth, the supply will be exhausted in a comparatively short time. The same is true of Spanish cedar, mahogany and other valuable trees. The data for the solution of these problems are only beginning to be accumulated. So far are we from knowing what must be done to insure a continued supply of the valuable forest products of South America, that even the botanical identity of the trees from which some of these products are obtained is as yet unknown. In the Amazon Valley it will require only 20 to 30 years to grow a crop of timber. The requirements of the various trees in regard to light, soil and moisture must be studied before intelligent management can begin. Fortunately for most of the countries of South America, much of their timber is still under government control, so that the opportunity to establish forestry experiment stations with the prospect of solving the important problems of forest conservation still presents. Beginnings have been made by Chile and Argentina in this direction.

Agreement to Limit Output of Quebracho Extract. CONSUL WILLIAM DAWSON, JR., Rosario, Argentina, Nov. 28. According to *La Nacion*, Buenos Aires, for November 24, manufacturers of quebracho extract have reached an agreement for the purpose of limiting production. This publication states that before the war quebracho extract was quoted at 80 gold pesos ($77.20) per metric ton. The increased demand for tanning extract due to the war brought about a steady rise in price, until early in 1916 quebracho extract reached 230 gold pesos ($221.95) per metric ton. The result was that extract factories considerably increased their output. On the other hand, substitutes such as oak, chestnut, etc., began to be used in larger quantities, while restrictions on purchases for Scandinavian countries tended at the same time to limit the demand. In a comparatively short time the price of quebracho extract dropped to 100 gold pesos ($96.50) per metric ton. The object of the agreement reached by Argentine and Paraguayan factories is, according to *La Nacion*, the reduction of their output to meet the world consumption, estimated at 130,000 tons. Extract will be delivered at a uniform price to one seller who will distribute profits pro rata among producers. The following concerns having a total output of 165,000 metric tons are reported to have entered the combine: La Forestal, Quebrachales Fusionados, Chaco y Paraguay, Las Palmas, La Formosa, and Fontana y Cia, in Argentina, and Carlos Casado, Puerto Sastre, Puerto Sarani, and Puerto Galileo, with factories in Paraguay. Of these companies the most important, which is the Forestal, is an English concern. The remainder work with Argentine capital. *La Nacion* estimates the capital invested in the quebracho industry in Argentina alone at 100,000,000 paper pesos ($42,460,000). Exports of quebracho extract from Argentina rose from 80,153 metric tons in 1914 to 100,213 tons in 1915, and will probably show a further increase during the present calendar year. The publication states that following the agreement reached among producers the price of quebracho extract rose to 150 gold pesos ($144.75) per ton. It adds that in order to encourage the home tanning industry Argentine consumers of extract will enjoy reduced rates.

South American Forests. H. M. CURRAN. *Proc. of the Society of Amer. Foresters,* October, 1916. With the exception of two small regions, South American forests are of broad-leafed hardwoods. From the point of view of forester or lumberman, these forests differ little from the hardwoods of our mountains and the Mississippi bottom lands. Here and there exceptional stands are found, but on the whole these forests run from 10,000 to 20,000 feet board measure to the acre. The common belief that tropical forests contain only very hard woods must also be dropped, for recent investigations show these forests to be composed of soft or medium hardwoods, which are as suitable for general construction as the pines and various conifers and hardwoods of our own forests.

South American forests may be roughly divided into four more or less distinct types, the species composing each varying from region to region, but the general effect of each type from Columbia to Argentina is much the same. The four principal types have, for convenience of description, been given the following names: dry forests, temperate forests, swamp forests, tropical rain forests. Better or more scientific names can be found and will come from the careful study now planned for these regions. Many minor yet distinct types must be passed over in this general survey. The conifers of northern Patagonia belonging to the temperate forests and the Brazilian conifers of the transition zone between temperate and rain forests are among the most interesting of the lesser types.

Dry Forests.—In the temperate or sub-tropical regions, both at high and low levels, there are immense areas where the rainfall is deficient or so unevenly distributed throughout the year as to cause long periods of drought. These areas are usually covered with some form of tree growth which at its best is a dense forest of comparatively few species. The trees are short boled, round headed, often armed with spines or thorns or short spurs like branches and harsh or bristle-pointed leaves. The trees usually do not exceed 50 feet in height, and in many regions the average is little over 25 feet. The commercial stem varies from 10 to 20 feet, with diameters of 12 to 24 inches common. These forests grade into chaparral on one side and on the other into tropical rain forests. Perhaps the best known representatives of this type are the quebracho-algarrobi forests of northern Argentina. They occupy the great semi-arid plain lying between the foothills of the Andes and the Parana and Paraguay Rivers and known as the Great Chaco. Other representatives of this type are the Catinga forests of Brazil and the coast forests of Colombia and Venezuela between Cartagena and the Island of Trinidad.

Temperate Forests.—This second type is found along the slopes of the Andes, where elevation and moisture combined with suitable soils make the growth of a temperate forest possible. This type is best developed in Patagonia and comes practically to sea level in Tierra del Fuego. Here in the south the trees are rather stunted and deformed by the winds, but in the mountains to the north and along the shore of the Patagonian Lakes they reach a splendid development and heavy stands are reported. These forests are of Antarctic beech and a few conifers. Three species of the beech would probably furnish 90 per cent. of the cut. Average stands are probably between 10,000 and 20,000 feet per acre, not allowing for defects. The forests are over-mature and so defective as to be of little commercial value. The trees reach heights of 100 to 125 feet and are 2 to 5 feet in diameter. The extension of this type along the Andes from Chili to Colombia can only be estimated. The great populations that have for thousands of years occupied this region drew on these forests fo fuel and construction timber and only second growth or scattered patches remain. These highland people have even worked down to the edges of the rain forests of the great Amazonian plain.

Swamp Forests.—This type, the third of the great divisions, may be divided into two sub-types—the tropical forests, occupying the salt-water swamps at the mouths of the great rivers forming one section, and the forests of the fresh-water swamp and bottom lands the other. The tidal swamp forests are typical mangrove areas like those found in other parts of the world and are rather restricted in area and practically destroyed. The fresh-water swamp forests occupy great areas and promise to be of commercial importance in the near future. The best known representatives of this type are the lowland forests that fringe the Amazon, the Orinoco, Parana, and Magdalena Rivers. These forests are similar in character, though differing in species from north to south. Many closely related species are found in all these forests and only the botanist would note a difference.

The overflowed areas along the river are a series of sandy or gravelly bars, small islands, sandy banks, wet open meadows or savannas, shallow ponds and lakes, and a network of minor waterways. They vary from a few miles in width to perhaps a hundred or more. At least once a year they are covered with water, with the possible exception of the very highest points. The rise of the water may be rapid or slow and remain a few hours or even months in the deepest part of the ponds and lakes. Usually the rise is gradual, the water flows through the many channels, fills ponds and lakes, and spreads thence to the forest, as in our own bottom lands. The water then gradually subsides, and only the deepest ponds and lakes and channels retain water during the drier period.

The forests of this area are very irregular in age, often very open, and growth is extremely rapid. Changes are so rapid in this region, each freshet making new land and destroying old, that only fast-growing species can obtain a footing over much of the area. The species common in this type are in the main soft-wooded, as soft or softer than our cottonwood, basswood, and yellow poplar, and many with but little color. They reach heights of over 100 feet in the best soils; probably 60 to 70 feet is an average, with diameters of 2 to 3 feet common. Certain of these species reach this height in 10 to 15 years and commercial diameters in much the same time. The dominant stand for any given region is usually of a very few species. In many cases four or five varieties of trees will furnish 75 per cent. or more of the commercial timber and the yield be 8,000 to 10,000 feet per acre.

Tropical Rain Forests.—This is the most important and the least known of all the types of South American forests, and, though it may seem paradoxical, yet its timbers are among the best known tropical woods. Mahogany, rosewood, Spanish cedar, Brazil wood are the products of these forests; but as only the edges of the great wooded areas have been reached by the lumberman and explorers, and even the Indians keep near the waterways, they may be said to be practically unknown.

This forest type in South America is probably the largest and most valuable body of timber in the world to-day. South America's future and many of the great problems of forest administration in Europe and North

America depend on how this forest is treated. If it is destroyed, as the forests of Argentina, Paraguay, and southern Brazil are being destroyed, it will mean economic ruin, probably also absolute physical ruin to land, climate, property, and life on a great part of the southern continent. If, on the other hand, it is protected and properly utilized, South America becomes the center of the world's prosperity in the years to come. The saving of this forest means also that Europe and North America will have time to repair their damaged forests, to perfect their organization, so as to meet demands without destroying the capital. Only by obtaining great supplies from these virgin forests of South America can this crucial time in the great struggle for forest conservation be safely passed. If, therefore, these forests are so valuable, can they supply at once the kind of timber demanded, or must the world learn to use new forms to supply its needs?

The tropical rain forests are composed of timber practically like those now in use and in most cases much better adapted for the uses to which they will be put than those now supplied by the American mill man. The time will come when we will look back with amusement to the dark ages, when we used yellow pine for boxes and railroad ties and redwood for shingles and vineyard stakes.

The woods of these tropical forests are in the main soft or of medium hardness and are suitable to replace pine for construction, oak for finish and furniture, hickory for wheels and handles, and ash for agricultural implements. From the infinite variety of these timbers we can find one for each industry more completely suited to its needs than the ones used to-day. From the point of view of the logger, these forests are ideal. Heavy stands are found over great areas on land as level as the southern pineries. Ten to 20,000 feet can be cut to the acre. Commercial diameters run between 2 and 3 feet and the clear lengths 50 feet or more. The total height of an average tree is well over 100 feet.

Chamois Skins. F. J. KOCH. *Leather Manufacturer*, Jan. 1917. pp. 9-12. The chamois skins of commerce, even those that come from France, are not chamois, but sheepskins, and the sheep from which they were taken were not French but Australian sheep. A Cincinnati dealer is quoted to the effect that the French chamois, in spite of meager shipments since the war began, sells for less than the domestic, and yet is of better quality. At the French factories, after removal of the wool, the skins are split. The skivers are used for "hat-sweats" and other purposes. The flesh split is the raw material for the manufacture of "chamois" leather. The author attributes the better quality of the French product to longer time spent in the oil. Chamois skins are sold in twenty-two sizes, from 6 by 8 inches up to 28 by 32 inches. Every line of industry in which wood or metal is polished is a consumer of chamois leather.

The name chamois, as is well-known, belongs of right to the Alpine antelope whose skin used to be tanned with oil, making a product similar to that now obtained by oil tannage of sheepskins. The chamois lives in the high Alps, and in the Carpathians and Pyrenees. It resembles in some respects the antelope of the Southwest, but has many goat-like characteristics. The horns are 6 or 7 inches long, the body about 3 feet 3 inches, and the height at the shoulder is about 2 feet. The whole body is covered with long hair, which hangs down at the sides, deep brown in winter and brownish fawn in summer. During the summer, the chamois lives high up on the mountains, being impatient of heat. In winter it comes down to the lower slopes, and it is at this season that hunters may pursue it with some hope of success. Up to the middle of the nineteenth century the chamois was fairly abundant in all the high mountain chains of Europe, but now, except where it is protected by rigid laws, it is very scarce.

COMMITTEE ON EFFECT OF HARD WATER ON TANNIN.

T. A. Faust, Chairman.

Some doubt has been thrown on the extent of the destruction of tannin by hard waters, and the writer was appointed Chairman of a Committee to investigate more extensively the effect of such waters in the tannery, so far as vegetable tanning materials are concerned.

The reaction occurring between the bicarbonates of the alkaline earths and tannin is well-known, but there appears to be a discrepancy somewhere between theory and practice, as the writer has not been able to find anything like the loss commonly believed to exist, and on mentioning the fact to other chemists, found that they obtained similar results.

The Chairman wrote to a number of the members of the Association along the above lines, incidentally requesting their co-operation, and found most of them very dubious as to any considerable destruction of tannin, and also found a rather unusual interest manifested in the problem.

In order to make this work more comprehensive, it was thought best to collect all possible data on the subject, and the Chairman requests that any members of the Association who have had any practical experience with this problem would kindly furnish such information to the Committee. It would be particularly valuable if some tanner who formerly used hard water, and is now using a soft water, could furnish some comparative data and analyses to show what difference was noticed when making such a change.

The Committee would also appreciate any information which the members abroad could supply, as it is believed that this problem has received more attention by our foreign members.

The nature of this investigation is rather an unusual one, and the writer realizes that in order to get any definite conclusions, it is necessary to have the co-operation of as many members as possible, and trusts that any who are interested in this work will lend their assistance.

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THE FORMIC-MERCURY PROCESS FOR STERILIZING AND CURING DRIED HIDES.

By Alfred Seymour-Jones.

Chairman of the International Commission for the Preservation, Cure and Disinfection of Hides and Skins.

Arising out of Mr. Oberfell's report on the Cure and Disinfection of hides, read at the thirteenth annual meeting of the American Leather Chemists' Association, Atlantic City, N. J., June 2, 1916, and the discussion which ensued, I desire, firstly, to express my own pleasure in reading the report and the discussion, and congratulations to the A. L. C. A. at inaugurating so important a discussion, thus departing from the monotony of the general procedure of such conferences, and my regret that it was impossible for me to have been present to join in the debate. As I have given a lifetime of thought and experiment with practice to the question of preservation, cure and disinfection of hides, and having evolved a process of cure and disinfection for dry hides, I feel I may be of some service to my colleagues of the A. L. C. A. by placing a few observations before them for their consideration and in the hope that by so doing I may assist in elucidating their problems.

Those of us who have labored in the field under review, are of the opinion that the extermination of this fell disease is possible and by applying simple remedies. It is a disease which is foreign to all white men's lands. That is, it is an imported disease. That by being imported it has secured a hold in certain areas is true, but those areas being known, the problem of extermination may be dealt with by other and well known means. The areas to which I refer are mainly the low lying marshy flats, mainly estuaries of rivers. The problem we have to consider is: How does the germ enter our countries?

The most reliable data regarding the incidence of industrial anthrax are those issued by the British Home Office, by Dr. Legge, who has made a special study of the question, and which returns, in so far as they bear upon agriculture, are confirmed by the British Board of Agriculture, all point to the following conclusions:

1. That dried hides from certain areas are the source of contagion.
2. That there is no certain evidence of wet salted hides being the cause.

If we accept those conclusions, then obviously it is our duty to prevent the importation of dried hides from those areas known to be infected, that is, the source of such supply. But to do this implies cutting off a valuable source of hide supply, therefore, is it possible to prevent contagion by converting those hides into wet salted hides at the port of embarkation, and perhaps sterilizing them at the same time?

Having had the pleasure and advantage of conferring with the authorities in Britain, I felt that it was our duty to devise a scheme which offered the maximum of advantages with the minimum of risk in importation of the disease. How would a scheme which involved the converting of dry hides back to the wet state assist in preventing the disease from being imported to farms? The Board of Agriculture has traced a direct connection between dry hides and animal food infection. Dried hides which have been shipped in the same ship with food stuffs, such as linseed, soya beans, and the like, are said to have infected such food stuffs. This must have been accomplished through the dust of such dry hides (infected with anthrax spores), being wafted through the ship during transit until they settled on some of the food stuff. It is of course not possible that all the food stuff will have become infected, but only an isolated patch, yet that patch of material will have passed through all the subsequent processes of manufacture and eventually found its way to an isolated farm, and been eaten by an isolated animal who would succumb to the disease. The danger of infection is mainly one of *dust* carrier.

In the light of all the evidence available, it would appear that provided in so far as dry hides are the "carriers," to convert them into wet salted hides, would eliminate the danger from our factories and farms. But it is not only dry hides which are the cause of the sporadic outbreaks at farms. New Zealand, a land which does not import hides of any description, had many outbreaks which they eventually traced to the bone manure imported from China and the Eastern lands. They made sterilization compulsory before importation. The bones are submitted to steam pressure under well defined conditions, which imposed considerable cost upon the exporters, nevertheless, it has been in operation for many years, and after it came into full operation, anthrax disappeared from that country, and I am informed that no further outbreaks have since occurred. Such conditions, imposed by a small country, should be also adopted and enforced by all civilized countries.

The conversion of dried hides to the wet condition was a serious problem and did not appear so easy of solution as it does to-day. The old method of stale soaks was foul, wasteful, and dangerous, and should not be tolerated by the public health authorities. The method suggested years ago by Prof. Procter, of employing a weak alkaline bath, did not meet the case although very useful and practicable. It was an old method which brought my thoughts to bear on the probable solution. In the days of my youth, we used to dry out all the skins out of drench which could not immediately be tanned, and wet them back in cold water as we required them. They wetted back easily due to their acid state. I then tried to reverse the process, *i. e.,* to wet back a dry skin in a weak acid solution, with excellent results. Those were the far-off days when we were limited to sulphuric, sulphurous and hydrochloric acids. Hydrochloric acid was the one employed, and experiments were carried out with the object of utilizing that acid in conjunction with salt, as a cure and sterilizer. Various conditions were set up with varying success. I found that sterilization could be accomplished under given conditions, which though workable were not practicable under conditions which would prevail with native labor in (say) China. Further, such a cure would give the hide a restricted market, as for many purposes the hide would be irretrievably damaged. Thus it was I turned down what is to-day known as the "Schattenfroh" process, more than twenty-five years ago. Time has confirmed the opinion I then formed, and that opinion is also held by those who have been exploring the field with me.

The scheme which can reasonably hope for success is one which involves the minimum of hide substance disturbance, and which the buyer can work through his tannery with the maximum of efficiency. My experiments proved to me that our tannery experience must guide us as to the acid to be used, and if one of the drench acids could be bought commercially, then we could hope for success. About fifteen years ago formic acid was placed on the world's markets, and as I had been experimenting with this acid among others as a hide softener, I decided to carry out a preliminary test on an extended scale with that acid. That test is described on pages 186-187 of the *Collegium*, 1904. It was a unique experiment, and had a wider bearing than the mere devising of a new pickle. It proved to many eminent tanners and others that it was possible to pickle a skin without altering the general character of the pelt. It proved that antiseptic conditions prevailed throughout, and that as a matter of fact the skins were sterilized. That trial gave me a sound foundation whereon to work and build up a scheme of curing and disinfecting dry hides which would be acceptable to the leather industry.

I do not desire to pursue this personal phase any further, but I felt that it was necessary to explain my position in regard to the Schattenfroh process. Prof. Schattenfroh and his colleagues have spent a great deal of time and money in pursuing their case, but unfortunately for them, no leather trade scientist or leather manufacturer of repute has seen fit to endorse it as a scheme which would be acceptable to the industry. It may be true, and it is true that under the conditions laid down by Schattenfroh, complete sterilization may be secured, but when the result is a destruction or partial destruction of the material for the purposes for which it is to be put, what avails the success in sterilization? The success of the Schattenfroh process rests entirely upon laboratory conditions. To transfer those conditions to practice and in the hands of ignorant natives, to maintain the conditions, even if acceptable, offers insurmountable difficulties. Although the Schattenfroh process is complicated and injurious to the hide, great credit is due to Prof. Schattenfroh for the excellent work he has done and for the effort made to elucidate a very difficult problem. I feel sure had Schattenfroh had experience of tannery conditions he would agree with me. The Schattenfroh process cannot be disconnected from Ponder's hatching-out theory.

The formic-mercury process has been evolved through years of patient research and practical experiment on lines which conform to practice. It may not be the final word on the question, and probably is not, but it does mark a very distinct advance in the direction of a final and permanent solution. It was a process devised for the cure and disinfection of dry hides only, and was never intended to be applied to all the varying phases of the problem. That fact is patent to all bacteriologists. The process has been severely tested by men eminent in leather trade science, like Prof. Procter, Dr. Constant W. Ponder, Dr. Georges Abt, of the Pasteur Institute, Dr. Gordon Parker, Dr. Baldracco, Prof. Eitner, Cav. Uff. Andreis, the Italian Government Commission of international experts, who awarded the process the first prize and by many men who were not versed in the science of our industry, and in all cases, they accord it the premier place for cure and sterilizing.

Using 1 per 1,000 of bichloride of mercury, it has been successful in completely sterilizing in certain hands, while partially failing in others. These were under laboratory conditions, yet all say provided the bichloride of mercury is strengthened, absolute sterilization ensues. The strength of 1 to 5,000 was adopted after prolonged research as affording the maximum of sterilization with the least amount of injury to the hide, and making the working conditions absolutely safe for the natives. Cost, too, had to be considered as all the acid and mercuric bichloride would of necessity have to be imported to the countries where the process was to be carried out.

The formic-mercury process gives under the most adverse laboratory conditions and using the strengths I have selected of bichloride of mercury gives not less than 90 per cent. of efficiency, a state higher than has been achieved by many of the antitoxin, serum therapy treatments in vogue to-day and in general practice among civilized nations. To attain the absolute or 100 per cent. of efficiency in such matters and at the same time without injury to the subject treated is a problem of supreme difficulty. The increasing of the strength of mercuric bichloride calls for additional expense, and with a certain amount of injury to the hide; for example, spoiling the color when tanned.

The investigators into this process are convinced that the amount of 1 part per 1,000 of bichloride of mercury will under the conditions which prevail in the infected areas, and under the conditions of transport and sale, completely sterilize dry hides against infection. The temperature of cold water in those countries is seldom below 80° F., and as the hides will be left in the formic-mercury bath for at least 2 to 3 days before immersing in the salt bath, the process of "hatching out" as suggested by Ponder will prevail. The acid will swell the spore, many of them will burst and thus sterilize themselves, while the rest will succumb to the acid on emerging as bacilli. The acid thoroughly cleanses the dirt and adhering filth off the hides and this remains behind as mud, which is the main carrier of the disease germs. The completely cleansed hide then enters the clean salt bath. The adding of the bichloride of mercury gives an additional security against any spores or bacilli remaining. It is necessary, perhaps, to make one point very clear to those who have not given attention to bacteriological study. Anthrax has two stages of existence, the bacillus and the spore. The bacilli are killed on drying the hide; the spores are not.

Anthrax spores *do not form* in the thickness of the hide or in the depths of the subcutaneous tissues, but they do form on the surface of any blood or other material which contains the bacilli, and which is exposed to air, if temperature and conditions of moisture be suitable. It has been found in practice that all this adhering matter is removed during the process of acid bath immersion, and washes off during removal from that bath leaving the hide in a creamy white condition apparently free of all contagion.

The laboratory tests except in the case of one investigator, have not been devised to meet the actual conditions prevailing in practice, and it is very difficult to devise laboratory conditions to agree with the actual. Nevertheless, severe as many of the laboratory conditions have been, they have omitted certain factors, (1) time, the tests having been confined to minutes or hours, against 'days in practice; (2) the salting has been omitted; (3) the temperature at which the conditions will be carried out have not agreed with the actual; (4) the fact has been lost sight of by some scientists that the prime factors in sterilizing are two: (*a*) burning, (*b*) tanning, *i. e.*, the conversion of the soluble into the more or less insoluble. The formic-mercury process relies upon tanning with a weak liquor to ensure complete sterilization, and all tanners know that weak liquors tan slowly, hence, the duration of the period of transit between the port of embarkation and the port of arrival is a strong factor which operates and should be taken into consideration. Where weak liquors are employed their potency largely depends upon the time and temperature factors.

The tests as to efficiency of this system have been carried out by animal experiments, and upon animals peculiarly sensitive to anthrax infection. This is manifestly unfair to man, who is, most fortunately, decidedly resistant to infection by anthrax. If this were not so, it would be a bad lookout for our workers. A process which is acceptable to any trade should not be discounted by bacteriologists because it kills one guinea pig in every ten tests. I have sterilized blood clots on Ponder's lines, and which contained anthrax spores of an especially virulent type, and accidentally inoculated myself without any injurious results, whereas the guinea pig so inoculated died after three weeks. The formic-mercury process was devised to save man from infection while being in contact with hides which presumably had been infected before shipment. The conversion of dry hides into wet-salted hides by this process achieves that result.

The opposition to the process will come from that quarter which does not desire to change prevailing conditions, because it interferes with the usual course of business, but even they will find that it offers considerable advantages to the profit side of the ledger. To the buyer it offers the great advantage of correct valuation of the hide. Sir William Howell Davies, M. P., a large tanner in Bristol, England, gave as his experience, evidence before the British Government Commission on foot-and-mouth disease and anthrax as follows: "It would be advantageous to us as tanners if we could buy hides in the condition in which they were brought after two days soaking in formic acid rather than in the flint-dried condition in which they are now brought to this country; as defects such as bad flaying and rotten damages would be seen at once (which is not the case when hides are flint-dried), and a better idea of their value can be formed."

In soaking back hides by the old method of stale soaks, the loss of valuable hide substance varied, but was always a very serious loss and unknown factor. This loss has happily to-day been removed in the bulk of yards tanning dried hides, by using the formic acid soaking bath, and it has been admirably shown by Blockey, at the Leathersellers Technical College, London, who carried out under Dr. Parker, that the loss of hide substance was a negligible quantity, and that the weights in tanned leather were higher and the quality better than by any other system.

The formic-mercury process was devised to meet the conditions I have described and to be applied by the merest tyro of a native at the port of embarkation without injury to either himself or to the hide, but to devise a method to meet all cases of anthrax infection and under all circumstances, is utopian, but the process will apply to all hides.

I cannot conclude this article better than quoting Dr. Constant W. Ponder, the eminent bacteriologist to the County of Kent, who in the *Lancet,* Nov. 4, 1911, under the title, "The Prevention of Anthrax Infection Due to Imported Hides and Skins (The Seymour-Jones Formic-Mercury Process)," writes: "A practical method having been suggested, how can its application be ensured to those goods which constitute a potential danger to our workmen? Civilized governments should forbid the importation of hides or skins unless (1) they have been submitted to the ordinary "wet-salting" process immediately after flaying; or (2) if cured by drying they have been converted back to the "wet-salted" state by the "formic-mercury" process before leaving the country of export. If such regulations were adhered to I am convinced we should hear no more of anthrax amongst the dock laborers and warehousemen in Bermondsey and Liverpool, nor of those sporadic cases which are continually cropping up in the tanneries in different parts of the country."

Personally, while I do not disagree with Dr. Ponder's advice, I do urge upon all civilized governments to make a start by making the scheme compulsory in those areas where anthrax is known to exist, and gradually to extend the order until all ports are equipped with the system. In this movement the enlightened government of the United States of America should give the world a lead. If they will, then the European nations who are now at death grips will follow when peace once more reigns.

THEORY OF VEGETABLE TANNING.*

By Henry Richardson Procter and John Arthur Wilson.

In spite of the fact that theories of tanning have formed the subject-matter of numerous controversies, no completely satisfactory theory has yet been promulgated, which is probably due largely to the lack of quantitative formulæ governing the supposed actions. It was in the hope of throwing light on the complicated phenomena of the tanning process that work was begun by one of us some eighteen years ago, on the action of dilute acid and salt solutions on gelatin. Since that time the work has steadily progressed, and mathematical formulæ have been derived governing the various parts of the tanning process. The theoretical development of this work is given in the following publications:

1. "The Action of Dilute Acids and Salt Solutions on Gelatin," by H. R. Procter, *Koll. Chem. Beihefte,* 1911, 2, p. 243; *J. Amer. Leather Chem. Assoc.,* 1911, p. 270.
2. "Colloid Chemistry and Tanning," by H. R. Procter, *Gedenkboek van Bemmelen,* 1910; *J. Amer. Leather Chem. Assoc.,* 1911, p. 23.
3. "The Equilibrium of Dilute Hydrochloric Acid and Gelatin," by H. R. Procter, *Trans. Chem. Society* (Br.), 1914, 105, p. 313; *J. Amer. Leather Chem. Assoc.,* 1914, p. 207.
4. "The Acid-Gelatin Equilibrium," by H. R. Procter and J. A. Wilson, *Trans. Chem. Society* (Br.), 1916, p. 307; *J. Amer. Leather Chem. Assoc.,* 1916, p. 261.
5. "The Swelling of Colloid Jellies," by H. R. Procter and J. A. Wilson, *J. Amer. Leather Chem. Assoc.,* 1916, p. 399.
6. "Theory of Colloids," by J. A. Wilson, *J. Amer. Chem. Soc.,* 1916, 38, p. 1982.

In these papers, by a process of generalization, the authors have derived quantitative equations which explain the swelling and contracting actions of electrolytes on colloid jellies, as well as the various effects of adding electrolytes to sols. In fact, the derived formulæ apply to the whole colloid state, and therefore should in themselves offer a quantitative explanation of the mechanism of tanning, which is the object of the present paper.

The tannins dissolve in water forming colloidal sols, in which the individual particles are negatively charged, so that, according to our theory, the surface layer of solution immediately surrounding the particles (which we shall hereafter designate merely as

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* *Transactions* of the (British) Chemical Society, 1916, pp. 1327-31.

the surface layer) must contain a certain concentration of positive ions bound by electro-chemical attractions to the negatively charged tannin. The tannin may acquire its charge by combining with a negative ion or by ionizing, as do soaps or Congo red; it is immaterial to the theory whichever is the case. Call the concentration of tannin particles $[T']$ and that of the positive ions bound by electro-chemical attractions to the tannin $[M+]$, and let some of the electrolyte MN be added to the solution. In the surface layer there will be a certain concentration of $M+$ bound by electro-chemical attractions to the tannin, as well as some $M+$ and N' not so bound, so that in this layer $[M+]$ and $[N']$ will be unequal, whilst in the bulk of solution they will necessarily be equal, a condition to which Donnan's work on membrane equilibria (*Zeitsch. Elektrochem.*, 1911, 17, 572) is applicable.

When equilibrium is established, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged, that is, no work will be done. The change here considered is the transfer of δn moles of $M+$ and N' from the bulk of solution to the surface layer. The work which equals zero is

$$\delta n R T \log\frac{[M^+]_{II}}{[M^+]_{I}} + \delta\eta R T \log\frac{[N']_{II}}{[N']_{I}} = 0.$$

(where $[M\ ]_{II}$ represents concentration of M^+ in the bulk of solution and $[M^+]_I$ its concentration in the surface layer, whence

$$[M^+]_{II} \times [N']_{II} = [M^+]_I \times [N']_I,$$

from which it follows that if only binary electrolytes are present, the products of concentration of any pair of diffusible and oppositely charged ions will be equal in surface layer and bulk of solution. In order to keep the mathematics as simple as possible only binary electrolytes will be considered, although it will be obvious that the reasoning can be extended to include, ions of any valency; for example, if the electrolyte MNx were present, then at equilibrium

$$[M^{x+}]_{II} \times [N']_{II}^{x} = [M^{x+}]_I \times [N']_I^{x},$$

Since any special case can readily be worked out algebraically, no useful purpose would be served by complicating the reasoning with higher equations.

The following system of notation has been adopted to keep the reasoning as closely allied as possible to that of our earlier papers (*loc. cit.*).

In the bulk of solution let

x = concentration of positive or negative ions.

In the surface layer let

y = concentration of negatively charged, diffusible ions;

z = concentration of positively charged ions bound by electro-chemical attractions to the tannin.

$\therefore y + z$ = concentration of positively charged ions.

From the law of equality of products just derived

$$x^2 = y(y + z).$$

The different distribution of ions in the surface layer and bulk of solution will result in a difference of potential, the formula for which is given by Donnan (*loc. cit.*) as follows:

$$E = \frac{RT}{F} \log \frac{1}{\lambda}.$$

But in our special case

$$\lambda = \frac{y}{x} = \frac{-z + \sqrt{4x^2 + y^2}}{2x}.$$

We may therefore write

$$E = \frac{RT}{F} \log \frac{2x}{-z + \sqrt{4x^2 + x^2}}$$

where z is either constant or has a limiting maximum value, and hence

$$\underset{x = \infty}{\text{limit}} \; E = \frac{RT}{F} \log \frac{2x}{\sqrt{4x^2}} = 0.$$

proving that the potential difference existing between surface layer and bulk of solution will diminish as the concentration of electrolytes in the solution is increased. When this difference of potential has been made sufficiently small, by the addition of electrolytes, a condition is established which is favorable to the coalescence of the particles, and consequently the tannin precipitates.

It is now necessary to refer to the papers dealing with colloid jellies (*loc. cit.*). Because of the different distributions of ions, a difference of potential must exist between the colloid jelly and the surrounding solution. When a hide is immersed in an acid solution, a highly ionizable salt of collagen is formed in which the collagen is positively charged, and therefore this potential difference will be expressed by the formula

$$E = \frac{RT}{F} \log \frac{-z + \sqrt{4x^2 + z^2}}{2x}.$$

where E is obviously of opposite sign to that in the case of tannin. In alkaline solution hide substance reacts with the resulting formation of ionizable salts, the collagen becoming negatively charged, in which case E would have the same sign as in the case of tannin.

It now becomes evident that if a hide is immersed in a slightly acid solution of tannin, as the tannin particles approach the substance of the hide, *electrical neutralization with the resulting co-precipitation of the two colloids must follow.* This is the fundamental action of vegetable tanning. Various tannins, however, differ chemically from one another, and consequently all would not produce the same value for z under a fixed set of conditions. The greatest difference of potential between surface layer and bulk of solution will be found in those tannins in which z has the greatest value. Such tannins would combine most rapidly with the hide and form the most stable leather, but would clearly not be suited for use excepting with hide which had been almost completely tanned. A table giving the values for z for the various known tannins under a fixed set of conditions would certainly be of great value, and it is hoped that these determinations may soon be made.

The rate of tanning will be a maximum for a given concentration of liquor when the potential differences are of opposite signs and the absolute value of each is a maximum. As the concentration of electrolytes in the solution is increased, the potential differences between the solution and both the jelly phase of the hide and the surface layer surrounding the tannin particles will decrease, lessening the rate of tanning; but if the concentration of electrolytes is increased sufficiently, the tannin must precipitate alone and the collagen shrink to a hard mass. In alkaline solutions both colloids have negative charges, and consequently will not combine, while in the presence of lime the negatively charged tannin particles are neutralized by calcium ions and a calcium compound of the tannin precipitates.

This reasoning clears up many points concerning the question of the function of acids in tan liquors and points out the important rôle played by salts, and appears to have almost infinite possibilities of extension in many industrial problems as well as in pure colloid chemistry. It is, for instance, obvious that the equations given are applicable without change to many, if not all cases of dyeing, and offer a full explanation of the functions of acids, or (with change of sign) of bases, and of neutral salts in these operations. It is also evident that the same laws are active in regard to the mineral tannages and the mordanting of fabrics, but as these are complicated by both chemical and colloidal changes it seems best to defer their consideration.

Summary.

It is shown that the combination of tannins and hide fiber, and the effect of acids and neutral salts in the tanning process, is explained by the existence of the electric potentials which Donnan has described and explained under the name of "membrane potentials." Equations are given with regard to the relation of the various concentrations involved, and it is mentioned that these are also applicable to dyeing.

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SOME SIZES AND FINISHES AND THEIR ANALYSIS *

By M. C. Lamb, F. C. S., and A. Harvey.

The authors having had occasion to make analyses of samples of the large number of animal and vegetable products used in the sizing and finishing of various textile fabrics, leather, etc., products which are often found to be subject to adulteration and sophistication, have experienced the fact that the amount of available data upon the subject is almost negligible. Analytical figures, so far as they are aware, that would enable comparison to be made with the figures obtained by the analysis of samples, are not to be found in any text book or standard work of reference for the majority of the products mentioned below, and in consequence unless the analyst is regularly employed in the analysis of the products enumerated, he is often at a loss to express an opinion upon a sample without going to the considerable trouble of making further analyses of a number of samples of known origin, for comparison purposes.

The authors beg to place on record the results of a number of analyses, which have been made with a view to suggesting standards that may possibly be considered worthy of adoption by any of their confreres who are interested in the analysis of sizes and finishes. In the course of the paper it has been thought advisable in order to make same as comprehensive and useful as possible to include various suggestions and particulars that have been collected by one of us during a somewhat lengthy experience, and other data obtained from a number of different sources.

Egg and Blood Albumen.—These nitrogenous products obtained by evaporation of egg white, and blood serum, at low temperatures, are largely used in the textile industry in the dyeing and printing of calico, and in the finishing of leather. The peculiar property of albumen is its coagulability at a low temperature (70° to 75° C.) and consequent insolublization, which is made use of in the forming of insoluble pigments as an adhesive rendered subsequently insoluble in the case of textile fabrics either by steaming or treatment with dilute acid. In the case of leather the albumens are used for the purpose of producing on the surface of the dyed leather a thin film which whilst assisting in the fix-

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* *S. and L. Rep.*, Jan. 18, 1917.

ation of the dyestuff also is capable of taking a very high polish when the leather is subsequently subjected to friction glazing.

The following are analyses of representative samples of blood and egg albumen of fair average commercial quality:

BLOOD ALBUMEN.

Moisture	= 21.35 per cent.	24.53 per cent.
Ash and Mineral Matter	= 8.41 per cent.	9.06 per cent.
Albumen	= 70.13 per cent.	65.73 per cent.
	99.79	99.32
Nitrogen	11.01 per cent.	10.32 per cent.
Color	straw yellow	brown

EGG ALBUMEN.

Ash (white fusible)	= 4.69 per cent.
Albumen	= 69.30 per cent.
Moisture	= 25.94 per cent.
	99.93 per cent.

In our experience the moisture, which is quite an important factor and liable to considerable variation, is best ascertained by carrying out same in an ordinary air oven at a temperature of 102° C. Care needs to be exercised when determining the amount of ash and mineral matter, because of its fusibility. The percentage amount of albumen is best determined by Kjeldahl; multiply the percentage of nitrogen found, by 6.37.

Samples of both blood and egg albumen should be completely soluble in a 1 per cent. solution of caustic soda. Blood albumen is liable to contain a proportion of insoluble matter, samples have been examined which were found to be almost entirely insoluble in water due to the fact that in their preparation the evaporation of the blood serum had been carried out at too high a temperature and the whole of the albumen had been coagulated and rendered insoluble. The percentage of insolubility is therefore a very important factor: a good quality blood or egg albumen should dissolve readily in water at 45° C. It is advisable when testing the solubility that the dry albumen should be added to the requisite quantity of water and that the operation should not be reversed as otherwise, particularly in the absence of mechanical agitation, the albumen will adhere to the bottom of the vessel and be difficult to detect and will dissolve extremely slowly, whereas by adding the dry material to the water and stirring continuously, this experience is obviated. Albumen is liable to adulteration with gelatine and alginic acid—zinc salts are often added to those albumens which are sold in solution form, for the purpose of increasing the viscosity of the solution, and to act as an antiseptic. Mineral adulterants are seldom added, in the author's experience, to albumen sold in the solid form. It is desirable to test egg albumen, particularly when purchased in the liquid form, for adulteration with blood albumen, Ganther suggested (J. Soc. of Dyers and Colourists, 1886, p. 47) the use of a mixture of 250 cc. caustic soda solution, 50 cc. copper sulphate, 700 cc. glacial acetic acid, but specified no particular strength of the individual solutions composing the reagent. We have endeavored to prepare this reagent, using varying strengths of copper sulphate and caustic soda solutions, but in no case did we succeed in obtaining a reagent, which would distinguish between egg albumen and blood albumen.

Allen (Vol. IV, p. 47) states that blood albumen containing the ordinary salts is unaffected by agitation with ether, whereas egg albumen gradually coagulates. This reaction is, however, reversed in the cases where no salts accompany the albumen.

Gelatine is best tested for by the addition to a dilute (2 per cent.) solution of the albumen, of a 1 to 2 per cent. solution of tannic acid; a copious precipitate will be formed if gelatine is present in any quantity.

Carrageen.—Carrageen (Irish moss) is very largely employed as a thickening agent, containing a large percentage of a viscous mucilage which is readily extracted by boiling.

The important factors in the analysis of this product are (*a*) percentage nitrogen, which should not be lower than 1.4 per cent. nor higher than 2.5 per cent., the percentage amount of moisture and the amount of mineral matter. The latter is liable to considerable variation and is indicative of the amount of salt present. The determination of the moisture should be carried out at a temperature not higher than 99° C. The percentage amount of sodium chloride should be determined.

The following is an analysis of a fair average commercial sample:

IRISH MOSS.

Moisture	=	20.9 per cent.
Ash	=	18.38 per cent.
Nitrogen	=	1.58 per cent.

Algin.—The gelatinous substance extracted by treatment of certain seaweeds, particularly laminaria, with caustic alkali and subsequently neutralizing the resulting sodium alginate by the addition of alginic acid obtained by precipitating a portion of sodium alginate with mineral acid, is now being somewhat largely employed in certain industries as a substitute for Irish moss. The amount of alginic anhydride present in commercial samples of the product will range between 4 and 6 per cent.

	(1)	(2)	(3)	(4)
Moisture	92.3	93.4	90.0	91.0
Alginic anhydride	5.6	3.8	6.3	4.7
Ash	2.0	2.6	3.8	4.0
	99.9	99.8	100.1	99.7

Gum Tragacanth.—Gum tragacanth on account of its high price is very liable to adulteration with lower quality gums. Owing to its acidic constitution tragacanth has a capacity for absorption of alcoholic caustic potash solutions and in consequence the saponification value carried out in identically the same manner as when making oil or fat analysis is a very important factor in determining its purity.

Good quality gum tragacanth will give saponification values ranging from 100 to 180. The percentage amounts of water will range from 18 to 22 per cent. and of mineral ash from 2.5 to 3.0 per cent. Adulteration of the genuine gum tragacanth and substitution of Indian gum tragacanth is very prevalent. The latter gives, when dissolved, a mucilage which is transparent and possesses an acid reaction, whereas the genuine gum produces an opaque mucilage which is quite neutral. Genuine gum tragacanth (*Astragalus gumifie*) gives a blue coloration with iodine, whereas the Indian gum does not.

A fairly reliable method for the detection of Indian gum in gum tragacanth is given by Emery (*J. Ind. and Eng. Chem.*, 1912, pp. 374-375). The test is based on the fact that Indian gum (*Sterculia urens* and *Cochlospermum gossypium*) yields on hydrolysis with phosphoric acid, acetic acid in large quantities. Thus the author in question found in several samples of sterculia acetic acid to the extent of 15.9 per cent., whereas Robinson has shown cochlospermum gossypium to contain 14.4 per cent. acetic acid.

In samples of genuine gum tragacanth examined by us, volatile acid has only been present to the extent of 1.8 per cent. to 2.4 per cent. so that where tragacanth gives a high percentage of volatile acid on hydrolysis, it points to adulteration with other gums.

The solubility of the gum is an important consideration. Gum tragacanth is only partly soluble and produces a viscous mucilage when dissolved in a 1 per cent. solution. Gum tragacanth is only completely soluble in water by prolonged boiling under pressure, whereas most other gums, *e. g.*, juniper, acacia, arabic, may be dissolved comparatively readily.

GUM TRAGACANTH.

Moisture (at 105° C.)	17.8 per-cent.
Ash (white)	2.97 per cent.

Gum Acacia.—This product (perhaps more commonly known as gum arabic) varies considerably in quality, same being dependent chiefly upon the source of origin, African gum arabic being nearly white in color and soluble in water, whereas Indian gum arabic is of a dark color and insoluble. The most common adulterant of this gum is dextrine.

Gum acacia may be detected from gum tragacanth by:

(*a*) The fact that it is readily soluble in both hot and cold water, whereas gum tragacanth is more insoluble.

(*b*) Gum acacia is precipitated by a solution of basic lead acetate, whereas gum tragacanth is not affected by this reagent. The specific gravity of gum arabic when dry (*i. e.*, at 100° C.) is 1.525. The mineral ash, consisting chiefly of calcium and magnesium oxides and potassium carbonate, is generally in the neighborhood of 3 per cent.

An important factor in the analysis of gum arabic is the acidity, which varies from between 2.5 to 3 per cent. of free arabic acid.

The following are analyses of gum arabic:

Gum Arabic.

Water	= 14.1 per cent.	18.07 per cent.
Ash	= 2.4 per cent.	2.66 per cent.

	[1] Acacia Pycnantha.	[1] A. Horrida.
Water	= 13.55 per cent.	15.34 per cent.
Ash	= 0.92 per cent.	2.59 per cent.
Insoluble matter	= 0.64 per cent.	0.98 per cent.

[1] Arch. Pharm., 1910, p. 171. J. S. C. I., 1910, p. 710.

Gum Tragasol.—The gummy exudation extracted from the locust bean is now largely used as a substitute for gum tragacanth and other gums, for thickening and sizing purposes. The following is a recent analysis:

Gum Tragasol.

Moisture	= 93.40 per cent.
Ash	= 0.09 per cent.
Gummy matter	= 6.51 per cent.
	100.00

Gum Juniper.

Moisture at 100° C.	= 2.65 per cent.
Ash (white)	= 0.10 per cent.

Casein.—The important constituents in the analysis of a sample of casein are moisture, fat and nitrogen. The percentage of casein is calculated from the percentage of nitrogen by estimating the total nitrogen determined by the Kjeldahl method, multiplied by 6.61. The sample should also be tested for solubility. This is best done by taking 10 grams with 50 cc. water rendered alkaline by the addition of 2 cc. of 30 per cent. ammonia, leaving the solution to stand for one hour and if the whole of the casein is not dissolved, gently heating.

The percentage amount of fatty matter, which usually varies from about 0.2 per cent. to 0.6 per cent., is estimated by extraction with petroleum ether in the ordinary way. The following is a representative analysis:

Casein.

Moisture	= 15.97 per cent.
Fat	= 0.35 per cent.
Ash (white fusible)	= 9.82 per cent.
Casein	= 74.60 per cent.
	100.74

GRAINS ON LEATHER.*

By F. E. Durrant.

As a preliminary to the consideration of the development of grains, natural and otherwise, which characterize so many styles of fancy leather, it is necessary to give a short survey of the structure of the skin which forms the foundation upon which the workman exercises his skill and ingenuity.

A glance at one of the many illustrations showing the structure of animal skin will show a foundation of fibers, not so compactly held together at their base as is the case as they approach the upper layers or grain surface. Surmounting this fibrous structure is seen a very thin and delicate layer known as the "Malpighian layer," which, as will be shown, plays a most important part in the production of grains. Above this layer is the outer skin or epidermis, which acts as a protector to the underlying dermis or true skin. In the process of leather manufacture intended for boot uppers and the colored fancy trades, the epidermis is most carefully removed, so that the Malpighian layer does not suffer injury.

Probably the original inducement to produce a grain upon fancy leathers arose from the appearance presented by dried-out leather when thrown flat upon the table. The grain surface would be seen to be more or less drawn and wrinkled. Investigation of the causes producing this effect reveals certain points well worth attention. The primary cause may be said to arise from skin structure itself. Its purpose is to cover and protect the vital organism of the animal, hence it is in form an envelope enclosing a body. This gives rise to the fact that the outer portion is larger in surface measurement than is the under or flesh side. Naturally it follows that the skin, therefore, when placed flat upon a table, the grain side should be forced into a series of small wrinkles possessing no uniformity in design, while the flesh side may be fully extended to its furthest limit. This effect is seen to be more pronounced in thick than in thin leather, and advantage is taken of this knowledge to produce varied sizes of natural grains by manual labor.

Doubtless attention was early drawn to the prominence of the grain appearing on rough dried leather, such, for instance, as the

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* *Leather World*, Dec. 4, 1916 and Jan. 11, 1917.

goat skin, and this would give a lead to an observant mind of the possibility of producing a regular grain surface by suitable measures being taken.

A skin pleated grain inside, and submitted to a little pressure, would further reveal a crease which changed the form of the prevailing drawn-up grain, and by following up this discovery by making, not one long crease, but a succession of these creases all in the same direction, the accomplishment of the long grain, more or less regular in effect, would result. Doubtless the appearance would not be satisfactory for several reasons. The inequality of the thickness of the skin would early be seen. To produce even grain, the substance of the skin must be, as far as can be attained, level and regular throughout. Where this is the work of the shaver, very great skill is needed.

It may here be said that originally the fancy leather finisher was a currier, and took pride in performing all the necessary work in producing a fine finished leather from the rough tanned article. Gradually there were changes introduced, and one man devoted himself entirely to shaving the skin, another to producing the grain. It has often been noticed how certain shavers and finishers have greater skill and special aptitude in performing respectively some class of work, and have adopted the expedient of exchanging their allotted portions or "draws" with each other on mutual terms. Doubtless this method was the origin of the dividing up of much work into sections and to the development of specialized skill and knowledge, bringing out higher trained workmen and better results.

Having discovered roughly the manner of forming a long grain by a succession of creases or wrinkles running parallel, the next step of turning the long into a square grain by making a series of similar creases, but at right angles to those already formed, would follow, and then it is easy to conceive how the corners of the square grain could be rounded off by careful manipulation in the creasing or graining to produce other formations. Roughly, this is probably the origin of the natural grain produced upon fancy leather. But much had to be accomplished before a really finished article was produced. Attention has been drawn to the regular thickness of the skin throughout as being one of the essential points needed to attain success. Next would be noticed that, whereas the first experiments in graining were made upon dry leather, that a slight pressure exerted from under the flesh side caused all the grain to disappear. To fix this grain, it was soon found that the work must be performed in the first stage upon skins in a dampened condition, and so giving the creases a deeper and firmer hold on the leather. Hence, after shaving and straining on boards to dry out flat, the leather is made fairly wet and piled a while. It is assumed that, where colored leather is being worked, the dyeing has taken place before or after shaving, whichever method is preferred.

Certain contrivances became necessary as the work progressed. and these took the form of hand boards, about 12 in. by 8, having a leather strap across the center from side to side, and between the strap and board the workman pushed his right hand. On the reverse or under side various ideas were used. Generally attached is a sheet of rubber, cork, linoleum, etc., and some have fluted or grooved wood, perforated tin—rough surface outward—just as the workman found it enabled him to accomplish the work in hand. For very heavy work, the arm board was introduced.

The production of grain by these means is followed by a considerable shrinkage in surface measurement. The flesh side is not extended to its fullest extent, consequently the grain is "tucked up," as it were, to cover the same area as the flesh. But to obtain the desired grain this is an unavoidable result.

To meet the demand for lower cost of grained leather, recourse was had to embossing. In the early stages a square copper negative or plate was obtained by depositing electrically a covering of copper upon a selected and prepared portion of finished leather. When a sufficient deposit of copper had been obtained, a backing of composite metal was provided to give it strength. This plate was afterwards fixed in a large screw press worked by hand. Leather placed beneath this copper plate and submitted to pressure became impressed with the design on the plate, and this without appreciable loss of size. A further development of the process resulted in larger plates being made, which were then converted into a roller, and thus, in a suitable machine, the work of embossing became continuous and less costly. Many rollers are engraved with a design which is not so expensive as the electrotyping method. The grain produced by embossing is, however, easily distinguished from the naturally worked-up grain and is of a much inferior character, although it meets with a demand which proves its usefulness. It certainly permits a less costly article, as sheep skin, to be used to produce imitations of very expensive leathers. The utility of embossing a grain upon a skin will be treated later from another point of view.

Attention has been drawn to the contraction of the flesh as a corollary in the production of a natural grain. One of the most prominent examples of this is the paste grain on skivers. Attempts to obtain a square grain by hand upon a skiver were futile, even upon the wetted skin; the creases were not permanent, and easily disappeared with a little pressure. Recourse was had to sizing the flesh to stiffen and hold the grain, and this eventually proved successful. A size of glue is made and used cold, being brushed into the flesh side. The skin is hung up to dry, and then there follows the seasoning, this comprising a solution of egg or blood albumen, with a little new milk and coloring of the same shade as the dyed skin. Before glazing, a finely fluted roller is used in the machine, followed by the smooth glass or agate. The need of this is to give a small square-dried pattern to the grain, which aids the workman to get a regularity by boarding which he otherwise cannot obtain. The roller does not turn round in its bed, but in action impresses long lines on the skin with every stroke of the machine. By crossing these lines at right angles, the square impression is obtained. Glazing over these lines follows. The skins are next boarded by hand, following the directions of the lines formed, the grain being pleated over itself. By this means a square grain is produced on the skiver, known as a paste grain, but the idea pervading the minds of those who first introduced this particular grain was to produce upon a sheep skin skiver the similar grain to the one obtained on moroccos known as the Turkey grain.

To finally fix the grain upon the skiver, it is necessary to sponge the flesh side with boiled starch, afterwards drying the leather in a hot stove. It is here where the shrinkage in size is most noticeable, but it is necessary to secure the prominence of the grain. In working to obtain this result upon skivers, it was early recognized that the skins must receive special treatment in the liming stage to obtain the best graining results.

It may here be remarked how the practically trained leather dresser gained good results, for by giving the skins more lime than usual, he produced a leather of a more spongy nature, which was found to be needed in the finishing stages, to be necessary to produce the best grain. In other words, the fiber structure of the skin must be rendered more open and less compact beneath the Malpighian layer to allow that layer to be wrinkled and tucked up into ridges.

Skins naturally of a solid character will not by boarding produce a satisfactory grain, nor will skins off young animals. The older and full-grown animal skins give the best results. The flanks of the skivers always give more or less trouble, from their particular softness and adhering flesh, producing a grain differing from the remainder of the skin.

To get regularity and to utilize skins otherwise unsuited to paste grain work, attention was turned to the embossing machine. A grain suitable for the purpose is cut in a copper or steel roller, and this is used to impress the form of the pattern upon the skiver before glazing. The result differs from the original hand-produced grain, being more uniform, but much waste is avoided in using up the skins, so the means may be said to be justified.

Seal skins, which are so largely used for bags and fancy articles of a small class, are valued for the large round grain they possess. It has been stated that to obtain a large grain, thick leather is needed. This is amply shown in the case of seal leather. It is of a soft, spongy nature, which renders it specially suitable to the production of a large grain. But there always existed a difficulty in obtaining a satisfactory result in the earlier productions of this article. Embedded in the skin were natural wrinkles, or "growth marks," as they were called, running in lines from the butt upwards and spreading outwards to some extent. When boarding the skin, these deep marks would make their appearance, and could not be eradicated. According to the number, so the classification of the finished leather was affected, which carried with it a less satisfactory profit. To avoid this objectionable marking, recourse was eventually had to the embossing machine. An electrotype of as perfect a grained skin as could be obtained was secured, and a roller made. Then before commencing the boarding of the seal skin, it was passed through the machine, which gave it the necessary first grain formation. The result was quite satisfactory. When finished, seal skins are split with the band knife machine to secure a thin leather bearing a bold, prominent grain.

When introducing chrome-tanned calf skins, it was found that the soft leather produced did not hold a smooth grain, as for instance calf kid, which it eventually replaced in the market. Chromed calf was covered with little wrinkles, so to get over the lack of a smooth fine grain the skins were boarded and a square grain given, to which was added a glaze. This is said to be the origin of the "box," or square grain, on chromed calf.

Apart from the embossed grains are others of a purely mechanical nature; such, for instance, are the long grains produced with a finely cut fluted roller. Used in a glazing machine, this roller first produces long parallel lines from side to side of the skin. By slightly changing the position of the skin, and again submitting it to the action of the roller, the original lines are crossed or split, as it is termed. A third splitting may be followed by glazing with a smooth roller. This is known as long grain. A variety may be produced by changing the position of the skins while rolling, also by using differently fluted or grooved rollers.

Very often leather is needed for some purposes, particularly shoe work, where the grain must be absolutely fine, without wrinkles, when quite flat on the table. To obtain this result, the leather is usually filled with more or less hard greases and fats which, forced into the fiber structure warm, harden when cooled. All possible expansion is forced out of the leather before the grease sets, and prevents the flesh drawing the grain afterwards into wrinkles. This preserves a fine smooth surface. But for some leathers grease is objectionable, and attention is turned to mucilages, such as are obtained from Irish moss, linseed, etc. With preparations of this kind, leathers, for example, as purse hides are treated. This attains a somewhat similar result to that secured by the use of stearines and hard fats, only no greasiness is present. This leather must not, however, be folded, or wrinkles appear in the grain and effectually spoil the particular finish which has been gained by much labor exercised on this kind of hide.

Very often the grain or Malpighian layer on the surface of the skin is damaged from various causes. Its extreme thinness renders it susceptible to be easily destroyed by careless working in the earlier stages of leather manufacture. Skins off young animals are more delicate in this respect than those taken from fully developed animals. Where this layer is damaged, a satisfactory natural grain is not always obtained. As a remedy, various compositions have been tried as a means to cover the damaged portions and allow a grain to be raised by boarding. The only one that has given any promise of success is the use of collodion, as the base of a mixture of other necessary articles which together will form a thin flexible covering over the defective space, while it does not penetrate the leather to form a solid patch, as this would prevent any grain resulting from boarding. The covering must be adhesive, and dry quickly, without any stickiness on the surface when dry, whilst it must be possible to give it the same color and polish as the rest of the skin. As a rule the whole of the skin is given a covering to obtain uniformity in appearance, but the expense entailed makes it questionable as to whether it pays to do this, and this is the factor which rules attempts to cover faults of this kind. The common practice is to "doctor up" damaged skins with some cheap composition composed of weak size and coloring; then, when dry, emboss a grain upon the surface so treated.

From the foregoing remarks it will be gathered what are the essential points to attain to obtain a satisfactory grain by hand or machine boarding, as different from embossing. First, the leather must be soft, otherwise the grain will be small and insignificant, if any is obtained. The softness must not be the result of violent action in a staking machine, by which the desired result is obtained by pulling the skin in various directions, and so breaking up and lacerating the fibers supporting the Malpighian layer. These fibers should be intact and not broken for this reason. When the skin comes from the drying boards, where it has been stretched and nailed to dry flat, the fibers are extended to their fullest capacity in every direction. Relaxation follows damping the leather, and as the fibers contract they exercise a pull upon the overlying Malpighian layer, which, as has been shown, covers a greater surface than the fibrous or flesh side. This contraction of the fiber causes a grain of irregular formation to appear. If the fibers are ruptured, little or no contraction follows damping the leather, and no grain appears. Boarding will not produce any satisfactory result. A little grain will appear where the fibers are still intact, but elsewhere the results are *nil*.

To obtain the best results, attention must not be centered solely on the finishing department. It is to the first stages of treatment in the lime yard, and here it is mainly where satisfactory grain production really originates. If the necessary amount of time, lime, and labor is given, suitable leather for the purpose will follow; if too little is done here, it is as disastrous as too much to obtain good effects. The subsequent stages all need care and attention to obtain a satisfactory result.

These remarks are intended as a guide to the colored or fancy leather branch of the trade, and do not apply in every particular to the heavier section. The principal skins forming the raw material in this portion of leather manufacture are goat and sheep, whilst amongst the rarer sources of supply may be mentioned seals. Calf skins, as a rule, are not grained; their claim to a fine natural grain is their special claim, and this is not disturbed except in the instance of chrome tannage for boots.

The result of these investigations only goes to prove how valuable is the knowledge attained and centered in the manufacturer who possesses it.

ABSTRACTS

Tanners Institute News, *Bulletin No. 31*, Feb. 7, 1917. Tanners Institute announces the completion of arrangements for the production of heavy leather in its school tannery this year. The students in the one-year course in Tanning and those of the one-year course in Applied Leather Chemistry are making use of these improved facilities, and they and future classes will receive due instruction in the tanning of heavy leathers. Practice in the tanning of the various other kinds of leather for which the school has long been well equipped will continue as heretofore to receive ample attention. It now becomes possible to give specialized instruction adapted to the particular needs of individual students where this seems advisable. The newly acquired facilities comprise a completely equipped model plant for sole leather and other heavy leathers. The equipment is up-to-date in every respect, and includes a suitable assortment of pits and machinery, all of which has been installed during the past year by the students as a feature of practical instruction. Some of the new equipment for heavy leather manufacture was donated by leather concerns or by tanning companies who have become interested in the progress of the school. In conducting the sole-leather tanning work, two packs per week are put into process, which makes it now possible to run a complete control system throughout the year, in accordance with best modern practice. The attention of sole and belting leather manufacturers especially is called to this new development in the school's heavy leather facilities, and it is believed that young men, whether sent by their employers or coming on their own initiative, will find a season's (nine months) course of instruction highly advantageous to their future advancement. Early application is advisable, as only a limited number of students can be accommodated. Address inquiries to The National Association of Tanners, 212 W. Washington St., Chicago, Ill., or 10 High St., Boston, Mass., or to Pratt Institute, Brooklyn, N. Y.

Cutch Production in Burma. *Jour. of the Royal Soc. of Arts*, Jan. 19, 1917, p. 172. The demand in the United States for crude dyes is being met, in part, by increased shipments of cutch from Burma. In 1915, 1,240,140 pounds of cutch were exported, in contrast with 237,440 pounds in 1914. In the manufacture of cutch no scientific process is employed, the industry being carried on exclusively by natives. It is obtained from the *Acacia catechu,* the trees being felled while green, the bark taken off, and the timber chopped up and boiled in large cauldrons. The liquid is drained off and solidifies as it is cooled. In making the better grades of cutch the heart wood only is utilized. It appears from a report by the United States Consul at Rangoon that cutch is brought into the market in several forms, the three principal ones being, (1) tablets, small rectangular blocks weighing from 1 to 2 pounds, (2) blocks, more or less square, weighing from 28 to 56 pounds, (3) baskets, a soft cutch. Tablet cutch is the best and basket the poorest. In recent years a larger business has been done in basket cutch than in the other two. On arrival at Rangoon the cutch is packed in wooden cases, usually containing 1 hundredweight net, and is then ready for export. Cutch trees are found throughout the whole of Burma, but the question of transportation makes cutch boiling unprofitable in many districts. Licenses for cutch manufacture are granted annually by the government, and the industry affords relief in seasons of bad harvests. The government increases or diminishes the number of licenses as necessity indicates. The principal producing districts of Burma are Prome, Thayetmyo, Myingyan, Minbu, Pegu, Yamethin, and Pyinmana. Cutch is used largely as a dye, also to some extent for tanning and as a preservative. In Burma, fishing nets and sails are steeped in it to protect them against the action of sea-water.

Activity of the Aden Hide and Skin Market. CONSUL ADDISON E. SOUTHARD, Aden, Arabia, in *Commerce Reports.* There has been a remarkable activity in the hide and skin market of Aden during the past three or four months, but this past week (Nov. 25) has witnessed unprecedented prices being paid for Arabian goatskins. The direct cause is said to be the demand from America and the local buyer now controlling the Aden goatskin market, by reason of being able to outbid his competitor, is reported to be buying on commission exclusively for an American client. Normally goatskins are bought at $6.50 to $7.50 per score, but prices paid this week by the above-mentioned buyer reached $12.33 per score. It is reported that $15 per score has been offered for Arabian skins, but so far there is no record of sales at that price. So keen is the demand for goatskins that sellers dispose of their goods without having to submit them to the usual examination or engage in the usual dickering about prices.

The bull market in Aden skins was started about six months ago, it is said, by the arrival of representatives of a firm that had done a large business in Red Sea ports. This firm announced that it was in the market for an unlimited supply of goatskins and would pay top prices. This firm and the local one above mentioned soon monopolized the skin market, the two older and most prominent American firms in the business in Aden ceasing temporarily to be active buyers. It is natural that the market should eventually break, but so long as the American tanners directly represented here find it necessary to control the Aden goatskin export for the reason, it is said, that they have fixed contracts to meet, prices will continue high. Aden markets are supplying this year an average of 300,000 goatskins per month.

With the wet season just closed in Abyssinia, which country is the source of many of the best skins marketed in Aden, increased shipments are expected from there. Political troubles in Abyssinia and some interruption to the railroad traffic from Jibuti inland has delayed skins coming to the coast, but the resumption of considerable shipments has already begun. The principal sources of goatskins in the Aden market are Arabia and Africa. From Arabia large shipments normally originate at Mocha, Jidda, Konfidah, Hodeida, and Ghizan, while the places of shipment of considerable quantities to Aden from Africa are Somaliland, Jibuti, and Obok, Abyssinia and Massaua, Dunkali coast, independent Somali ports, and Italian East Africa. Normally Arabian and African ports supply each about one-half. Most of the African skins are sun-dried, known to the trade as flints, while Arabian skins are brine-cured. Due to expertness in skinning, the Abyssinians send skins that are regarded as the best. Somali skins are also highly regarded as being free from knife cuts and as containing the largest number of primes. The Abyssinian skins are generally of superior weight and condition, although a season either too dry or too wet affects the quality. The supply of African skins from Italian East Africa and Eritrea will possibly be affected by a decree published by the Italian Government in Eritrea on September 21, prohibiting the export of skins from there to all countries except Italy. At this time the effect on the supply of skins at Aden is not marked, and it is possible that it will not be, as some of the skins heretofore brought out through the Italian African ports will reach the coast at other points, due to the unwillingness of producers to change from the old and well-established Aden buyers to those supplying exclusively the Italian markets.

Most of the Arabian skins are exported from Aden as Mochas, but are bought by local buyers under trade names taken from the place of origin, such as Ghizans, Jiddas, Konfidahs, etc. The principal African skins are classified as Mogadiscios, Berberas, Somalis, Massauas, Harrars, Abyssinians, Gallahs, and Dunkalis. Of these the Mogadiscios and Massauas may be affected by the prohibition issued by the Italian Government of Eritrea above referred to. Classifications of skins exported to America and Europe from Aden is usually into firsts and seconds. A class consisting of culls and, in general, all skins or pieces of skins rejected goes principally to the Indian market.

The following table shows the exports of goatskins from Aden by countries for the fiscal years ended March 31, 1914, 1915 and 1916. It will be seen that the United States bought in 1915-16 nearly 80 per cent. of the total export of goatskins from Aden and made 5 per cent. greater direct purchases than in the preceding year. In addition, Aden goatskins are re-exported to the United States from foreign countries. An increased value for the export for 1916-17 is predicted, due to the present high prices and generally active state of the market.

	1913-14		1914-15		1915-16	
Countries	Hundred-weight	Value	Hundred-weight	Value	Hundred-weight	Value
France	6,044	$143,112	3,281	$85,619	1,214	$33,277
Germany	115	2,722	34	656	——	——
India	3,688	29,374	3,363	28,412	1;617	21,320
Italy	599	20,305	6	316	355	11,253
United Kingdom	3,377	106,351	1,743	47,667	6,750	177,921
United States	39,512	1,234,761	32,040	915,877	34,593	962,370
All other countries	17	317	76	1,934	——	——
Total	55,352	$1,536,942	40,543	$1,080,491	44,529	$1,206,141

The number of skins exported in the fiscal year 1913-14 was 4,268,167; 1914-15, 3,243,391, and 1915-16, 3,641,560.

Sheepskins play a less important part in the Aden market than goatskins, but they form an important item of export. The best skins are the flints from the Somali Coast, but considerable quantities of the brine-cured Arabian skins are in the market. Sheepskin exports are about two-thirds as great as goatskins. The United States took more in 1916 than in 1915, as will be noted from the following table. The next largest buyer was the United Kingdom, but it is said many of the skins going there are re-exportetd to the United States. The total exports were more for 1915-16 than for the previous year. Arrivals of sheepskins of good quality are just beginning, and find an active market at high prices. At present the Arabian skins are selling in the Aden market at about $7.50 per score, and the African skins at about $14 per score. The principal purchases are being made by or for American houses. About a year and a half ago the Arabian skins were bringing in the local market not more than $3 per score and the Africans $11 per score. Sheepskins sold here are classified as white, black, and red heads, the black heads coming mainly from the African Coast and being considered the best. The destination of the exports of sheepskins during the three fiscal years ended March 31, 1916, follows:

	1913-14		1914-15		1915-16	
Countries	Hundred-weight	Value	Hundred-weight	Value	Hundred-weight	Value
France	6,073	$182,293	2,356	$102,755	274	$9,959
Germany and Austria	653	12,660	160	4,602	——	——
India	2,607	21,311	1,632	14,128	1,289	9,817
Italy	371	11,848	30	1,166	59	1,784
United Kingdom	8,717	331,311	9,580	308,138	13,086	349,798
United States	3,785	175,042	7,397	273,574	12,548	447,320
All other countries	963	35,172	217	13,292	——	——
Total	23,169	$769,637	21,372	$717,655	27,256	$818,678

The number of sheepskins exported during the fiscal year 1913-14 was 1,853,523; 1914-15, 1,709,866; and 1915-16, 2,182,911.

The United States plays a considerably less important part in the Aden cowhide market than in the skin market. The Aden hide market is supplied largely from Abyssinia through Jibuti and Italian East Africa. In 1916 Italy led all countries in the purchase of hides in this market, taking nearly five times as much as the United Kingdom, which is the next best customer for Aden hide exports. In 1915 the purchases of the United Kingdom far exceeded those of Italy. The United States bought $6,618 worth of hides in this market in the fiscal year 1915-16, compared with $2,430 worth in the preceding year. The value of the hide exports from Aden for 1915-16 was less than for the preceding fiscal year, and present indications are that the present fiscal year will not exceed the last one. Just at present the market is showing more activity, although it is understood that considerable shipments are being made direct from African ports to Italy. Present prices are steady at about 20 cents a pound at Jibuti. There have been no recent large sales in Aden, as the owners can get better prices in Jibuti.

The following table gives the destination of hides exported from Aden for the three fiscal years ended March 31, 1916:

Countries	1913-14		1914-15		1915-16	
	Hundred-weight	Value	Hundred-weight	Value	Hundred-weight	Value
France	13,735	$244,472	9,857	$195,498	2,866	$68,893
Germany and Austria	12,486	309,971	3,563	85,589	——	——
India	1,364	11,426	1,617	15,037	1,632	10,636
Italy	9,478	189,749	11,846	242,704	26,958	711,218
United Kingdom	15,535	617,890	22,393	626,469	5,175	154,207
United States	——	——	83	2,430	289	6,618
All other countries	2,742	81,580	3,572	82,314	376	4,375
Total	55,340	$1,455,088	52,931	$1,250,041	37,296	$955,947

The number of hides exported during the fiscal year 1913-14 was 553,397; 1914-15, 529,303; and 1915-16, 372,986.

Skins constitute an average of 14½ per cent. of Aden's total annual exports and hides about 10 per cent. of the total. Thus hides and skins comprise together about 24½ per cent. of the total exports, ranking far ahead of any other item. The United States took directly in 1915-16 about 80 per cent. of the total goatskin exports and 55 per cent. of the sheepskin exports, but took less than 1 per cent. of the cowhide exports. It is stated that the hides marketed here weigh so unevenly and give such unequal results in tanning that American tanners are not inclined to buy them. Even at this time of active buying available freight space is said to be uncertain and while considerable shipments have already gone forward large stocks are piling up, more rapidly than freight space is being made available. A continuance of this condition is said to be certain to bring about a break in the present inflated prices. (See p. 103.)

Burma Conquering Cattle Disease. CONSUL W. RODERICK DORSEY, Rangoon, in *Commerce Reports,* Nov. 20. The report of the Civil Veterinary Department of Burma for the year ended March 31, 1916, as summed up in a resolution of the Government of Burma in the Agricultural Department, shows a period of satisfactory improvement in the conservation of domestic animals. The Province was singularly free from cattle disease. For the fifth successive year there was a decrease in the reported number of deaths from contagious sickness; the total, 7,210 in an estimated cattle population of 6,000,000, was the lowest on record and just over one-fifth of the average for the ten years preceding. Rinderpest, the chief scourge, claimed 3,589 victims, or a little more than one-eighth of the average for that period. The mortality was practically confined to Akyab and the districts bordering on the Shan States, China, and Siam. It is believed that with effective supervision and control over imported cattle, the prominence of this disease in Burma will disappear. The department reports that 1,782 cattle died from foot-and-mouth disease, and 1,839 from anthrax, hemorrhagic septicemia, and black quarter. The last two are not differentiated by villagers or headmen, but are considered as different manifestations of anthrax. There were twenty-one more of these cases than in 1914-15. The assistants of the Civil Veterinary Department visited 24,787 villages and treated 94,761 sick animals, both totals being the highest on record. Touring by inspectors created an adequate standard. Reports of outbreaks are now more promptly made, and the benefits of early segregation are more widely realized. Still closer relations between the Agricultural Department and cattle owners may be expected from the spread of cattle insurance societies on co-operative lines. The system of insurance adopted encourages the better treatment of cattle and the resort to expert assistance in case of sickness. The total expenditure incurred by the department was $89,220.

Japan's Leather Industry. CONSUL M. D. KIRJASSOFF, YOKOHAMA in *Commerce Reports,* Nov. 22. Leather manufactories in Japan which maintain large plants are:

Nippon Hikaku Kaisha, capital 2,500,000 yen ($1,246,250), Senju Machi, Minami Katsushika Gun, Tokyo Prefecture.
Meiji Shikaku Kaisha, Azuma Mura, Minami Katsushika Gun, Tokyo Prefecture.
Sakura Gumi, capital 100,000 yen ($49,850), Owari Cho Itchome, Ginza, Tokyo.
Toyo Seikaku Kaisha, capital 300,000 yen ($149,550), Toyosaki Cho, Nishinari Gun, Osaka Prefecture.
Nitta Taikaku Seikaku Sho, capital 600,000 yen ($299,100), Kuboyoshi Cho, Minami Namba, Nishi Ku, Osaka.
Nakai Chrome Leather Company, output in 1914, 1,200,000 yen ($598,200), Osaka.
Osaka Taikaku Seizo Sho, Osaka.
Murakami Shoten, capital 150,000 yen ($74,775), Osaka.
Teikoku Chotai Kaisha, capital 150,000 yen ($74,775), Osaka.
Sanyo Hikaku Kaisha, Himeji.
Taisho Hikaku Chotai Kaisha, capital 1,000,000 yen ($498,500), Shiokoji, Kyoto.
Chosen Hikaku Kaisha, Kei-Ki-Do, Chosen (Korea).

The output of leather in Japan during 1914, the latest year for which figures are available, was as follows: Tokyo Prefecture, 4,082,234 yen ($2,034,994); Osaka Prefecture, 2,291,364 yen ($1,142,245); Hyogo Prefecture, 1,005,164 yen ($501,074); Wakayama Prefecture, 1,110,508 yen ($553,588); other, 654,238 yen ($326,138); total, 9,143,508 yen ($4,558,039). The leather imports for that year totaled 1,952,176 yen ($973,375), while the exports amounted to 868,691 yen ($433,042). The present capacity of the leather factories of Japan, according to value, is estimated at about three times that of 1914. The price has risen by about 50 per cent., however, so that the present actual output in quantity is about twice that of 1914.

East African Trade in Goat and Sheep Skins. CONSUL H. P. STARRETT, Mombasa, British East Africa, in *Commerce Reports.* During the fiscal year 1914-15 (the last available detailed statistics) the total exports of goatskins amounted to 13,465 hundredweight of 112 pounds, valued at $267,900, of which 75 per cent. went to the United States and 20 per cent. to France. In the same year the exports of sheepskins amounted to 2,497 hundredweight, valued at $19,343, most of the product going to India, France, and the United States in about equal quantities. Goatskins are shipped in lots containing three grades, 15 per cent. of the total being of grade 1 (weighing 115 pounds per 100 pieces for the heavy and from 70 to 80 pounds per 100 pieces for the light weights, 60 per cent. being of the second grade, 20 per cent. of the third grade, and about 5 per cent. being kidskins, weighing from 40 to 45 pounds per 100 pieces. The present export market price for goatskins in mixed lots as above is 28 rupees ($9.08) per 20 skins. Sheepskins are also shipped in mixed lots containing three grades. The first grade represents 10 per cent. of the whole, the second grade 50 per cent. and the third grade 40 per cent. The present market price for sheepskins is 10 rupees ($3.24) per 20 skins in the Mombasa market. The export duty on skins is 10 per cent. *ad valorem*; and the present freight rate to New York is 120 shillings ($29.20) plus 20 and 10 per cent. per cubic ton; to Liverpool, Genoa, or Marseille 75 shillings ($18.25) plus 20 and 10 per cent. per cubic ton.

Supplies of European Hides after the War. *Commerce Reports.* An American firm which has employed certain extra plump hides of French, Swiss, and Italian origin in the manufacture of belting, packings, and various kinds of mechanical leathers, and has found its sources of supply curtailed by embargoes, recently made inquiries regarding the probable future production of these hides. In response investigations of the subject were conducted by Consuls General A. M. Thackara at Paris and F. B. Keene at Zurich. In their opinion it is probable that whenever the embargoes are removed the hides will be procurable in adequate quantities.

New Method for Soling Boots. CONSUL HOMER M. BYINGTON, Leeds, England, in *Commerce Reports.* The attention of the Leeds consulate has been called to a recently patented method of manufacturing boot soles from scrap leather. It is claimed that the soles are non-suction, non-slipping, and water-proof, and can be produced at a much lower cost than the ordinary leather sole. Owners of plants for heel building, it is believed, will find themselves in a position to conveniently adopt the new process. It is also claimed that the novelty of the patent may be enhanced by an ingenious arrangement of strips of rubber attached to a thin layer of canvas, the rubber strips fitting into the interstices of the leather sections. This is said to give a pleasing resiliency to the step of the wearer and to do away with the aching of the feet sometimes produced by purely rubber soles.

South American Timber Resources and their Relation to the World's Timber Supply. RAPHAEL ZON, of the U. S. Forest Service. *Geographical Review,* Oct., 1916. The commercial value of the vast forests of South

America is still very little known. The number of species is large, especially in the river bottoms. If the number of commercially useful trees is relatively small and these are scattered among a large number whose value is little or nothing, the cost of logging may be so great as to make the exploitation of such forests unprofitable. This has seemed to be the case heretofore with the tropical forests which have been the source of some of our well-known woods, but recent researches make it probable that among the unknown woods of these forests may be many which can be used for purposes similar to those for which coniferous woods have been supposed to be the only suitable material. Our present knowledge of the technical properties of the majority of the woods of the tropical forests is slight. Only three species are at present known which are suitable for building and similar uses. These are the Parana pine, the Chilean pine and the Spanish cedar. The total forest area of nearly 2,000,000,000 acres may be roughly divided into six regions. (1) the Parana pine region of southeastern Brazil, comprising 200,000,000 acres. Some stands of this pine cut from 15,000 to 20,000 board feet per acre. (2) The antarctic beech region, including some 61,000,000 acres. This forest contains beside the Chilean pine some larch and cedar. (3) The tropical and sub-tropical hardwoods which occupy far the largest area, some 1,200,000,000 acres. The most valuable tree of this forest is the Spanish cedar, which is found scattered among other tropical hardwoods over large areas. The annual cut in Brazil amounts to 47,000,000 board feet. (4) The hardwoods of which quebracho is the most important representative are found chiefly in northern Argentina. The available quantity of quebracho is estimated at 168,000,000 tons. The present rate of cutting is about 1,000,000 tons per year, obtained by cutting over 500,000 acres. (5) Greenheart, which is associated with mora, is the most important tree of British Guiana, which is the only region where it is being cut extensively. The greenheart seldom extends more than 50 miles inland and never more than 100 miles. The wood is used in building ships and docks because it is immune from the attack of the teredo. The annual cut is from 200,000 to 400,000 cubic feet. The tree is found over a range of some 150,000,000 acres. The timber resources of South America are not inexhaustible. Attention has been called repeatedly to the danger of extinction of the quebracho, since little or no check has been placed on the cutting of this tree. Not only the quebracho, but other valuable trees are in danger of extinction from reckless cutting and inadequate forestry laws. The coniferous woods of South America are not more than sufficient to supply her growing population, therefore their preservation is a matter of serious importance. It is important that the tropical hardwood forests be explored, so that their resources may be intelligently estimated and utilized.

Goat and Sheep Skins Cheaper. CONSUL ADDISON E. SOUTHARD, Aden, Arabia, Jan. 15, in *Commerce Reports.* The upward tendency of the prices paid for goat and sheepskins in the local market, reported by this consulate under date of November 27 (see page 96, this issue), apparently reached its limit at the end of the year. So far as can be learned, the highest price paid for skins was 55 rupees ($17.84) per score, which is more than twice the normal price. Sales at this figure were reported during the last week in December. Beginning the new year prices started to fall, and prime skins can to-day be bought in Aden for 35 rupees ($11.35) per score, as against 55 rupees ($17.84) per score paid less than a month ago. The tendency is still downward, and well-known buyers predict a return to the normal price of 20 to 25 rupees ($6.49 to $8.11) per score. Most of the experienced dealers have temporarily ceased buying. It is said that probably only one local firm stands to lose heavily, because of large stocks acquired at the high prices prevailing just before the break came. Other firms will have some loss.

Several causes are reported as responsible for the decline in prices, but the four principal ones seem to be as follows: (1) Large stocks purchased and accumulated, awaiting freight space, which is scarce and costly. One firm with unusually large stocks is said to have recently bid $130 per ton on space for skins from Aden to New York. Even at that figure the firm was able to secure only a limited amount of space. (2) Heavier arrivals from Abyssinia and Somaliland, which always occur during the winter months. (3) Scarcity of ready cash to pay native sellers of skins. (4) A weakening of the demand under the abnormal advance in prices. The demand has not yet recovered, and it is predicted that prices must and will decline still more before there is a recovery.

The declared export returns at this consulate show that for the nine months from April 1, 1916 (the beginning of the current fiscal year in Aden), to December 31, 1916, the number of goat and sheepskins shipped to America was 3,571,565, valued at $2,355,122, as against 3,773,726 skins, valued at $1,409,460, for the entire year ended March 31, 1916.

PATENTS.

Tanning Compound. U. S. Patent 1,210,259. GEORGE T. BALL, Foss, Oklahoma. A mixture of August Flower (which one not stated) Gambier and Glauber salt.

Tanning Fur Skins. U. S. Patent 1,210,968. The mixture used contains alum, salt, borax, fermented flour paste, yeast, alcohol and water in specified proportions.

Spring Roll for Leather-working Machines. U. S. Patent 1,210,041. E. N. BERGSTROM, East Lynn, Mass.

Machine for Handling Hides or Leather in Bulk. U. S. Patent 1,210,700. CARLETON RUHE, Olean, N. Y. This machine is designed to replace the man with the hook in taking stock out of vats.

Artificial Leather, British Patent 102,114. A. E. ALEXANDER, London, Duratex Co., Newark, N. J. Relates to the production of artificial leather, and consists in applying to a fabric base a coating containing nitrated cotton and a vegetable oil and a superimposed baked coating of a leather-japanning composition. The preferred vegetable oil is rape-seed oil, and a number of coatings of the nitrated cotton and oil solution may be applied, the proportion of oil varying for each coating and being such that the oil will not be set free under the baking temperature employed; a specific example of this method of coating is described, and it is also stated that leather fiber may be incorporated with the solution. An example of a suitable leather-japanning composition is described and comprises boiled linseed oil, naphtha, and an opaque pigment ground in oil, and the baking temperature used after this coating is applied is stated to be 150° to 180° F. The material may be embossed to imitate leather, and Spanish or antique effects may then be produced by applying a composition of vegetable oil, vegetable gums, and coloring matter in a suitable solvent, partly allowing to dry, and wiping off the composition from the protruding parts of the surface.

Liquid Dressing for Leather. U. S. Patent 1,214,157. H. A. HAMEISTER, Elkhart Lake, Wis. The dressing is made of rosin, linseed oil and pitch.

Toggle for use in Stretching Leather. U. S. Patent 1,212,485 A. G. HILL, Chelsea, Mass.

Leather Glazing Machine. U. S. Patent 1,214,460. W. B. HICKEY, Sapulpa, Okla.

Crippling Machine. U. S. Patent 1,214,219. C., RAUSCH, Leipzig, Germany.

Leather Brushing Machine. U. S. Patent 1,213,908. CARLETON RUHE, Olean, N. Y.

Skin, Hide and Leather Working Machine. U. S. Patent 1,214,852. FRANCIS WAYLAND, Salem, Mass.

Leather Boarding Machine. British Patent 102,320. P. R. BARKER, Otley, Yorkshire.

Artificial Leather. U. S. Patent 1,217,123. L. LILIENFELD, Vienna. The ingredients are 100 parts nitrocellulose, to which a "colloiding agent" is added, and from 50 to 200 parts of a phenol ester.

Machine for Making Leather of Uniform Thickness. U. S. Patent 1,216,053. H. A. BELL, Indianapolis. The active part of the machine is a rotary scraper.

Leather Working Machine. U. S. Patent 1,215,866. W. C. ROCHE, Beverly, Mass., assignor to the Turner Tanning Machinery Co.

Leather. British Patent 14,543. R. PARKER AND A. H. PATTEN, Yeovil, Somersetshire. "The object is to produce a skin having all the qualities of reindeer leather from inferior skins, such as Cape sheepskins." The skin is split, into three parts and one of them treated with alum, salt, flour, egg-yolk, grape sugar, starch, glycerine, tartar emetic and tannic acid.

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ELECTIONS.

ACTIVE.

Charles William Reilly, England-Walton Laboratory, 307 New St., Philadelphia, Pa.

Joseph C. Dickson, Canton, Haywood County, N. C.

Claude Smith, Barngarth, Cartmel, Grange over Sands, England.

F. G. Alexander Enna, The University, Leather Dept., Leeds, England.

ASSOCIATE.

Dwight W. Cooke, % Reed Laboratories, 227 Fulton St., New York, N. Y.

Francis P. Howden, 255 Lafayette Ave., Brooklyn, N. Y.

James Randall, Low Mill, Ulverstone, Lancashire, England.

CHANGES OF ADDRESS.

Philip W. Tompkins, to 331 California St., San Francisco, Cal.

H. L. Pierson, to ℅ Waterbury Clock Co., Waterbury, Conn.

Erwin J. Kern, to 1084 Eighth St., Milwaukee, Wis. In announcing the election of Mr. Kern as an active member in the February issue, his name was wrongly spelled as Edwin instead of Erwin.

BOUND VOLUMES.

See notice on third page of cover.

CORRECTION.

In the official methods as printed in the Nov., 1916 JOURNAL, page 551, Analysis of Liquors, paragraph 18, Non-tannins, heading of the second column of the table, read "dry powder per 200 cc." instead of "dry powder per 100 cc." In the booklet the same error occurs, top of page 17.

COUNCIL MEETING.

The Council met at the Chemists' Club, New York City, Feb. 24. Present: Messrs. Oberfell, Eachus, Reed, Alsop, Faust, Small and Veitch. The Secretary was instructed to give notice to delinquent members that unless their dues were paid by March 31, the JOURNAL would be discontinued to their addresses. It was agreed to make special effort to obtain papers pertaining to disinfection of hides. W. K. Alsop, Editor of the JOURNAL, submitted a report. One matter mentioned in this report was the fact of the increasing scarcity of some of the back numbers. The Council authorized the publication of the notice which appears on the third page of cover in the March number and also in this number. Mr. Reed brought up the question of the standardization of kaolin. It was decided that a preliminary investigation be conducted by R. W. Frey, of the Bureau of Chemistry. The time for the annual meeting was agreed on. (This has been changed as announced on next page.) The President was authorized to appoint a Program Committee. Nominations were made for members of Council.

FOURTEENTH ANNUAL MEETING. DATE CHANGED.

The notice in regard to the fourteenth annual meeting given on the slip attached to the outside of the March number was premature. When the Committee of Arrangements set about securing a place, they found that on account of a large convention to be held in Atlantic City during the week selected, no accommodations could be secured in any of the beach-front hotels. The time has therefore been set for a week later, June 7, 8, 9. The place is the southwest solarium of the Marlborough-Blenheim. Those expecting to attend are requested to write direct to the management of the hotel for reservations. Rates are given below.

The Program Committee are not ready to report, but some valuable papers are already promised. The subject of one of these is anthrax sterilization, embracing description of recent research in this line.

RATES PER DAY, MARLBOROUGH-BLENHEIM, ATLANTIC CITY.

	Amer. plan	Eur. plan
Double room without bath, two persons....	$9, $10	$5, $6
Double room with bath, two persons.......	$10, $11, $12	$6, $7, $8
Large ocean front room, two persons......	$16, $18	$12, $14
Single room without bath, one person.. ...	$5, $6	$3, $4
Single room with bath, one person........	$6, $7, $8	$4, $5, $6

THEORIES OF LEATHER CHEMISTRY.

By John Arthur Wilson.

The development of every branch of chemistry has assumed such proportions in recent years as to encourage an attempt to explain the mechanism of some of the various operations of the tanning process. On account of the extreme complexity of many of the problems only a comparatively small amount of work has been done along these lines, but it is to be hoped that by greater co-operation and freer discussion among the leather chemists we shall finally achieve results unexcelled in the field of industrial chemistry. An opinion seems to be prevalent that the real obstacle in the way of progress is our ignorance of the chemical composition and constitution of hide-fiber. Following the reading of a paper by Mr. Wm. Harrison[1] some time ago, a similar statement was made concerning the finishing of wool. Mr. Harrison pointed out, however, that "if the chemical composition of wool were known, it did not follow that it would be of any assistance in wool finishing. To illustrate the point, he said that for many years chemists had known exactly the chemical composition of barium sulphate, but that knowledge had given no idea of the numerous physical or colloidal states in which the substance exists; for that purpose, in recent years, a special study had been made of the colloidal state." Although the exact compositions of some of the substances with which the tanning process is concerned are not yet known, there may still be available sufficient data to give a satisfactory hypothesis upon which to work. The subject is rich in problems of various sorts, of which only a few will be dealt with in the present paper, but it is hoped that advantage will be taken of the opportunities which they offer for fruitful discussion and criticism.

A hide is composed chiefly of proteins, which are condensation products of amino acids. The combination of several amino acids results in the formation of what is called a polypeptide,

$$3NH_2.R.COOH \rightleftharpoons NH_2.R.CO.NH.R.CO.NH.R.COOH + 2H_2O$$

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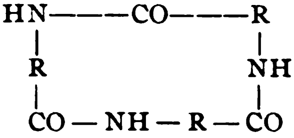
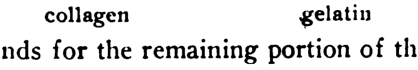
[1] The Chemistry and Physics of Finishing, *Textile Inst. Journal*, **7**, 2 (1916).

A protein differs from this principally in the fact that its molecules are composed of much greater numbers of amino acids. It is not necessary that a protein possess free carboxyl groups; by dehydration the tripeptide represented above would become an anhydride possessing no free amino or carboxyl group,



To differentiate between such proteins and those possessing terminal carboxyl or amino groups might be difficult were it not for the discovery of the selective actions of trypsin and pepsin. According to Plimmer,[2] "trypsin will hydrolyze a chain of amino acids with a terminal amino or carboxyl group. Pepsin will open the anhydride ring at one or more junctions and give several proteoses and peptones with free terminal NH_2 and COOH groups capable of being attacked by trypsin. Those proteins which are resistant to the action of trypsin until they have been acted upon by pepsin will have all their units contained in the anhydride ring."

It is well known that hide-fiber, or collagen, is hydrolyzed but very little, if at all, by trypsin, whereas it is acted upon by pepsin. On the other hand, gelatin is readily hydrolyzed by trypsin and yet these two proteins are almost identical in chemical composition. Collagen evidently has all its units contained in the anhydride ring, while gelatin has, in part at least, an open-chain structure with terminal amino and carboxyl groups. The conversion of collagen into gelatin is probably a case of hydrolysis, which might be represented thus:



$$R\left\langle\begin{matrix} NH \\ | \\ CO \end{matrix}\right. + H_2O \rightleftharpoons NH_2.R.COOH$$

collagen gelatin

Where R stands for the remaining portion of the protein molecule. The conception that gelatin is a hydrolyzed form of collagen is, of course, not new.

A fact that has come to the attention of leather chemists in

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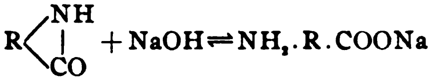
[2] The Chemical Constitution of the Proteins, Part II, p. 11 (Second edition, Longmans, Green & Co.).

recent years is that an unhairing action can be produced by means of tryptic enzymes in which the Malpighian layer is attacked and the hair carries away with it patches of the outer or corneous layer of the epidermis. Young and tender hairs are attackable by trypsin to some extent, but older keratin, such as that found in horn, resists its action. It is possible that newly-formed keratins have an open-chain structure, rendering them attackable by trypsin, but that, upon aging, they undergo a process of dehydration, represented by the above equation reversed. In unhairing by means of trypsin, the collagen is not attacked, but Mr. J. T. Wood has observed that if a hide be "over-limed," it then becomes attackable by trypsin, which confirms the above reasoning.

The closed-ring structure of collagen offers an explanation of why this protein is more resistant to the action of alkalies than the keratins of the epidermis and hair, but even collagen is readily decomposed if the alkali be of sufficient strength. In the first place the action between sodium hydroxide and collagen is probably one of combination, expressed as follows:



$$R\left\langle\begin{matrix}NH\\ |\\ CO\end{matrix}\right. + NaOH \rightleftharpoons NH_2.R.COONa$$

It is probable, when collagen and water are in equilibrium, that there is always a very small quantity of the protein present in the hydrolyzed form, so that the action represented above takes place in stages, following the laws of ionic equilibria.

A considerable amount of discussion has arisen over the question of whether or not a sterile lime has any unhairing action. It might seem, since sterile solutions of lye and sodium sulphide are capable of producing unhairing, that lime should likewise have this property, excepting insofar as it is limited by its lesser solubility and degree of ionization. In the following paragraphs it will be shown that the tendency for a diacid base to produce decomposition of a protein is less than that for a monacid base. While this will not settle the dispute as to the unhairing properties of lime, it should make clear the reason for the marked difference in action between lime and alkalies with monovalent cations.

The most obvious action of an alkali upon a protein is the neutralization of carboxyl groups with the formation of water and a salt of the protein. Collagen may be considered as an anhydride and its combination with alkalies as expressed by the above equation. In the case of monacid bases, we should expect the formation of highly ionizable salts of the protein with subsequent swelling or decomposition, depending upon the nature of the protein. The question of swelling and contracting is one of great importance, but it will not be dealt with here in detail because it has been treated very fully in a paper entitled, *The Swelling of Colloid Jellies*,[3] to which the reader is referred. The degree of swelling is dependent upon the amount of *ionized* protein salt formed, excepting insofar as other electrolytes present tend to produce contraction of the hide or jelly. A strong base like NaOH will have much more nearly completely neutralized the carboxyl groups of a particular protein, when equilibrium has been established, than would a weak base like ammonia, which is shown more clearly by a consideration of the law of mass action. The ionization-K's for any alkali MeOH and any protein, considered as an acid, may be represented as follows:

$$[OH'] = \frac{K[MeOH]}{[Me^+]}$$

$$[H^+] = \frac{K'[protein]}{[protein\text{-}ion']}$$

The brackets indicate that concentration is meant. The product of hydrion and hydroxidion concentrations at equilibrium must equal the ionization-K for water, and hence

$$[H^{+}] \times [OH'] = 10^{-14} = \frac{KK'\,[Me\,OH] \times [protein]}{[Me^+] \times [protein\text{-}ion]}$$

$$\text{or } [Me^+] \times [protein\text{-}ion'] = 10^{14}KK^{1}\,[MeOH] \times [protein]$$

The value of K for NaOH is of the order of unity and that for NH_4OH of the order of 10^{-5}, while for our case K′ may be taken as of the order of 10^{-12}, so that it will be readily seen that the amount of protein salt formed by NaOH, at equilibrium, will be much greater than would be formed by an equivalent concentration of ammonia. This means, in the case of elastic gels, such as collagen and gelatin, that dilute solutions of highly ionizable, monacid bases should produce much swelling, while

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[3] H. R. Procter and J. A. Wilson, This Journal, 11, 399 (1916).

slightly ionizable bases should produce but little, even in fairly concentrated solutions. Diacid bases should produce less swelling than monacid bases because of the lesser degree of ionization of salts dissociating into two divalent ions; for example, the calcium salt of collagen is probably ionized to a lesser extent than the sodium salt and therefore its gel should swell to a lesser extent. How great this difference of degree of ionization may be can be roughly estimated by recalling that salts of the type of $ZnSO_4$ and $CuSO_4$ are ionized to the extent of only about 25 per cent., while salts of the type of NaCl and KCl are almost completely ionized in dilute solutions. Protein salts of triacid bases are probably ionized only to a slight extent and consequently their gels should swell but very little.

The swelling of these gels of protein salts is due to the tendency of their cations to diffuse into the surrounding solution, which they are prevented from doing because of the electrochemical attractions of their colloid anions, which are held together by cohesive forces, of which tensile strength is one manifestation. A possibility which now presents itself is that, while the cohesive forces holding the protein molecules together may be great enough to resist the pull of the cations, the individual amino-acid groups to which the cations are attached may not be held to the rest of their molecules with sufficient force to prevent their being torn away, with the resultant decomposition of the protein. In different proteins it is unlikely that the amino-acid groups to which the cations are attached are held to the rest of their molecules with equal forces and hence we should expect some proteins to be more readily decomposed by alkalies than others.

While NaOH and NH_4OH should produce very different degrees of swelling, they would not necessarily produce very different degrees of decomposition, for the pull of an ammonium ion upon an amino-acid group would be as great as that of a sodium ion, because equal concentrations of each produce the same osmotic pressure. But the case of a divalent cation is essentially different. *It possesses no greater osmotic pressure than a monovalent ion. but is bound to the protein by two amino-acid groups instead of only one,* and hence, in the protein salt of a diacid base, the forces opposing decomposition would be twice as great as in one of a monacid base, even if both salts were ionized to the same extent. Since salts dissociating into two divalent ions are generally less ionized than those yielding only monovalent ions, *the tendency for a diacid base to produce decomposition would be considerably less than for a monacid base of equivalent concentration.*

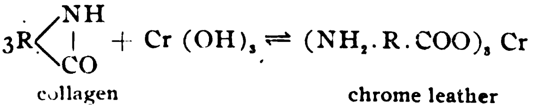
This reasoning is apparently borne out in practice. Sodium hydroxide produces much swelling in a hide, while ammonia produces but little and yet both bases show marked tendencies to dissolve hide substance. Calcium hydroxide produces less swelling of hide for equivalent concentrations than does sodium hydroxide and yet it has a lesser solvent action than the much weaker base ammonia. The actions of ammonia, lye, and sodium sulphide upon the protein of the Malpighian layer of a hide result in the formation of protein salts yielding monovalent cations, so that the increased unhairing action produced by adding these alkalies to the limes is evidently due to more than the mere increase of hydroxyl-ion concentration. Experiment seems to show that various cations of the same valency produce different degrees of swelling and decomposition, but the author is of the opinion that this can be accounted for by the different degrees of ionization of the bases and protein salts concerned.

In considering the differences in rate of unhairing produced by sodium and ammonium hydroxides, it is necessary to take into consideration the effect of the swelling of a hide upon the ease of unhairing. Swelling apparently hinders the unhairing action, which may be due partly to the fact that a swollen hide tends to retain the hair by a sort of pinching action and partly to the fact that the alkalies in the surrounding liquor must penetrate through a greater distance of swollen hide. The rate of diffusion of electrolytes in a collagen gel may be nearly as great as in water, but in the case of the gel we are not able to agitate the solution so readily as with pure aqueous solutions. If a concentrated solution of sodium hydroxide be carefully covered with a layer of water, it will take a very long time for the alkali to diffuse completely, unless the solution be agitated in some way. Another point to consider is that, as a protein becomes more acid in character, the difference in rate of decomposition, produced by strong and weak alkalies, should become less, while experimental results with tryptic digestion seem to indicate that the protein of the

Malpighian layer is richer in terminal amino and carboxyl groups than the proteins of the rest of the hide.

In dealing with this subject, it would be wrong to assume that alkalies are necessary to produce unhairing. Some time ago, Mr. J. T. Wood sent to the author a piece of calf skin which had been sterilized by the Seymour-Jones process. It had been acted upon by the acid continually for 70 days; it was somewhat swollen and the grain rather tender, but it could be unhaired with great ease. Mr. Wood says, however, that the unhairing effect was well shown in 8 days. Six months later the condition of the skin, which had been kept in the acid solution all this time, appeared not to have changed very appreciably, although there had been some loss of hide substance. The experiment is interesting, at least from a theoretical standpoint.

The reasoning regarding monacid and diacid bases can be carried a step farther by a consideration of triacid bases, such as the hydroxides of chromium, aluminum and iron. In a protein salt of such a base, the cation is bound to the protein by three amino-acid groups, and since the degree of ionization of such a salt is probably very small, little decomposition or swelling upon immersion in water would be expected. Such a compound should be extremely stable and certainly much more resistant to the action of water in continued washing than the protein salts of monacid and diacid bases. Chrome leather may not be such a salt, but it has the chief characteristics that would be expected in such a salt, and in the absence of a better theory, the author sees no objection to considering alum, chrome, and iron leathers as collagen salts of triacid bases. In actual tanning there is probably first a fixation of basic salts and to some extent a precipitation of metallic hydroxide upon the hide fibers. The "aging" of mineral-tanned leathers may be caused by slow combination between the collagen and metallic hydroxide precipitated upon the fibers, expressible as follows:



$$3R\left\langle\begin{matrix}NH\\ |\\ CO\end{matrix}\right. + Cr\,(OH)_3 \rightleftharpoons (NH_2.R.COO)_3\,Cr$$

It should be noted that the above equation is not intended to imply that one molecule of collagen combines with only one equivalent of the metal; in a protein molecule there are many groups of the type —NH.CO—. The equation is given thus only for the sake of simplicity. It is given as a reversible equilibrium because the chromium can be removed almost completely by digesting the leather with the salt of a hydroxy-acid, such as Rochelle salt.[4].

This theory of chrome tanning raises an extremely interesting point regarding the minimum ratio of chromic oxide to hide substance required to make leather. Working on the assumption that gelatin is a diacid base, Procter[5] has found its molecular weight to be 839, giving it the formula $C_{35}H_{57}O_{13}N_{11}$. The author, working in Procter's laboratory, found that assuming gelatin to act as monacid in dilute acid solutions its molecular weight would be 768, giving the formula $C_{32}H_{52}O_{12}N_{10}$. Although there are a number of facts supporting the view that gelatin acts as a monacid base in dilute acid solutions, some further work will be required to settle this point definitely. It appears evident from work done that the figure 768 represents, approximately at least, either the molecular weight or some multiple of the equivalent weight of gelatin. If the equation given for the conversion of collagen into gelatin is correct, the molecular weight of the former is 750, in which case the smallest amount of chromic oxide required to convert 100 grams of collagen into the chromium salt would be

$$\frac{152 \times 100}{6 \times 750} = 3.38 \text{ grams}$$

The figure for gelatin would obviously be 3.30 grams. In referring to the work of Lumière and Seyewetz,[6] Wood[7] says that "they state that gelatin fixes a maximum quantity of sesquioxide of chromium of between 3.2 and 3.5 grams per 100 grams of gelatin, whatever be the chromium salt employed. I have been unable to confirm this but find that the quantity of chrome fixed by gelatin depends on the concentration of the chrome solution, and on the basicity of the salt used." These apparently contra-

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[4] See *J. S. C. I.*, **35**, 156 (1916); This JOURNAL, **11**, 173 (1916).

[5] *J. Chem. Society*, **105**, 313, (1914); This JOURNAL, **9**, 207 (1916).

[6] *Bull Soc. Chim.*, **29**, 1077 (1903).

[7] The Compounds of Gelatin and Tannin, *J. S. C. I.*, **25**, 384, (1908); This JOURNAL, **3**, 183 (1908).

dictory results may be due to differences in the conditions of the experiments. If the gelatin acted only as a monobasic acid, we should expect the results obtained by Lumière and Seyewetz, while if conditions were such as to favor hydrolysis of the gelatin with the formation of more terminal amino and carboxyl groups, the gelatin would become capable of combining with more chromic oxide, the maximum amount fixed by 100 grams under any given set of conditions always being some multiple of 3.3 grams. Whether or not Wood's figure of 13.6 is approximately such a multiple merely by chance, can be determined by further investigation. In a recent publication Lamb and Harvey[8] state that "it is a well known fact that, unless the leather gives 2.8 per cent. to 3.0 per cent. chromic oxide, it will be invariably undertanned." These figures appear to be based upon the dry, degreased leather and would obviously be increased slightly if based only upon the actual hide substance. Perhaps we shall some day speak of monochrome, dichrome and polychrome leathers as representing definite chemical compounds.

The theory of vegetable tanning has been treated from a colloid-chemical standpoint by H. R. Procter and the author and appears elsewhere,[9] but it is well to consider its relation to chrome tanning. An attempt will be made to explain the mechanism of vegetable tanning from a purely chemical point of view, in order that it may prove more satisfactory to those not familiar with colloid equilibria. It is hoped that the loss in accuracy may be compensated by greater simplicity. Those who prefer the more exact treatment are referred to the paper mentioned. According to this theory, vegetable tanning consists of the coprecipitation of the oppositely charged colloids, collagen and tannin. The collagen first combines with acid from the liquor forming an ionizable salt of which the colloid ion is positively charged. It has actually been demonstrated that the tannins dissolve in water, forming sols in which the tannin particles are negatively charged. If the acid present in the tan liquor be represented by HA, then its combination with collagen takes place thus:

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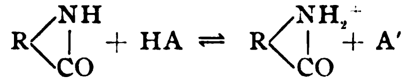
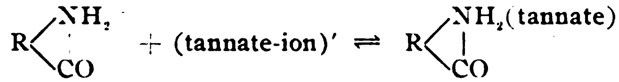
[8] Estimation of Chromic Oxide in Chrome Tanned Leather, *Collegium* (London edition) 201, 1916; This JOURNAL 11, 571 (1916).

[9] *J. Chem. Soc.*, 109, 1327 (1916). This J. 12, 76, (1917).



$$R\left\langle\begin{matrix}NH\\ |\\ CO\end{matrix}\right. + HA \rightleftharpoons R\left\langle\begin{matrix}NH_2^+\\ |\\ CO\end{matrix}\right. + A'$$

and the subsequent coprecipitation of collagen and tannin as follows:



$$R\left\langle\begin{matrix}NH_2\\ |\\ CO\end{matrix}\right. + (\text{tannate-ion})' \rightleftharpoons R\left\langle\begin{matrix}NH_2(\text{tannate})\\ |\\ CO\end{matrix}\right.$$

vegetable-tanned leather

In mineral-tanned leathers the metal is combined with the carboxyl groups, while in vegetable-tanned leather the tannin is combined with the amino groups. This strongly suggests the possibility that the two methods of tanning are to some extent independent of one another and that a piece of leather tanned by one method may remain as capable of being tanned by the other method as though it were still raw pelt. Confirmation of this reasoning is to be found in Wood's important paper on *The Compounds of Gelatin and Tannin,*[10] in which he shows that "the chroming of gelatin does not interfere with the absorption of tannin, as a sheet of heavily chromed gelatin will absorb as much tannin as before chroming." In detannizing by means of chromed hide-powder in the present official method for analysis of tanning materials, it is assumed that the chroming of hide powder does not interfere with its power to combine with the tannins.

A simpler and possibly more satisfactory explanation of the amphoteric nature of collagen and gelatin is to be found in a consideration of the chemical properties of glycocoll (amino-acetic acid), which forms more than 16 per cent. of these proteins. When glycocoll is dissolved in water, the amino group reacts with water, forming a hydroxide, corresponding to ammonium hydroxide,

$$NH_2.CH_2.COOH + H_2O \rightleftharpoons HO.NH_3.CH_2.COOH$$

As an acid, glycocoll hydroxide is as highly ionizable as acetic, while at the same time it is as highly ionizable as a base as ammonium hydroxide. In consequence of the slight degree of dis-

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[10] Loc. cit.

sociation of water, the compound exists in aqueous solution chiefly in the form of a salt,

$$\mathrm{HO.NH_3.CH_2.COOH} \rightleftharpoons \underbrace{\mathrm{NH_3.CH_2.COO}} + \mathrm{H_2O}$$

The addition of sodium hydroxide represses the ionization of this compound as a base and forms, almost to completion, the sodium salt, which is probably as highly ionizable as sodium acetate. On the other hand, hydrochloric acid represses the ionization of glycocoll as an acid and forms, almost to completion, a chloride of glycocoll, which is ionized to about the same extent as ammonium chloride. If this amphoteric character of the amino acid still persists in the protein, we should expect to find gelatin positively charged in acid solution and negatively charged in alkaline solution, and it is a significant fact that Billitzer[11] has found this to be the case.

Discussion of the actions of alkalies of metals of different valencies would not be complete without a consideration of tetracid bases, such as $Zr(OH)_4$. If a collagen salt of such a metal were formed, such that each of the four bonds was attached to an amino-acid group, the product should be a leather even more stable than those produced by triacid bases. The difficulty lies in the production of such a salt. If the sodium salt of collagen were ionized only to a very slight extent, the production of a mineral-tanned leather would be a fairly simple matter, but collagen salts of either alkali or alkaline earth metals are too highly ionizable to be suitable for use as leather. The difficulties encountered with metals of higher valency are due to the facts that their hydroxides are very difficultly soluble and slightly ionizable, which explains why such care is required in chrome and alum tannages to get just the right degree of basicity. If the solution is too strongly acid, no combination between metal and hide will take place; if not sufficiently acid, basic salts of the metal are precipitated. The hydroxides of trivalent and tetravalent metals are amphoteric and therefore the ease with which they produce leather will depend upon how strongly marked are their acid or basic characters.

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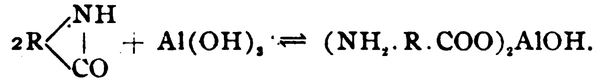
[11] *Z. phys. Chem.*, 51, 157 (1905).

A striking example of this is to be found in the differences of action of chrome and alum in their respective tannages. It will be recalled, in qualitative analysis, that aluminum hydroxide can be separated from the hydroxides of chromium and iron by digestion with strong alkali, which shows that the hydroxide of aluminum is a stronger acid than the others. The more basic character of chromium hydroxide will result in a readier combination with the hide and therefore a set of conditions that would just permit the combination of all three bonds of the chromium with carboxyl groups of the protein would permit not more than two bonds of the aluminum to combine with the collagen, thus:



$$2R\left\langle\begin{matrix}NH\\ |\\ CO\end{matrix}\right. + Al(OH)_3 \rightleftharpoons (NH_2.R.COO)_2AlOH.$$

While investigating the action of aluminum salts upon gelatin, A. and L. Lumière[12] found that "the quantity of alumina combined with the gelatin increases with the weight of salt employed, until 3.6 per cent. of alumina is combined; beyond that point there is no increase." Where only two bonds of the aluminum are combined with the gelatin, one molecule of Al_2O_3 represents only four equivalents. It is, therefore, evident from the theory that, under conditions such that gelatin acts as a monobasic acid, the amount of Al_2O_3 fixed by 100 grams of gelatin in the presence of an excess of the aluminum salt would be

$$\frac{102 \times 100}{4 \times 768} = 3.32 \text{ grams},$$

which is not far short of the maximum which the Lumières have determined by experiment. A leather in which the aluminum was bound to the collagen by only two bonds, as that shown in the above equation, would probably be very little more stable or resistant to washing than the calcium salt of collagen, which offers an explanation as to why aging or drying is so essential to make alum leathers resistant to washing; upon drying for a sufficiently long time, the third bond of the aluminum probably combines with the collagen.

In view of these considerations the difficulties to be overcome

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[12] *Brit. J. Phot.*, **53**, 573 (1906); abst., *J. S. C. I.* **25**, 770 (1906)

in making zirconium, titanium, or silicon leathers become more apparent. The hydroxides of these metals are much more pronouncedly acid than those of the trivalent metals. If these hydroxides were precipitated upon the fibers of a hide, a leather might be produced upon aging; but even then it is unlikely that all four bonds would be attached to carboxyl groups, as the metal would probably retain one or more of its hydroxide groups. Some indication is here given of the value which may accrue from a more extended knowledge of the various physical constants of the hydroxides of the trivalent and tetravalent metals.

The question of the mechanism of fat-liquoring and dyeing is probably intimately associated with that of the mechanism of vegetable tanning, in that it is concerned largely with colloid-chemical reactions in which oppositely charged colloids are coprecipitated. There are, however, methods of stuffing and dyeing so numerous and complicated as to make any detailed considerations far beyond the scope of the present paper. It will, nevertheless, be of advantage to consider the mechanism of the stuffing of chrome leather by means of an emulsion of an oil in a solution of a soap, say sodium stearate. The finely divided globules of oil adsorb some stearate ions, thus becoming negatively charged. It is obviously this electrical charge which prevents the coalescence of the oil particles. Wet chrome leather containing a small amount of hydrochloric acid ionizes as follows:

$$(\mathrm{Cl.NH_3.R.COO})_3\mathrm{Cr} \rightleftharpoons (\mathrm{NH_3.R.COO})_3\mathrm{Cr}^{+++} + 3\mathrm{Cl}'$$

If this leather be treated with the emulsion mentioned above, combination will take place between the positively charged leather and negatively charged oil particles, thus:

$$(\mathrm{NH_3.R.COO})_3\mathrm{Cr}^{+++} + 3\,(\text{oil-stearate})' \rightleftharpoons (\text{oil-stearate}\text{—}\mathrm{NH_3\,R.COO})_3\mathrm{Cr}.$$

In this case it is evidently required that the leather be in a slightly acid condition at the time of fat-liquoring, for otherwise it will not assume a positive charge by ionizing as a salt of the acid, and it is important to note that, if the leather is not slightly acid, it will not combine satisfactorily with the oil, while if it is strongly acid, the soap is decomposed and the emulsion broken up.

Equations of the type given above are apt to be misleading to the extent of suggesting that the finished leather should contain its various components in definite proportions. As in the equations given for tanning, quantitative exactness was sacrificed for greater simplicity. In the coprecipitation of oppositely charged colloids, electrical forces are concerned whose magnitudes are dependent for their values not only upon the concentrations of the colloidal particles, but also upon the nature and concentrations of the various electrolytes present in the solution, and since these factors can be varied continuously within certain limits, so the proportion of components making up the finished leather can also be varied continuously within limits. In a paper entitled *Theory of Colloids*,[13] the author has given quantitative formulas showing the relation existing between the concentration of electrolytes present in the solution and the difference of potential between the bulk of solution and that portion immediately in contact with the surfaces of the colloidal particles. Reference to this paper may give the above equations a deeper significance.

Those desiring a simpler explanation might consider an aqueous solution of acetic acid. The ratio of concentration of hydrogen ions to that of the non-ionized acid is not constant but varies according to the equation.

$$[H^+]^2 = 0.000018\ [CH_3COOH],$$

which represents a parabolic curve. If sodium acetate is added to the solution, the relations become still more complicated, since the concentrations of hydrogen and acetate ions are no longer equal. It is evident that the ions and molecules in solutions of electrolytes are not present in definite proportions, but in proportions depending upon the concentrations of all the electrolytes present. It requires only a step further to appreciate why the proportions of components of a leather which is in equilibrium with one solution will be different from those of a leather in equilibrium with a similar solution of different concentration.

The foregoing treatment of theories pertaining to leather chemistry is far from exhaustive and the reasoning not even detailed; that will require the united efforts of many workers. An attempt has been made to bring a little nearer to solution some of

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[13] *J. Amer. Chem. Soc.*, **38**, 1982 (1916) This J., p. 122.

the fundamental problems confronting the leather chemist. Some phases of the work present almost insurmountable difficulties, but there are others simple enough for any chemist to discuss intelligently. General discussion and criticism, if given with the sole purpose of approaching nearer to the absolute truth, would undoubtedly prove of immense value to all interested in gaining a deeper insight into the mechanism of the various operations of the tanning process.

The author expresses his thanks to Mr. Douglas McCandlish for kindly criticism and suggestions during the preparation of the manuscript.

THEORY OF COLLOIDS.*

By John Arthur Wilson.

The object of the present paper is the promulgation of further reasoning in favor of the "complex" theory of colloid formation and the elucidation of the very interesting and important conclusions which follow. The fundamental assumption of this theory is that the colloidal state in sols owes its stability to the formation of a complex between the particles of the disperse phase and certain substances present or formed in the dispersion medium during the preparation of the colloid. The sols of the noble metals have been cited as an argument against this theory, but Beans and Eastlack[1] have shown that the presence of chloride, bromide, iodide, or hydroxide ions in concentrations from 0.00005 N to 0.005 N has a marked stabilizing effect on gold sols and that the colloid particles become negatively charged. In concluding, these authors consider that the electrical synthesis of colloids consists of a thermo-mechanical dispersion of the metal, followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium.

The assumption of the formation of such a complex between any colloid particles and electrolytes present in the dispersion medium is not unreasonable. Carbon is a typical *adsorbing* agent and happily one, the stability of whose compounds has been extensively investigated. The data leading to the formulation of

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* *J. Am. Chem. Soc.*, **38**, 1982, (1916).

[1] *J. Amer. Chem. Soc.*, **37**, 2667–83 (1915).

Baeyer's Strain Theory indicates that the four valencies of the carbon atom are directed toward the vertices of a regular tetrahedron, of which the carbon atom is the center. This being true, any atom *within* a given particle of carbon will attract and be attracted by the atoms immediately surrounding it, but one at the surface is attracted only towards atoms of the particle and consequently has one or more of its valencies directed away from the particle, and therefore unsatisfied. In a lump of carbon this free or residual valency might be relatively insignificant but would increase to huge proportions as the carbon became more and more highly dispersed. It is probable that every substance possesses a certain amount of residual valency at its surface, which tends to cause it to combine with substances approaching its surface. As in chemical combination in general, such combination is probably selective. Indeed, Beans and Eastlack (*Loc. cit.*) have shown that the presence of fluoride ions does not stabilize gold sols, while Lenher[2] has shown that gold fluoride is incapable of existence, not only in the presence of water, but under ordinary laboratory conditions.

Apparently the colloid particle takes its electrical charge from the ions with which it combines, or in some cases, acquires a charge by ionizing itself. Such a charge seems to be necessary to the stability of the colloid state in sols, which is explained to some extent by the fact that particles with like charges tend to repel each other, thus preventing coalescence.

Associated with any charged particle there will be a number of ions of opposite charge, which cannot be separated from the surface of the particle, excepting by very small distances, or by being replaced by other ions of the same sign, which means that the distribution of ions in the layer of solution surrounding the particle will be different from that in the bulk of the dispersion medium, a condition to which Donnan's[3] work on membrane equilibria can be applied. Donnan considers an aqueous solution of a salt, NaR, such as Congo red, in contact with a membrane which is impermeable to the anion R' and the non-ionized salt, but will allow Na^+ or an other ion to pass freely through it. On the other side is an aqueous solution of sodium chloride, which will diffuse from its solution II into the solution I of NaR. When equilibrium is established, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged, *i. e.*, no work will be done. The change here considered is the transfer of δn moles of Na^+ and Cl' from II to I. The work which equals zero is

$$\delta n \text{ RT} \log \frac{[Na^+]_{II}}{[Na^+]_{I}} + \delta n \text{ RT} \log \frac{[Cl^-]_{II}}{[Cl^-]^{I}} = 0$$

or

$$[Na^+]_{II} \times [Cl^-]_{II} = [Na^+]_{I} \times [Cl^-]_{I} \, .$$

By a continuation of this reasoning it can be shown that whatever diffusible binary electrolytes be added to solution II, when equilibrium is established, the *products* of concentrations of any pair of diffusible and oppositely-charged ions will be equal in the two solutions.

If a substance is dispersed to the colloid state in a solution of the electrolyte MN and combines with a portion of M^+ (not necessarily in equivalent quantity from a chemical standpoint), then at the surface of the colloid particles there will be a certain concentration of N' bound by electrochemical attractions to the colloid. This surface layer of solution will also contain M^+ and N^- and will thus bear the same relation to the bulk of solution as did solution I to solution II in Donnan's work just quoted, and consequently the product $[M^+] \times [N^-]$ will be equal in the surface layer and bulk of solution, and since the concentrations of M^+ and N^- are *unequal* in the surface layer and *equal* in the bulk of solution, *the total concentration of ions will be greater in the former than in the latter.*

In the bulk of solution let x = concentration of positive or negative ions.

In the surface layer surrounding particle let y = concentration of ions of same sign as charge on the colloid particle.

z = concentration of ions bound to the colloid by electrochemical attractions.

Therefore $y + z$ = concentration of ions of opposite sign to that on the colloid particle.

Let e = excess of concentration of diffusible ions of the surface layer over that of the bulk of solution.

In order to keep the reasoning as simple as possible only

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[1] *J. Am. Chem. Soc.* **25**, 1136 (1903).

[2] *Z. Electrochemie*, **17**, 572 (1911).

binary electrolytes will be considered, although it will be obvious that the reasoning can be extended to include ions of any valency. From the law of "equality of products" just discussed

$$x^2 = y(y + z)$$

and since

$$2x + e = 2y + z$$

$$z = \sqrt{4ex + c^2}.$$

If unit quantity of colloid and unit volume are considered, z *represents the quantity of electrolyte combined with the colloid.* But the generally accepted *empirical* formula for *adsorption* (using the same system of notation) is

$$z = kx^{1/p}$$

where p represents a constant, usually *about* 2, so that generally

$$z = k\sqrt{x}.$$

The similarity of the equations is striking and in certain cases, and within limits, they would give similar curves, but they are not identical, and here it should be noted that the latter formula is at best only empirical, while the former follows from well-founded assumptions.

The different distribution of ions in the surface layer and bulk of solution will result in a difference of potential, the formula for which is given by Donnan[4] as follows:

$$E = \frac{RT}{F} \log \frac{1}{\lambda}$$

Or, in the notation adopted in this paper,

$$E = \frac{RT}{F} \log \frac{x}{y} = \frac{RT}{F} \log \frac{2x}{-z + \sqrt{4x^2 + z^2}}.$$

But z has a limiting maximum value, since the amount of electrolyte which can combine with a colloid of definite degree of dispersion is limited by the amount of residual valency at the surface, or, in the case of an ionizing colloid, the portion ionized cannot exceed the whole. Hence,

$$\overset{\text{limit}}{x = \infty}\; E = \frac{RT}{F} \log \frac{2x}{\sqrt{4x^2}} = 0,$$

proving that the difference of potential existing between the surface layer surrounding the colloid particle and the bulk of solu-

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[4] *Loc. cit.*

tion will diminish as the concentration of electrolyte is increased, after the combination of colloid and electrolyte has reached *or neared* its maximum. When this difference of potential has become sufficiently small a condition is established which is favorable to the coalescence of the particles. Assuming that a given potential difference is required for the maintenance of the colloid state in sols, the amount of electrolyte required for precipitation of the colloid will depend upon the maximum value for z. In the case of suspensoids this is probably very small, while for many emulsoids it is known to be comparatively high.

Where a charged particle combines directly with an ion of opposite sign, precipitation must follow. The cause of the coprecipitation of oppositely-charged colloids is equally obvious, but it might be well to point out in passing that the rate of this precipitation might be controlled by suitable regulation of the concentration of electrolytes in the dispersion medium. Similar lines of reasoning explaining the swelling and contracting action of electrolytes upon colloid jellies have been worked out by H. R. Procter and the author and appear elsewhere.[5] Whatever herein expressed may seem opposed to the generally accepted views on colloids can be tested as the formulas derived are quantitative in character. The author expresses the hope that they may lead a step nearer to the goal of colloid chemists.

MILWAUKEE, WIS.

NOTE ON ADSORPTION.

By John Arthur Wilson.

In the paper on "Theory of Colloids," which is reprinted in this issue, the subject of adsorption is touched upon, but its importance to leather chemists should make a little further development of interest. If the theory is to prove satisfactory, it must explain negative as well as positive adsorption. Exactly the same notation will be used as in the paper just mentioned.

Both positive and negative adsorptions have been observed, but the cause of the latter has been a matter of much speculation. Negative adsorption has been regarded as a positive adsorption of the solvent instead of the solute, but such a view is unneces-

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[5] *J. Chem. Soc.* (British) **109**, 307 (1916); *J. Am. Leather Chem. Assoc.*, **11**, 399, (1916).

sary and even superfluous in sols of ionizing colloids where the added electrolyte does not interact chemically with the colloid. If a substance is dispersed to the colloid state in a solution of a binary electrolyte and acquires an electrical charge by combining only with ions of the same sign, we should have a case of positive adsorption. The excess of concentration of ions of the surface layer over that of the bulk of solution equals e, while the equivalent of a concentration of z ions is actually combined with the colloid, making a total excess of $z + e$ for the surface of the colloid, which in terms of molar concentration would be one-half of this amount. Probably in its strictest sense, the portion of electrolyte adsorbed, which we may call a, would be represented by the *apparent* excess of concentration of the electrolyte at the surface of the colloid over its concentration in the bulk of solution in which case

$$a = \frac{z + e}{2}$$

If we now consider an *ionizing* colloid dissolved in a solution of a binary electrolyte with which it does not interact chemically, the portion of electrolyte adsorbed will be represented by

$$a' = \frac{e - z}{2}$$

since from the total excess of ions of the surface layer e, must be subtracted that portion, z, derived from the colloid itself and not from the electrolyte. But this quantity a' *must be negative,* since z is greater than e, for at $x = 0$, $z = e$, while as x increases, e must decrease, thus becoming less than z, which is constant, since in this discussion all ionization is considered to be practically total.

As regards absolute values it is obvious that a will always be greater, and a' will always be less than $\frac{z}{2}$. In very dilute solutions where the value of e approximates that of z, the absolute value of a will be nearly equal to z, while that of a' will be almost negligibly small. This is strongly confirmed by actual experiments, since negative adsorption has generally been found too slight to determine with any great accuracy, while positive adsorption is often comparatively great.

THE ACTIVATED SLUDGE PROCESS OF SEWAGE PURIFICATION.*

By Edward Ardern, M.Sc.

The rise and development of this method of sewage purification has been described in a series of three papers, entitled "The Oxidation of Sewage Without the Aid of Filters,"[1] presented to this section of the Society during the past two years.

It was observed from the first that the purification process was subject to disturbance in the presence of certain trade-wastes of inhibitory character.

For the purpose of investigating the effect of such trade effluents on the activated sludge process, the experimental plant employed previously when working with the Manchester sewage received at the Main Outfall Works, Davyhulme (a strong trade sewage), was transferred in July, 1915, to the Withington Sewage Works, Chorlton-cum-Hardy, where a purely domestic sewage is dealt with.

The preliminary results obtained during the period the activated sludge was being "built up" were, however, so remarkable that it was decided to postpone the trade-effluent trials pending a careful survey of the possibilities of the activated sludge process as applied to the purification of a weak domestic sewage free from manufacturers' effluents.

This communication is concerned with a brief account of the results of the investigation, which has extended over a period of 15 months. The plant employed consisted of wooden casks of 200 liters capacity (net). The aeration was effected by diffusing the air through a porous tile placed on the bottom of the cask. The air supply was always sufficient to maintain complete admixture and circulation of the sludge and sewage. The floating matters and grit had been removed from the sewage dealt with by prior screening and adequate detritus tank treatment.

The method of "building up" the activated sludge was that described in the last paper[2] on the subject. For a period of 9 days from the commencement of operations the cask was filled

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* *J. S. C. I.* Jan. 31, 1917, pp. 65-8.

[1] Ardern and Lockett, *J. S. C. I.* May 30, 1914; Dec. 15, 1914; Sept. 30, 1915. Abstr. this J., 1914, p. 331; 1915, p. 647.

[2] Arden and Lockett *J. S. C. I.* Sept. 30, 1915.

once each day, an aeration of 21 hours being allowed. The remaining 3 hours was occupied by quiescent settlement of the accumulated suspended matters, discharge of effluent, and refilling with sewage.

Subsequently the aeration period was reduced and the number of fillings rapidly increased without diminution in the purification effected, so that after the experiment had been in progress 18 days, four fillings per day were allowed with an average of four hours' aeration. After operating for a fortnight in this manner the average aeration period was reduced to 2⅗ hours, and five fillings per day allowed for a period of 11 days. Eventually the cask received six fillings per day, with the following aeration periods: three fillings 1 hour, and the other three fillings, 2 hours, 3 hours, and 4 hours respectively, or an average aeration period of 2 hours.

Working in the manner described above, 15 per cent. by volume (measured after 2 hours' settlement) of partially activated sludge, *i. e.*, 30 liters or 6.6 gallons, were obtained from 2,970 gallons of sewage dealt with during the first 31 days, which was increased to 31 per cent., *i. e.*, 62 liters or 13.6 gallons, in the succeeding 12 days. At this point 5,180 gallons of sewage had been treated in the cask. On this basis, the sludge production is equal to about 12 tons per million gallons of sewage treated.

The results obtained during this initial period were of such a character that it became of interest to determine whether they could be maintained indefinitely without regard to the establishment of active nitrifying organisms in the sludge. At this stage, therefore, the partially activated sludge which had been accumulated was divided equally between two casks, one of which was operated with six fillings per day as previously, while the other was worked in such a manner as to allow a development of nitrifying organisms.

For this purpose, the first filling of sewage was aerated continuously until the free and saline ammonia content of the sewage had disappeared and nitrification was complete, which required 48 hours' aeration. Subsequent fillings were likewise aerated until the sewage was completely nitrified; the aeration period required during the following 9 days, varying from 8 to

23 hours, dependent on the strength of sewage treated. Later it was found easily possible to allow two fillings per day with an average aeration period of 10 hours, and within 14 days of commencing to establish nitrifying organisms three fillings were being given (6 hours' aeration) with the production of highly nitrified effluents. Finally the quantity of sewage dealt with was increased by allowing four fillings per day with an average aeration period of 4 hours, at the same time maintaining a highly purified and well nitrified effluent.

It may be noted that nitrifying organisms were much more readily established in the sludge obtained from the Withington sewage than in that produced from the trade sewage at Davyhulme, *e. g.*, the first filling of Davyhulme sewage usually requires 15 days' aeration in contact with the partially activated sludge for somplete nitrification. Further, there is no ammoniacal fermentation of the sludge meanwhile or production of turbid effluents, and the alkalinity of the sewage is always sufficient to allow nitrification to proceed to completion.

During this period of complete maturing of the activated sludge, the cask containing the partially activated sludge continued to receive six fillings per day, but the total aeration periods had been reduced from 12 hours to 10 hours, divided as follows: Four fillings 1 hour aeration and two fillings 3 hours' aeration, when the sewage was at its maximum strength, or an average of 1⅔ hours' aeration per filling.

The average results obtained from the operation of the casks containing the two types of sludge over a prolonged period, embracing a great variation in temperature conditions, are given in the following table. The volume of sludge in each case varied from 20 to 25 per cent., and the volume of purified effluent discharged after each filling was equal to 75 per cent. of the total capacity of the cask.

No. 1 cask contained partially activated sludge and No. 2 cask fully activated sludge.

In general, the effiuents obtained from the two casks were equally well clarified, although in some cases, especially during prolonged dry weather, when a stronger sewage was dealt with, the effluent yielded by the partially activated sludge exhibited a faint turbidity, whereas those from the fully activated sludge were invariable perfectly clarified.

RESULTS IN PARTS PER 100,000.

	Screened sewage	No. 1 effluent	Screened sewage	No. 2 effluent
4 Hours' oxygen absorption	3.34	0.70	3.40	0.64
Free and saline ammonia	2.61	1.66	2.64	0.35
Albuminoid ammonia	0.71	0.11	0.70	0.08
Nitrite and nitrate (as NH_3)	—	0.41	—	1.40
Dissolved oxygen absorption (Royal Commission test)	--	1.20	—	0.84
No. of fillings per day		6	—	4
Average aeration period	—	$1\frac{2}{3}$ hrs.	—	4 hrs.
Volume of sewage dealt with per day	—	187 gal.	—	125 gal.

The above results show that except for a somewhat lower albuminoid ammonia content, which is reflected in a reduced dissolved oxygen absorption, the difference between the effluent yielded by the fully activated sludge and that obtained from the partially activated sludge is confined to the amount of nitrification. Their importance lies in the fact that they demonstrate that the activity of the sludge, so far as oxidation of carbonaceous matter and clarification is concerned, can be maintained without reference to the degree of nitrification.

This result is contrary to the experience gained in the earlier experiments when working with the trade sewage at Davyhulme; and means that if nitrification is not required, and it is certainly not essential, high-class effluents, easily within the standard suggested by the Royal Commission on Sewage Disposal, can be produced from domestic sewage by the activated sludge process, with a considerably reduced aeration period at consequently lower cost.

In view of this material difference between results obtained at Withington and Davyhulme, obviously it was important to ascertain whether similar differences were to be found with regard to the question of the effect of temperature on the purification process. Operations with the two types of sludge were therefore extended throughout the winter and summer months.

In the following tables are given the results obtained when working (in each case) with from 20 per cent. to 25 per cent. by volume of sludge (measured after 2 hours' settlement) and removal of effluent after each period to the extent of 75 per cent. of the contents of the cask.

RESULTS IN PARTS PER 100,000.

	Feb. and March, 1916. Temperature 5° to 10° C.			Aug. and Sep., 1916. Temperature 16° to 19° C		
	Sewage	Effluent No. 1	Effluent No. 2	Sewage	Effluent No. 1	Effluent No. 2
4 Hours' oxygen absorption	3.30	0.74	0.63	3.76	0.69	0.64
Free and saline ammonia	1.90	1.53	0.44	2.77	0.60	0.20
Albuminoid ammonia	0.64	0.12	0.10	0.74	0.09	0.07
Nitrite and nitrate (as NH_3)	—	0.37	1.37	—	0.67	1.44
Dissolved oxygen absorption (Royal Commission test)	—	1.11	0.87	—	1.14	0.81
No. of fillings per day	—	6	4	—	6	4
Average aeration period	—	1⅔ hrs.	4 hrs.	—	1⅔ hrs.	4 hrs.
Volume of sewage dealt with per day	—	187 gal.	125 gal.	—	187 gal.	125 gal.
Percentage purification calculated on:						
4 hrs. oxygen absorption test	—	78	81	—	82	83
Albuminoid ammonia test	—	81	84	—	88	91

There was no appreciable difference in appearance between the effluents obtained during the winter and summer months; in each case, they were invariably well clarified and contained only very small quantities of suspended matter. It will be seen that the purification was not materially retarded by the low temperature experienced during February and March. In the case of the partially activated sludge, however, there was a considerably reduced nitrification effect.

In the light of these results it would appear that the detrimental effect of low temperatures (below 10° C.) found when working with the Davyhulme sewage must be ascribed to the lowered vitality of the organisms present in the sludge, due to the constant presence of inhibitory trade waste, which renders them more susceptible to changes in temperature.

Activated Sludge.—In the following table is given an average analysis of the activated sludge obtained from the Withington sewage together with comparative figures for the sludge produced from the Manchester sewage at Davyhulme, and from the Salford sewage.

The activated sludge produced from the Withington sewage thus has an appreciably higher nitrogen content than either the Manchester or Salford sludge, due to some extent to the fact that the percentage of mineral matter is considerably less.

ANALYSIS of ACTIVATED SLUDGE (DRY).

	Withington	Manchester*	Salford†
	%	%	%
Loss on ignition	70.4	64.7	54.5
Mineral matter	29.6	35.3	45.5
Total nitrogen (as N)	6.0	4.6	3.75
Phoshate (as P_2O_5)	4.2	2.6	2.1
Greasy matter, etc.—ether extract	7.3	5.8	4.8

As stated in previous papers, the high percentage of nitrogen in activated sludge is one of the most important features of the process, in view of its direct concern with the question of the conservation of nitrogen.

SUMMARY OF RESULTS.

The results of the present investigation may be summarized as follows:

1. That contrary to the opinion formed as the result of earlier experiments when working with a strong trade sewage, the maintenance of the activity of the sludge is not dependent on the stage to which nitrification is carried.

2. That when dealing with a sewage free from inhibitory trade effluents no appreciable loss of efficiency need be anticipated in England during the winter months.

3. While the problem of disposal of the sludge remains to be fully developed, it would certainly appear from known data that the cost of dewatering and drying will be more than repaid by the value of the resultant dried sludge.

The investigation in regard to the effect of various trade effluents on the purification process is now well advanced and it is hoped that the results obtained will shortly be available for publication.

In conclusion the author has to thank Mr. H. Edwards (Withington Works Manager) for exercising general supervision, Mr. G. Smith (laboratory attendant) for intelligent operation of the experimental plant, and Mr. C. Jepson, B.Sc., for able assistance in the analytical work involved. He is indebted to the Rivers Committee, Manchester Corporation, for permission to publish these results.

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* Ardern and Lockett (*J. S. C. I.* 1914, p. 523; This J., 1914, p. 331.)

† S. E. Melling (*J. S. C. I.* No. 23, Vol. XXXIII.).

DISCUSSION.

Mr. Hoseason inquired what was the effect of auto-digestion on the sludge and whether it was then more difficult to obtain a stable effluent.

Mr. S. E. Melling was doubtful whether nitrification was, in all circumstances, vital. His experience of the continuous flow method of operation appeared to indicate that, by the use of 25 per cent. by volume of activated sludge, very satisfactory purification, notably in the colder winter months, could be obtained and maintained, practically without nitrification. He understood that the only effect of nitrification was to improve the stream into which the effluent passed by providing it with potential oxygen, which, however, was not the prime object of sewage purification. The point was, whether the elimination of the ultimate stage or more or less complete nitrification, would result in an appreciable saving of time, thus effecting economy in air consumption. One or two hours' treatment by the fill-and-draw method gave results very similar to those quoted in the paper, and conformed very satisfactorily to the suggested dissolved oxygen test of the Royal Commission. At the same time, the activity of the sludge was well maintained throughout. The figure of 3.8 per cent. of nitrogen (Salford sludge) given in the paper was now increased to 4.5 per cent. or thereabouts, and for all seasons of the year. Was it not possible to recover directly the nitrogen in the form of sulphate of ammonia? There was a very appreciable excess of nitrogen as compared with peat, and the latter, containing 2.0 per cent. of nitrogen and 40 per cent. of moisture, had, he believed, amply repaid for the recovery as the sulphate.

Mr. William Thomson asked whether it would be practicable to mix activated sludge with charred peat so that the large quantity of nitrifying bacteria in the sludge could be made available for the culture of vegetation. The charred peat would no doubt aid in the air drying of the sludge. He had Professor Bottomley's experiments in mind.

Mr. Percy Gaunt inquired whether any difference in nitrogen content had been observed between the sludge employed for the maximum purification and the sludge employed for the less complete purification.

Mr. Ardern in reply said the effect of auto-digestion of the sludge was to produce turbid effluents. In the absence of disturbance due to the presence of certain trade effluents, it was only met with during the initial period when nitrifying organisms were being established in the sludge by prolonged aeration periods. He agreed with Mr. Melling that nitrification was not essential and consequently in view of the fact, which had been established, that the activity of the sludge could be maintained without reference to the degree of nitrification, thoroughly well purified effluents could be obtained with a considerably shorter aeration period than was at first thought necessary, with consequent reduction in cost. He believed that the recovery of nitrogen by distillation of activated sludge was a practical proposition, but his view was that it would be better to utilize the dried sludge direct as a fertilizer. Its fertilizing value had been thoroughly demonstrated by Dr. Bartow (Illinos University) and Mrs. Mumford (Manchester University). Activated sludge could, of course, be mixed with peat (either before or after inoculation) as suggested by Mr. Thomson, but seeing that the sludge itself contained appreciably more nitrogen than peat, it did not appear desirable to do so. This suggestion, of course, raised the important question of soil inoculation which had been investigated by Professor Bottomley and others. He believed that the best results would be obtained by the direct use on the land of activated sludge with its normally high bacterial content, as there was every reason for believing that in addition to nitrifying organisms the sludge also contained nitrogen-fixing organisms. In devising means for drying or partically drying the sludge endeavor should therefore be made to avoid sterilization.

The practical difficulty was, however, to maintain the organisms in the sludge in an active state, particularly as the demand for manures was seasonal whereas the production of sludge would be regular all the year round. He had not observed any material difference in the nitrogen content of the partially and completely activated sludge.

ABSTRACTS.

Observations on Dr. Moeller's Views of the Nature and Constitution of Vegetable Tanning Materials. R. LAUFFMAN. *Ledertechniche Rundschau*, No. 37, 1916; *Collegium*, 1916, pp. 417-20, Nov. issue. In his articles on peptization in tanning solutions and the vegetable tanning colloids (see Abstr., this J., 1916, p. 592) Dr. Moeller has developed in connection with a new theory of tanning, views in regard to the nature and constitution of tannins and tanning solutions which differ widely from those commonly accepted. The new views rest upon the researches of P. P. von Weimarn on the colloid condition of substances. According to Moeller tanning properties can never be shown by true solutions, but only by peptized sols. Further, all tanning materials contain gels which by the agency of a soluble substance, the peptizer, is peptized in water solution to a sol. In all vegetable tanning materials the peptizer is the same, namely tannin. The peptized substance, in the case of the catechol tan-stuffs, consists of catechin and its polymerization products; in the case of the pyrogallol tan-stuffs, of ellagic acid and its polymerization products; in the case of mixed tan-stuffs, partly of ellagic acid and partly of catechin. The pyrogallol materials have much tannin in proportion to the ellagic acid and are in a condition of complete peptization. On the contrary, the catechol tan-stuffs consist mainly of phlobaphenes and only to a small extent of tannin, and are therefore only partly peptized. Moeller believes also that ellagic acid, catechin and their polymerization products, which he groups under the term "phlobaphenes," are contained ready-formed in the plant organism. In water leaching, the phlobaphenes are peptized by the tannin while the latter is going into solution. The quantity of phlobaphenes in a tanning solution remains always the same. The separations which subsequently take place in the tanning solution are not due, as has been supposed, to the formation of ellagic acid or phlobaphenes by oxidation or hydrolysis, but simply to the re-separation of the catechin or ellagic acid which had been present all along in a peptized state, and are precipitated by the destruction of the peptization equilibrium.

In order to observe peptization phenomena in the case of vegetable tanning materials Moeller proceeds as follows: He prepares ellagic acid and phlobaphenes by pouring a hot alcoholic infusion of a tanning material into water, and washes with water the precipitate so obtained. He then determines how much of this freshly prepared material is peptized by a solution of tannin. By a series of experiments with tannin solutions of different strengths, Moeller found that dilute solutions were able to peptize much greater quantities of gel than concentrated solutions, and that the peptizing power of tannin is much greater for phlobaphenes than for ellagic acid. These and a number of similar experiments designed to determine peptization equilibrium, form in the main the basis on which Moeller rests his view of the constitution of the tan-stuffs and the properties of tanning solutions. Against these experiments and conclusions, a number of important objections must be urged.

First of all, Moeller's statement that the separations which take place in tannin infusions are only the settling out of substances which were already present in the plant, rests simply upon assumption, for it is not possible to observe with certainty whether any change of substance takes place before or during the separation. Further, it is quite as impossible to determine whether the ellagic acid, etc., prepared by the usual methods of purification from tannin infusions were contained in this condition in the plants, or whether these products result from transformation of other substances. Moeller himself admits that the phlobaphenes thus obtained are not the original materials, saying that the phlobaphenes of the catechol tan-stuffs have not as yet been obtained in crystalline form, "since they are, so to speak, changed under the hand of the analyst." The question must be answered whether or not the ellagic acid and catechin phlobaphenes prepared by Moeller through separation and purification from tan-stuff infusions are already transformation products from other materials originally present in the natural tan-stuff, before his experiments on the solution of these prepared materials in tannin solution, forming artificial "tan-stuff sols," can have any convincing weight. If the ellagic acid and phlobaphenes are transformation products, evidence obtained from such experiments would give no true picture of the behavior of the corresponding original material in the presence of tannin solution. If it is found in a laboratory experiment that ellagic acid is better peptized than catechin phlobaphenes, it is not admissible to draw from this observed fact any conclusion in regard to the constitution of the natural tan-stuff, nor to infer that pyrogallol tans contain along with ellagic acid excess quantities of tannin, and that catechol tans have chiefly phlobaphenes, and along with them a small proportion of tannin. If it be true as Moeller alleges that the methods of examination now at our disposal do not suffice to show the very small amount of tannin which is present in solutions of the catechol tan-stuffs, we are left with no means of showing that the substances heretofore regarded as pure catechol tans, which do not give the reactions for pyrogallol tannin, contain tannin at all. For the purposes of his theory, Moeller assumes in considering catechol tan-stuffs that unrecognizable tannins are present in this group. On the other hand, he leaves out of account such an important case as that of chebulinic acid, which Paessler and Hoffman (*Ledertech. Rundschau*, 1913, p. 129; this JOURNAL, 1913, p. 268) have shown to be present in considerable quantities along with ellagic acid in the "bloom" deposited from an infusion of myrobalans. According to Moeller's peptization theory, this chebulinic acid ought to play an important part in peptization. Many other results obtained in the examination of tanning materials contradict the explanation which Moeller offers of the nature and constitution of the tan-stuffs. If, for example, catechol tan-stuffs consist mainly of the products of condensation or polymerization of phlobaphenes, we should not expect to find, on applying Stiasny's test with formaldehyde and hydrochloric acid, the extraordinarily easy facility of reaction which is observed in the solutions of these tans.

Moeller remarks in regard to the methods of examination for tan-stuffs at present in use that the qualitative tests are entirely insufficient and the quantitative determination with hide powder can only give information of the total amount of peptizer and peptized substance present. He also claims that the tanning value or quality of a tan-stuff can only be determined by examining the colloid condition of the tannin infusion and the behavior of this infusion in regard to colloid-chemical reactions. It must be admitted that the means now available for the qualitative examination of tan-stuffs, particularly commercial extracts, are very incomplete. It is also true that the qualitative tests are practically almost valueless for determining what sort of a solution a tan-stuff infusion is, and how the reactions which take place in it are brought about. It is a fact, however, that the tests now in use suffice to divide tannins into two pretty well-defined groups, catechol and pyrogallol tans, and to show the same two groups either in natural materials which contain both, or in artificial mixtures. It is to be expected that the methods of qualitative testing of materials will be further developed and improved, and it is sure that in this work colloid-chemical reactions will afford valuable help. The quantitative method of tannin determination by means of hide powder is not only able to furnish a measure of the total material having tanning power, but also from the percentage of tannin, from the proportion between tannin and non-tans and from the quantity of insolubles, to enable many conclusions to be drawn in regard to the tanning properties of tanning materials and extracts. Thus Moeller's assertion that in regard to the quality of a tanning material, only an investigation of the colloid properties of its solution can lead to any conclusion, is contradicted. Further, such important properties of a material as the "feel" and color of the resulting leather can neither be determined by a quantitative tannin determination with hide powder nor by colloid-chemical researches, but only by a properly carried out experiment with animal skin. Moeller's views in regard to the constitution, qualities and tanning effects of vegetable tanning materials and solutions are notably lacking in any sufficient experimental basis. They rest almost entirely on speculative considerations, and will hardly displace views heretofore held which are based on experimental research. L. B.

The Insufficiency of the Methods of Tannin Investigation. W. MOELLER. *Ledertech. Rundschau*, Nos. 41, 42 and 43, 1916; *Collegium*, 1916, 420-27 and 462-76. This long paper was written in answer to the preceding. He disputes Lauffmann's assertion that his (M.'s) theory rests on insufficient experimental evidence. He attacks the validity of qualitative tests in general, using as an example a case which had been extensively discussed some years earlier. An extract said to consist of 80 per cent. oak and 20 per cent. quebracho was examined by two laboratories and certified as containing no quebracho. Fourteen pages are devoted to a review of this old dispute. The rest of the paper, more than six pages, deals with the hide-powder method. L. B.

The Tannins of the Oak Tree. Valonia. ANONYMOUS in *Shoe and Leather Reporter* for Feb. 15, 1917. Valonia is commonly not extracted alone, but in mixture with barks or myrobalans. The different texture of the material helps to prevent the valonia from caking. Some tanners extract valonia without grinding, which results in slower and less complete extraction. Some crush the cups instead of grinding. The author asserts that the extraction should aim to avoid removing coloring matter. (In the case of such materials as valonia and quebracho, where the coloring matter removed by drastic leaching is yellow, not all tanners will agree with the author.) He quotes the table from "Principles of Leather Manufacture" showing best yield at from 150° to 176° F.

Recent Improvements in the Art of Glass-making. Circular sent out by ALLEN ROGERS, Chairman, Press and Publicitv Committee, A. C. S. The first glass noted is the heat-conducting and shock-resisting "pyrex" glass, used in the manufacture of both chemical and culinary ware. Another is the new glass for electric light bulbs in which potash is replaced by soda, with no loss of strength or transparency.

The Metric System. Circular from the same Committee as the preceding abstract. (This one is signed E. H., which we judge from the style of the text means Ellwood Hendrick. Text follows in full.)

For years the various scientific bodies of the country, including the American Chemical Society, American Electrochemical Society, American Society for Testing Materials and others have been trying to get the metric system adopted in the United States. At the last convocation of the American Association for the Advancement of Science a special conference was held on the subject, at which some interesting features were brought out. Full papers are published in the March *Scientific Monthly*.

Professor Kennelly of Harvard observed that whereas the metric system employs only two units of measurement, the meter and the gram, we have about forty units and these are entangled in measures of length, area, volume, and in dry, liquid, cord, apothecaries' avoirdupois, troy and what not other standards until dire confusion has resulted. The metric system is international and is employed in all Europe and America except Great Britain and her colonies, Russia and the United States. There is no question as to which system will finally be adopted by all countries; the only question is how much longer the United States and England will delay.

All accurate and scientific work in all countries is measured by the metric system, and all electrical measurements and electric light bills are already recorded in the international scale. Every nickel five-cent piece weighs 5 grams and is 2 centimeters in diameter.

On the other hand, American wet and dry gallons, quarts and pints differ from each other and also from British standards. A bushel is a measure of volume, but it is also a measure of weight, and while the volume is constant the weights vary in the different states. A bushel of rye, for instance, is 56 pounds in most states, 54 in California and 50 in Maine. A bushel of barley is 48 pounds in the majority of states, but 45 in Arizona, 46 in Oregon, 47 in Pennsylvania, Kentucky, Georgia and Alabama and 50 in California. A bushel of buckwheat is 40 pounds in California and 56 in Kentucky with many variations in other states, while the standard for shelled corn varies from 50 to 58 pounds per bushel.

Mr. William C. Wells, Chief Statistician of the Pan-American Union, contributed the above figures and pointed out the need of the metric system in selling manufactured goods. Raw materials, he said, sell themselves and the buyer does not mind figuring so long as he can get what he wants at the market price. But manufactured goods do not sell themselves. They are really competitive and the ultimate consumer, living where the metric system prevails, will not buy a 15½ collar, a No. 8 shoe, an inch chisel, cloth a yard wide or a nut threaded to the inch scale.

Although Russia has not formally adopted the metric system, practically all her imports are measured to that gauge and her people are coming around to it. Since the war even in domestic trade in England the metric system is also coming rapidly into use.

It is held that any intelligent child can learn and carry in his mind in three lessons the whole metric system, and that any reasonably intelligent adult can master it in one hour or less of serious study. On the other hand, it would be easier to commit the multiplication table up to one hundred to memory than to learn all the details of the confusing system of weights and measures current in this country.

Mr. Wells explains also that invariably when the metric system has been adopted the old folks with closed minds use their familiar terms for new measurements. Thus the quart becomes the liter, the pint the half-liter, and the pound the half-kilogram. And the young people have trained their minds by learning to remember more useful information than that a mile has 8 furlongs, a furlong 40 rods, a rod 2¾ fathoms, a fathom 2 yards, a yard 3 feet, a foot 12 inches and an inch 3 barleycorns. Also that, among other enlightening revelations, a pound has 16 ounces if it isn't troy weight, an ounce 16 drams and a dram 27½ grains.

The use of our present system is very like giving the chief engineer of a great works a pigs-in-the-clover puzzle to solve during his busy hour.

The Wrong Solvent. By ELWOOD HENDRICK. (Another contribution from the Publicity Committee.) The soya bean is one of the most promising of vegetables. It provides oil and food for man and beast. Given enough soya beans and granted the art of preparing them so developed that they might be served as food having sufficient diversity and palatableness, neither meat nor fish nor fat would be needed. In this respect the Germans did not prepare for war and a blockade. It is marvelously prolific, and so valuable is the oil expressed from it that nearly every state in the Union is making experiments with soya beans in its agricultural experimental stations. The oil is used as a substitute for linseed oil which, owing to the uncertainty of the flax crop, is more speculative than mining stocks in its value. The oil may also be hardened into an edible, hard fat, while the pulp or oil cake is one of the very best kinds of cattle feed.

In order to get as much as possible of the oil out of the meal the pressed pulp is sometimes further extracted by means of a solvent which will dissolve out the oil remaining after the beans have been pressed. Naphtha is good enough, but care must be taken to remove it entirely from the meal. Cattle do not take to the smell of naphtha, although they thrive mightily on their new fodder when it has been thoroughly removed. Now tri-chlor-ethylene is another good solvent for soya bean oil; it is not offensive in odor and it is not poisonous when given to cattle in comparatively large doses. Neither is it inflammable or explosive. Off-hand it would appear that tri-chlor-ethylene was better and safer in every way than naphtha, but it appears that when it has been used as a solvent for the oil in the pressed meal or cake a considerable number of cattle have died from eating it. Now since the cake is grand feed for cattle and the tri-chlor-ethylene is not poisonous, something must have happened and it appears probable that a chemical reaction takes place between these two harmless bodies which produces a poison. It is not yet known what the reaction is.

Fish Skins for Leather. ANONYMOUS in *Hide and Leather* for Mar. 3, 1917. The writer had visited the Peabody Museum, Salem, Mass., and describes some of the samples of fish skin seen there. Most of those named are seal, whale or walrus, which would scarcely be called fish by a biologist. One article described is a costume formerly the property of an Hawaiian king, of thin glossy material said to be fish skin leather.

Near-skin Shoes. E. F. HARKINS in *Boston Transcript*, through *Hide and Leather*, Mar. 3, under title "Calf No Longer Needed." The shoe described has imitation leather upper made from a fabric base covered with a rubberized product. Sole and heel are of fiber, and box toe of the same. Insole and welt of felt. The fiber is a by-product of the automobile business.

Sulphite-cellulose Extracts. A. HARVEY. *Leather World*, Feb. 8, 1917, pp. 73-4. Review of processes of manufacture, followed by abstracts of experiments and opinions in regard to the value of the extract and methods of recognizing it.

The Extraction of Sumac. ANONYMOUS, *Leather World*, Feb. 8, p. 76. If sumac is extracted at the boiling temperature, from 20 to 30 per cent. of the tannin may be lost. The correct temperature is from 120° to 140° F. If the infusion is kept for any length of time before using, it is liable to loss of tannin from fermentation.

Forestry Work In New Zealand. CONSUL GENERAL ALFRED A. WINSLOW, Auckland, in *Commerce Reports*. The principal Government forestry nursery and reserve of New Zealand is at Rotorua. Mr. H. A

Goudie, General Superintendent for the North Island, has given the American consul general an opportunity to study the nursery and plantation, where the first forestry work was begun in 1898. Since that date 58,459,000 forest trees have been propagated in this nursery out of a total of 104,835,900 for the entire Dominion since the beginning of the industry; and more than 14,700 acres of trees have been planted on the two adjoining reserves, out of a total of 27,217 acres for the Dominion. The soil for the nursery is thoroughly prepared by being cultivated and fertilized until it becomes a rich black sandy loam before planting is begun. It is then laid out in beds about 8 feet wide and 100 feet long into which seeds for about 200,000 plants each are sown. A very great majority of the plants are cultivated until they are two years old, when they are transferred to the plantations, or sold to individual growers at the cost of production. The output of the nursery for the past few years has varied from 2,600,000 to 6,000,000 plants. Only seven Government forest plantations of any importance are maintained in this Dominion. The largest two are just south of Rotorua and cover more than 21,000 acres. About two-thirds of this area has been planted with trees averaging 32 square feet to the tree. The work is thoroughly done, and it is calculated that at the end of 30 years some good saw logs may profitably be cut from the eucalyptus and the more rapidly growing pine forests. Meanwhile many trees which are cut to thin out the timber may be used for poles, posts, sleepers, etc., while considerable firewood is sold annually from the plantations. The total cost of the plantations to March 31, 1916, had been $1,092,431. During the year ended with March, 1916, much less work than usual was done in Government forestry. The clearing and preparing of the ground in the two large plantations near Rotorua is done by prison labor. It is estimated that at the end of 30 years the native forests of New Zealand will have been exhausted. The annual consumption of lumber will then require the cut from at least 20,000 acres of timber lands, which means that about that area must be planted annually before many years if the supply is to be provided by this country. In this the general public is beginning to realize that it can materially help by planting small patches on farms and along partition fences, and the Government proposes to supply the small trees at cost.

Rapid and Ultra-Rapid Tannage. NICOLAS FLAMEL. *Revue général des Sciences,* 1916, Dec. 30, pp. 720-4. In 1830 was published a second edition of a book by M. Dessables, entitled "The Art of Making and Improving All Kinds of Leather," in which the author undertakes to apply science to leather problems, with special reference to rapid tannage. Leather is of wide application in military equipment. Good leather for soles cannot be made in a hurry, especially if it is to be used in wet and muddy trenches. The old process of making sole leather was a very slow one. At the time of the wars of the First Republic and the Empire there were attempts to shorten the time of tannage. The name of Seguin is generally coupled with the first process for rapid tannage. There was in reality a group of men at work on the problem, both in England and France. In his book, "The Art of the Tanner," published in 1764, the astronomer Lalande suggested means to shorten the time of tannage, tannage by flotation, preparation of extracts, the employment of heat and the use of such salts as alum.

Preiffer announced in 1777 that he could convert the heaviest cattle hides into excellent leather without tan in six or eight weeks with the products of distillation of coal or peat, and by the aid of heat. The hides, cleansed in the usual manner, are placed in vats two-thirds full of the earlier products of distillation and one-third of water. The vats are heated to blood heat and after twelve hours the hides unhair readily. They are now, after scudding, placed in a bath made up of the later products of distillation, diluted with one-fourth water. (This suggests the phenol tannage of recent experiments.)

Seguin realized the importance of certain processes and sought to perfect them. Plumping was secured by the aid of dilute sulphuric acid, a practice then in use in England and mentioned by MacBride. The tannage was effected in vats, the hides being immersed in solutions of tannin prepared beforehand, means being used to keep the hides apart. As the tannage progressed, stronger and stronger liquors are used. To avoid useless absorption of tannin the heads and flanks were cut off. The committee appointed by the Convention assisted at the experiments which extended over three months at St. Denis, and then at new experiments at Mousseaux, destined further to expedite the tannage. A report was made in 1795 and was very favorable. The needs of the army in the field increasing, every means of accelerating tannage was of interest. Again the Seguin process was applied on a large scale by order of the First Consul. In 1801 Dieudonné boasted of the superiority of the leathers made by Ducrocq.

On all sides, particularly in England, the example of Seguin was followed in efforts to accelerate tannage. William Desmond was granted a patent in 1797 for a process similar to Seguin's. The *Annales de Chimie*, of which Lavoisier was one of the founders, in the first three volumes of the *Repertoire des Arts*, contains many processes of tannage. (1) A new method by Mr. Ashton. He used mineral astringents instead of tannin, preparations of copper, iron, zinc and sulphur. He made sole leather in six weeks. (2) Leather was rendered water-proof by the use of a drying oil and metallic oxides or gum-resins. (3) The new method of Dr. MacBride, in which lime water was used instead of ordinary water, (4) A memoir by Swayne on the use of oak leaves in tanning. (This memoir was reprinted in this JOURNAL for April, 1911.) (5) An improvement by J. Tucker. He raised the temperature of the liquors.

In 1808, the *Société pour d'Encouragement l'Industrie nationale*, which in the past as well as recent time has always striven for the development of French industries, gave its interest and support to the work of *Favier*. As commissioners to observe the tanning experiments of Favier, the learned Society designated Audibert, Bardel and d'Arcet. The closing passage of their report, after noting that the earlier experiments of Seguin and others seemed to have been forgotten, states that M. Favier sought to abbreviate the time of tannage of sole leather from fifteen months or even two years, without loss of quality. They report that M. Favier had made in two months leather which, although somewhat brittle and of poor finish on the grain, was nevertheless well tanned and equal in quality to much of the leather on the market.

Nearly 40 years elapsed before any further mention of rapid tannage appears. A. Turnbull, in 1847, says in his "New Process of Tannage" that it is surprising that tanning has not felt the impulse that other industries have received from chemical science. He remarks that the many processes which have been proposed for shortening the time have only done so at the expense of the quality of the product. He used a sugar solution saturated with lime, thus causing the hides to absorb much more lime than usual. The hides were delimed and tanned in the absence of air "to prevent the formation of gallic acid, which dissolves gelatin and changes the quality of the leather." He claimed great economy from his process. "In ordinary tannage 50 kilos of fresh hide make 22.5 kilos of leather, and 25 kilos of finished leather require 150 kilos of oak bark." By his method, 50 kilos of fresh hide make 30 kilos of leather, using only 50 kilos of bark, only 14 days being required. The advantages claimed are short time, better quality and less cost besides larger yield.

Durand, 1859, made a tanning extract from lentisco and myrtle.

None of these experiments had any permanent result. Rightly or wrongly, but as experiment has shown chiefly wrongly, it was supposed that the effect of electricity on the tanning process would be to hasten the union of hide and tannin. The idea is seductive. The house of Durio attempted to effect a rapid tannage by the aid of the electric current. They took out a patent in 1882, after several years of experiments.

M. Placide Peltereau, president of the *Syndicat général des cuirs,* in his report on the Exposition of 1900, estimates the results of the new rapid processes. Speaking of the beautiful leathers made by the slow process with oak bark, he says "They combine all the qualities of a fine and compact tannage (due to the slow assimilation of the tannin), the shade, the firmness without brittleness, the smooth finish on flesh and grain." Of the leathers made by the "moderately accelerated" methods, using extracts with bark, he says, "At a price somewhat less than the other, generally of fairly good quality and appearance, although they have not the shade nor the 'cut' of pure oak leathers, these are nevertheless the leathers of to-day and will be, more and more, the leathers of the future" But in regard to the leathers produced by ultra-rapid tannage with extracts, M. Peltereau remains skeptical. He quotes the opinion of Procter, "These leathers are hard rather than solid. It is possible that the best sole leathers cannot be made by rapid tannage."

The war has made the need for rapid tannage acute. The disadvantages in the case of harness leather are not so great as in the case of sole leather, because the former is not subjected to such hard use, and is protected by grease And the poorer the sole leather is, the more rapidly it wears out, and the sooner must it be replaced. Why must good tannage be slow? In general, the speed of reaction between a liquid and a solid depends on certain factors, among which are (1) the active surface of the solid (porosity, etc.), (2) degree of concentration, (3) temperature, (4) chemical energy, (5) the physico-chemical constitution of the solid body, (6) agitation, (7) electric energy in the case of conducting bodies, (8) osmotic pressure, (9) permeability of the cell walls, (10) migration of ions under the action of electric current, (11) pressure, etc., etc. If the process involves molecular physics instead of chemical reaction, the factors are the same, excepting chemical energy. It is probable that leather is a mixture of complexes, of compounds and of solid solutions.

The tannins are substances of feeble reaction, and if the walls of the hide-cells are permeable, like the parchment used by Graham in his beautiful researches on osmose, those of leather are less permeable. In so far as the tannin has penetrated and converted the hide into leather, to that extent is its further penetration hindered. In the vats, there is no agitation and the temperature is low. In this slow tannage, the progress can be watched by making a cut. If there is no "green streak" left in the middle, the leather is tanned through. With thick and heavy hides, this takes many months. At first glance one might conclude that to cause the tannin to penetrate the hide was the only end to be achieved in order to produce good leather. All the patents aiming at this end utilize the following: Increasing concentration of tan liquor, agitation, heat, if agitation does not heat it enough, and sometimes the employment of acids or other substances. The employment of liquors of increasing concentration is a natural development of the old tanning process. If a hide is immersed in a liquor richer than itself in tannin, tannin will be absorbed. If the hide is richer in tannin than the liquor it will lose tannin, in virtue of the law of osmosis. The effect of agitation is so great that if it were necessary, sand could be made to penetrate the leather. Heat accelerates all the processes. The purpose of acids is to swell the hide and aid the penetration of the liquors. As an illustration of the effect of agitation, note a patent of Stark & Co., 1891. They apply tannin in powdered form, and it is forced into the hide in a few hours, forming a paste with the moisture of the hide.

Pressure has also been resorted to. An English patent places the hides in an autoclave under a pressure of 5 or 6 atmospheres and changes the liquors every 24 hours. In Italy the same process has been patented by the firm of Alimonda at Spezzia. The action of vacuum has also been utilized. The hides are placed in a vessel from which the air is afterward exhausted and the liquor then introduced. The action of pressure or vacuum is further hastened by rotation. Acids and other materials are added to the liquors. By the use of these various means, tannage has been effected in less than 48 hours. But is the leather the same as that obtained by slow tannage? Actual experience shows that it is not. Tannage occupying three or six months produces a leather intermediate in character between the slow-tanned product and that from the extra-rapid processes. Can we recognize the different products, and can their value be compared by tests? The second question cannot as yet be answered positively. Tests have been made, and others are in progress, but no results have been published as yet. The other is not easy to answer either. Rapidly tanned leathers will in general contain a larger percentage of water-soluble materials than those more slowly tanned. But even slowly tanned leathers are often heavily charged with uncombined tannin by dry-dipping and similar processes, so this difference is not distinctive or certain. L. B.

PATENTS.

Purifying Sewage. British Patent 14,733. E. Long, Manchester. A modification of the activated sludge process in which a mixture of activated sluge, sewage and air is sprayed into a mixing chamber where it is emulsified by violent agitation. It is then delivered to a tank, from another part of which a stream is fed again to the emulsifying apparatus. The sewage may thus be circulated until the desired degree of purification is accomplished.

Tanning Material. U. S. Patent 1,216,612. OTTO SCHMIDT, assignor to the Badische Company. The process involves converting difficultly soluble materials into more soluble form by treatment with a soluble condensation product of naphthalene, formaldehyde and sulphuric acid, free from hydroxyl groups and containing at least one sulphonic acid group. The said condensation product is prepared from 10 parts naphthalene, 10 parts sulphuric acid and 4.3 parts 30 per cent. formaldehyde.

Leather Substitute. British Patent 15,269. A. L. NIELSEN, Copenhagen. The cloth from worn-out automobile tires is the material. Several layers are united by heat and pressure, after devulcanization. A layer of rubber may be applied to one or both sides.

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CORRECTION.

In the Alfred Seymour-Jones paper on the formic-mercury process in the March JOURNAL, on p. 72, first line of second paragraph, for "Using 1 per 1,000," read "Using 1 per 5,000." Also in second line from bottom, substitute 5,000 for 1,000.

TENTATIVE PROGRAM 14TH ANNUAL MEETING.

The meeting will be held at the Marlborough-Blenheim, Atlantic City. See April number for hotel rates, etc.

THURSDAY MORNING.

Opening Remarks	C. R. Oberfell
Report of Secretary and Treasurer	H. C. Reed

Committee Reports:
- Comparative Analysis..............................R. H. Wisdom
- The Testing of Dyes for Leather......................G. T. Creese
- Solubility of Hide in Salt Solution and Effect of Alkali on Soaking Dry Hides..................................Dr. L. Balderston

THURSDAY AFTERNOON.

Nigrosines....................................Dr. J. Merritt Matthews

Committee Reports:
- Analysis of Sulphonated Oils..........................W. K. Alsop
- Effect of Hard Water on Tannins.......................T. A. Faust
- Sulphuric Acid in Leather...........................C. R. Oberfell
- Specifications for Kaolin..............................R. W. Frey
- Analysis of Tannery Effluent............................W. A. Fox

Studies Conducted by the Public Health Service in Regard to the Sanitary Disposal of Tannery Wastes
H. B. Hommon, Sanitary Chemist, P. H. S.

The Public Health Service built an experimental disposal system at an important tannery where these studies were conducted.

FRIDAY MORNING.

Chemistry of the Manufacture of Tanning Extracts from Waste Sulphite-Cellulose Liquors ....H. H. Hurt

Anthrax Symposium:
- Anthrax............................Dr. A. S. Ross, Camden, N. J.
- Practice and Theory on Treatment and Diagnosis of Anthrax
  Dr. H. Z. Frisbie, Elkland, Pa.
- The Nature of Anthrax and Anti-Anthrax Serum
  Dr. John Reichel of H. K. Mulford Co.
- Studies on the Disinfection of Tannery Wastes.......A. M. Buswell
- Anthrax and Disinfection of Hides...................V. A. Wallin
- Anthrax Sterilization (by Title).............Alfred Seymour-Jones
- Discussion..........Dr. Hickman of the Bureau of Animal Industry

FRIDAY AFTERNOON.

Tanners and Chemists "Round Table" discussion.

Drum Tannage ....Oskar Riethof

SATURDAY MORNING.

Borax and Boric Acid in the Tannery and Currying Shop....H. L. Harris

Discussion of recently advanced ideas on "Theory of Leather Formation"

John Arthur Wilson
Dr. L. Balderston
Robert W. Griffith
Dr. William Klaber
H. C. Reed
F. H. Small
Dr. Allen Rogers
J. H. Yocum

Saturday Afternoon.

Executive Session.
Election of Members of the Council.
Council Meeting.

CAESALPINIA CORIARIA.

By Miles Haman.

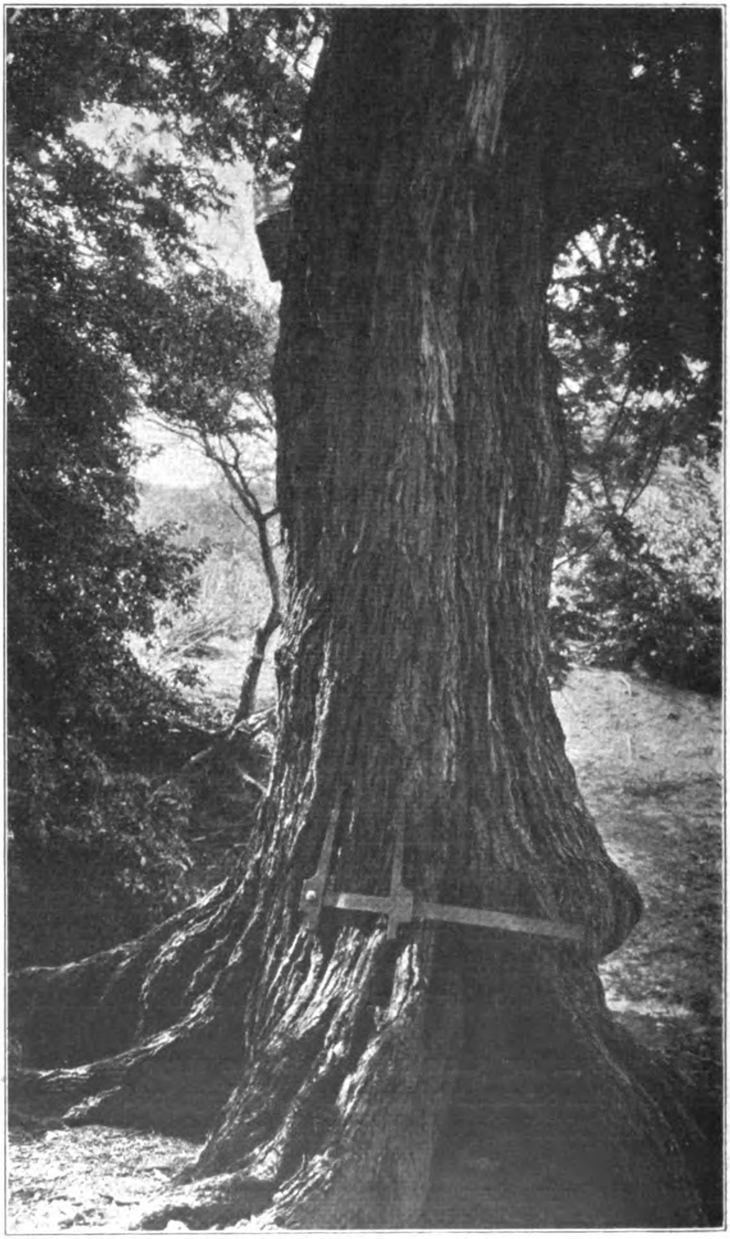
Illustrations from photographs by the author.

The increasing demand in American markets for the product of this well known tree, commonly called Dividivi, makes it of interest to describe the conditions under which it grows on the island of Curaçao, Dutch West Indies. In all parts of the island, from the tops of the hills to the sea-beaches, this tree is found. It occurs on coral-limestone rock as well as on soils formed from the disintegrated igneous rock, but reaches its best development in low-lying, protected sites, where the soil is not too dry. It sometimes occurs singly as a short-boled, wind-distorted tree or shrub, and again in sheltered valleys as a stocky-boled, wide-spreading tree reaching diameters of nearly 2 feet and heights of 25 to 30 feet.

In March the trees are yellow with the opening blossoms borne in dense clusters, half hidden by the dark green leaves. Later the tree is a mass of curled green pods turning to a rich golden or chestnut brown, and ripening in May and June, when they are picked by the negroes. Later the pods are sorted in the storehouses of the large estates and sent by burro-cart to the city. Here it is stored and shipped to various ports in the United States. The quality and quantity of the crop varies greatly with the locality and size of the tree. June to September sees the bulk of the production, for the crop is not all matured at the same time.

The accompanying photographs show the shape of the individual trees, the character of the bark and foliage, and the appearance of the Dividivi growing together with the Curaçao maiz (sorghum).

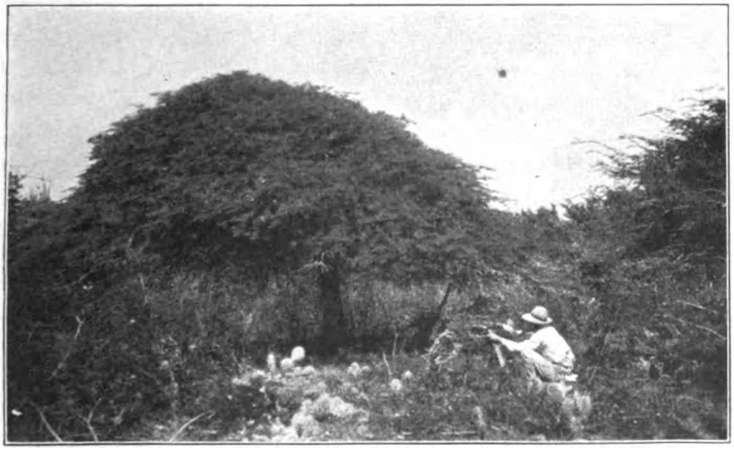
Besides its value as a producer of tanning material Dividivi furnishes an excellent food for the goat, and his love for the tree has in the past very seriously hindered its reproduction.



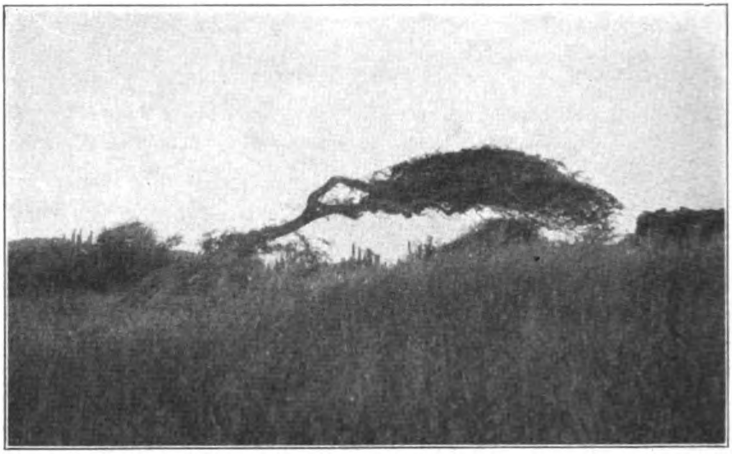
Trunk of Large Dividivi Tree. Diameter 21 Inches.

Dividivi:—Growing on Good Agricultural Land.

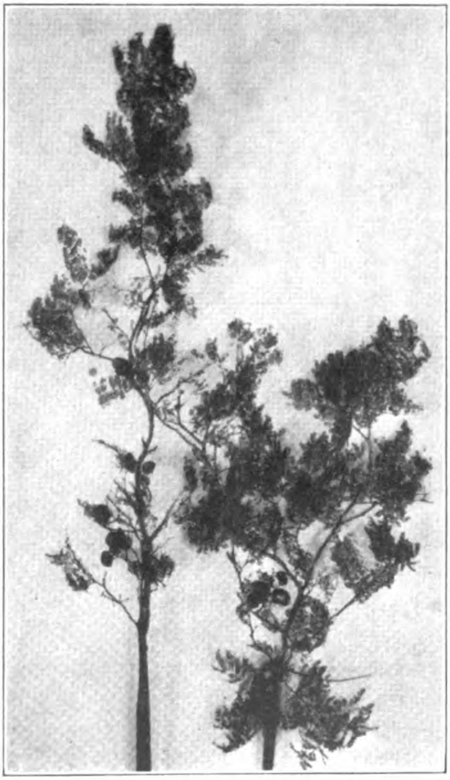
The high price for the product of Dividivi of late years has increased the interest of the planter and farmer in the tree, and in consequence many of them are planning to protect their trees from grazing and increase the number on the plantation. The wood of this tree is also valuable and furnishes a dark, very heavy, hard and durable material for a variety of uses.



Typical Dividivi Tree Growing on Good Soil in a Sheltered Valley.



Characteristic Habit of Dividivi Growing on Exposed Sites.



Fruit and Foliage of Dividivi.

A CONSTANT SAND-FEED.

By J. S. Rogers and R. W. Frey,

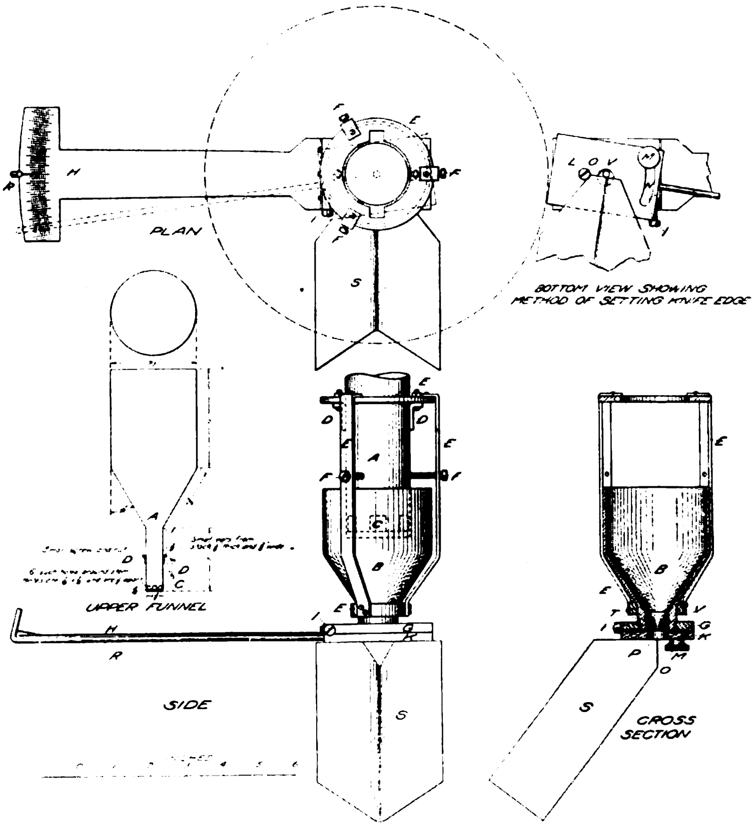
Assistant Chemists, Leather and Paper Laboratory, Bureau of Chemistry, Department of Agriculture, Washington, D. C.

While developing a machine for testing the wearing quality of heavy leathers it became necessary to devise an apparatus which would give a reasonably constant flow of sand. During the preliminary work several devices, which will be only briefly described, were tried with but little success.

The first one consisted of a small belt conveyor, fitted with cups, which it was hoped would supply sand from a bin to a small funnel in such a manner as to maintain a constant level in the latter. This failed because of the slipping of the belt, unequal filling of the cups, and stoppage of the funnel. A paddle wheel revolving in a metal jacket supplied at its base by sand from a hopper, was tried next. The jacket was provided with a slot through which the sand was ejected by the wheel on to a spreading or distributing plate. This proved unsatisfactory because of irregular ejection of the sand. It was thought that this could be remedied by maintaining a constant level of sand in the hopper, which, however, did not overcome the trouble.

It was finally decided that the best chance of obtaining satisfactory results would be furnished by a device which would deliver the sand in the form of a continuous stream such as is given by flowing through a funnel. Bearing this in mind and also the necessity of reducing the possibilities of stoppage and of overcoming the varying effects from changes in the level of sand in the supply hopper, the apparatus described below was developed. Since this sand-feed, or possibly some modification of it, may be of use to others, it seems desirable to describe it in detail.

The apparatus consists essentially of two funnels *A* and *B*. The upper large funnel *A* may be made of tin or brass and serves as a reservoir or hopper. The stem of this funnel is closed off at the bottom, but has a ring of similar and equally spaced holes *C* in the walls and as near the end of the stem as possible. By this arrangement the weight and packing effects of the high column of sand in *A* are almost entirely removed and at the same time the sand flows through the side openings *C* in such a manner as to maintain a practically constant level in the lower funnel *B*.



Details of Sand-feed Apparatus.

This lower funnel is suspended under the stem of *A* in such a way that it can be removed and replaced in exactly the same original position. Furthermore, the support must be such as to hold the lower funnel firmly in place, and not allow any swaying or displacement from the vertical position. In the apparatus shown here this is accomplished by means of the ears *D*, the frame *E* and the guide screws *F*.

The lower funnel *B* is of brass, with the exception of the apex of the cone and the lining of the funnel stem. These parts are made from a tool steel bushing *T*, the upper end of which forms the apex of the cone and is machined in such a manner as to form a smooth unbroken continuation of the walls of the brass cone. This bushing, made of hardened steel to prevent excessive wear and consequent enlargement of the aperture, is replaceable and so designed as to give the funnel a very short stem. The end of the funnel stem screws into the center of the plate *G* until it is flush with the lower surface of the latter. The scale *H* and the bumper screw *I*, the purpose of which will be stated later, are both attached to *G*. The bottom plate *K* is similar in size to *G* and is supported from the latter by means of pivot *L*, and set screw *M* which works in the slot *N*. In the center of *K* is a circular opening *O*, larger than the aperture *V* of the funnel. This opening is divided by a hard steel knife edge *P*, which is firmly fastened with its upper edge somewhat below the top of the plate. There is also attached to one end of *K* a long pointer arm *R*, which plays over the scale *H*.

By turning the lower plate on the pivot the knife edge is made to move across the aperture of the funnel, thus dividing the stream of sand. In this manner any desired division of the flow can be obtained and can be duplicated by setting the needle at the same point on the scale. If the plate is turned far enough the sand can be entirely shut off. It has been found that the needle must be reset very accurately to duplicate the desired division of the stream and to aid in this resetting the screw *I*, referred to above, is arranged so that the head acts as a stop for the bottom or pivot plate. Of course, the screw must be first adjusted to agree with the desired reading on the scale.

There is fastened to the knife edge a small chute *S*, which deflects or carries off one portion of the divided stream, thus giving what has been termed a "direct stream" and a "deflected stream." The direct stream is used on the abrasion plate, being distributed on the latter in a very uniform layer by means of a baffle plate. There is no reason, however, why either one or possibly both could not be used if desired. Since it was found in the preliminary work that an aperture of suitable size to give as small a stream of sand as required would invariably become clogged by the bridging of the sand grains, a large opening was used which then made necessary the knife edge split-off described above. Besides solving this difficulty, the split-off affords a means of keeping a check on the sand feed as explained below.

The total flow of the sand is the sum of the direct and deflected streams and is constant within reasonable limits. Knowing the total rate and the deflected rate, a simple subtraction will give the rate of flow of sand on the abrasion plate. In this way all that need be done while the feed is in operation during a test is to weigh the sand deflected in a definite period. This will also show the accuracy of the set of the knife edge and any partial stoppage of the aperture of the funnel which sometimes occurs due to foreign particles in the sand. As now used the sand deflected every 15 or 30 minutes during the entire test is weighed and from this the amount of sand flowing on the plate during those intervals is determined. This may not be necessary but is, however, a good precaution.

It may be stated here that any enlargement of the aperture of the funnel is no serious objection. Even should this become great enough to materially affect the total flow, which would be detected in the occasional checking up, it could be very easily corrected, for by a slight change in the set of the knife edge to give the direct flow desired, or to duplicate the flow used in previous tests. There has been no measurable increase in the size of the aperture of the apparatus which has been in use for several months.

To obtain good results it is absolutely necessary that the sand be carefully sifted to uniform fineness and be kept clean and free from foreign matter. This last point cannot be too strongly emphasized as the introduction of a small piece of string, wood, lint, etc., may seriously affect the flow or even entirely stop it. The sand used for this work is purchased as being of 30-40 fineness; it is resifted through standard 30 mesh on to standard 40 mesh. That which passes the 30 mesh but remains on the 40 mesh, is used.

The support for the entire apparatus is more or less a matter of choice, depending somewhat upon the conditions under which it is to be used. It should, however, be very strong and so firmly built that it prevents appreciable vibration and also accidental disturbance of the various parts.

Some results obtained with this apparatus are given below. It has been found advisable in operating the feed to keep the hopper well filled by adding sand every 30 to 45 minutes, as too great a change in the height of the column of sand influences the total flow to a slight extent. The figures given were obtained on one large lot of sand. It need hardly be added that the apparatus should be checked up on every new shipment of sand and also after taking down and reassembling.

TABLE I.—CONTINUOUS RUNNING—WEIGHT OF SAND FROM EACH STREAM AT INTERVALS.

Time min.	Pointer position graduation	Sand from direct stream grams	Sand from deflected stream grams	Total flow grams
15	6.0	1,106	1,116	2,222
15	6.0	1,105	1,122	2,227
15	6.0	1,107	1,120	2,227
15	6.0	1,102	1,120	2,222
30	6.0	2,209	2,249	4,458
30	6.0	2,208	2,256	4,464
15	8.0	1,282	943	2,225
15	8.0	1,286	945	2,231
15	8.0	1,290	940	2,230
15	8.0	1,289	941	2,230
30	8.0	2,578	1,880	4,458
30	8.0	2,573	1,886	4,459

Average total flow for 15 min. = 2,228 grams.

TABLE II.—SAND SHUT OFF AND POINTER RESET AFTER EACH COLLECTION.

Time min.	Pointer position graduation	Sand from direct stream grams	Sand from deflected stream grams	Total flow grams
15	8.0	1,281	944	2,225
15	8.0	1,286	940	2,226
15	8.0	1,290	931	2,221
15	8.0	1,276	945	2,221
30	8.0	2,566	1,886	4,452
30	8.0	2,564	1,883	4,447

TABLE III.—COMPARISON OF CALCULATED DIRECT STREAM WITH WEIGHED DIRECT STREAM.

Predetermined total flow equal to 2,228 grams per 15 min.

Time min.*	Deflected stream weighed grams*	Direct stream weighed grams*	Direct stream calculated grams*
15	1,116	1,106	1,112
15	1,122	1,105	1,106
15	1,120	1,107	1,108
15	1,120	1,102	1,108
30	2,249	2,209	2,207
30	2,256	2,208	2,200
15	943	1,282	1,285
15	945	1,286	1,283
15	940	1,290	1,288
15	941	1,289	1,287
30	1,880	2,578	2,576
30	1,886	2,573	2,570

* Results taken from Table I.

SUMMARY.

With the apparatus just described the enlarged aperture and knife edge split-off make it possible to secure a fine stream of sand without danger of stoppage from bridging of the grains of sand. The construction of the hopper stem practically removes the influence of the weight and packing action of the sand, besides maintaining it at a constant level in the funnel. Table I shows that a reasonably uniform flow of sand may be obtained. Having once secured the desired division of the total stream, no difficulty is experienced in resetting to duplicate the flow. (See Table II.) Weights of the deflected stream serve as a satisfactory check upon the amount of sand delivered by the direct stream. (See Table III.)

In conclusion, appreciation is expressed for suggestions offered by F. P. Veitch during this work.

COMPARATIVE TESTS WITH MANGROVE AND WATTLE BARKS.*

By F. A. Coombs, F. Alcock and A. Stelling.

The mangrove barks are now being used in large quantities by tanners who are producing sole-leather. These barks have a very high tannin value and very large supplies are available for the production of leather.

In a previous paper (*J. S. C. I.*, 1912, p. 212), we gave the tannin values of some Australian mangrove barks. After examining the mangrove trees in Cairns and Cooktown districts, North Queensland, we found that *Rhizophora mucronata* represents fully 75 per cent. of the trees suitable for stripping, the remainder consisting largely of *Brugiera gymnorrhiza* and *Ceriops candolleana.* For commercial reasons strippers are not likely to take the bark from the different species and keep each one in a special grade. The above three species (Specimens identified by Dr. J. Shirley, Brisbane) grow in a very mixed state and buyers can assume that bark from these districts consists of an excess of *R. mucronata* and small varying proportions *B. gymnorrhiza* and *C. candolleana.* The majority of the mangrove bark

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*J. S. C. I., February 28, 1917, pp. 188–92.

from German East Africa (See Paessler. *Collegium,* 1912; *J. S. C. I.,* 1912, 446; this J., 1912, pp. 46-8) is also taken from the above three species.

We have used the commercial mangrove bark for our tanning experiments, and *B. gymnorrhiza, R. mucronata,* and *C. candolleana* were examined by the aid of the usual qualitative tests.

The color and precipitation tests gave results which did not differ from those described by other workers for mangrove bark. The solubility tests for mangrove tannins have not received a great deal of attention from leather chemists, and the results given for these tannins may have been obtained from one or a mixture of the genera which are described as mangroves.

The following values have been given (Leather Chemists Book, Leeds University) for mangrove: Ethyl acetate figure, 0 to 5; alcohol figure, 0 to 5, and gallic acid value 0.68.

These differ to a certain extent when compared with our results shown below.

	C. candolleana	*R. mucronata*
Ethyl acetate figure....	20 to 25	7
Alcohol figure.........	0	0
Gallic acid value.......	0.785, 0.738, 0.692, 0.657	0.600, 0.595, 0.501, 0.479

	B. gymnorrhiza
Ethyl acetate..................	4
Alcohol figure..................	11, 12, 24
Gallic acid value..............	0.450, 0.385, 0.381, 0.359

Procter and his students have carried out a considerable amount of work in connection with the oxidation of tannins with permanganate and the results obtained are useful as qualitative tests for the recognition of various tannins. He gives the gallic acid value of 1 g. of chestnut tannin as varying between 0.56 and 0.66 and of valonia tannin as varying between 0.55 and 0.63.

These variations are common to mangrove and apparently no constant figure can be given which represents the gallic acid value of these tannins. The gallic acid value of mangrove tannins apparently reaches the maximum with *C. candolleana* and the minimum with *B. gymnorrhiza.* Procter states that the phlobaphenes or reds are probably anhydrides of their respective tannic acids, and it is a well-known fact that the catechol tannins change on exposure to heat or light from a medium to a dark red color. This change brings about a more complicated and larger molecular aggregate; and as this aggregate increases, its solubility in water decreases, until it finally reaches the state known as insoluble reds or phlobaphenes. The tannins in wattle and mangrove barks appear to exist as variable molecular aggregates ranging from the parent body or unit molecule, to the insoluble red; and it is probable that the oxidation values would differ for the unit molecule and the difficultly soluble reds. The tannin from *B. gymnorrhiza* has a low oxidation figure and probably a high molecular aggregate. Mallet bark tannins also have a low oxidation value .(gallic acid value, 0.288) and the rate of penetration is slow.

Recently Bennett (*J. S. C. I.*, 1914, 1182; this J., 1915, pp. 87-101) suggested certain changes in the I. A. L. T. C. official method for estimating tannins. He believes that the present method returns a high percentage of non-tans, and we are confronted with the problem that certain substances exist which are tannins or non-tannins according to the ratio, within certain limits, between hide-powder and tannin.

The non-tannins have a low oxidation figure and it would probably throw some light on the subject if oxidation figures were obtained for tannins and non-tannins from one sample of bark using both the official and Bennett's revised methods for estimating the tannin. Such results would show if the substances under dispute were akin to tannin or non-tannin, and we might get a better view of the value of the gallic acid figure.

The leather-forming properties of mangrove barks were tested by an experimental process described in *Collegium* (October 12, 1916; *J. S. C. I.*, 1916, 1028; this J., 1916, pp. 573-85).

Two duplicate tests were carried out for comparative purposes, and wattle bark was used for the standard tannage. The mangrove bark has already been described and the wattle bark was the same as the tanners use under the name of Adelaide bark (*Acacia pycnantha*).

The hide is cut into sections of equal area and numbered as shown in the diagram. The sections are approximately 1 ft. 9 in. square and they are soaked, limed, and tanned in upright vats measuring 2 ft. × 2 ft. × 4 in. Two sections are suspended in each vat and about 32 liters of liquor is required to cover them.

The sections 1 and 5, 2 and 6, 3 and 7, and 4 and 8 are approximately constant in area, thickness (substance) from grain to flesh, and in general structure.

The first two sections, Nos. 1 and 5, are both soaked, limed, and delimed in the same vat at the same time; therefore, temperature, time, and constituents of all liquors are constant for these two pieces until they reach the tan liquors. Then they are separated, and No. 1 goes into wattle bark liquors and No. 5 into mangrove liquors. Under skilled control these two sections are approximately constant until they reach the tan liquors, and then if any variation occurs, it will be due to a difference either in the process of tanning or in the tanning materials. In this experimental work the tanning process has been kept approximately constant for both duplicate tests, so that if the hide sections be constant the variations can be traced to difference in the tan liquors (acidity, non-tans, etc.), or in the structure of the tannin molecule. What has been said of No. 1 and 5 applies also to the groups Nos. 2 and 6, 3 and 7, and 4 and 8, but it is hardly necessary to point out to practical men that No. 1 will differ from all others with the single exception of No. 5 section, and likewise No. 4 will differ from all except No. 8 section.

Sections 1 and 5, and 2 and 6 were used for the first test and the other two pairs were used for the second. For both, the soaking occupied two days with two changes of water; liming 7 days in one fresh lime liquor; wash pits (after dehairing, etc.) 2 days with two changes of water; and deliming, one hour in lactic acid solution (2 g. per liter).

The tanning process was continued at a constant tannin strength for both tests.

Acidity of the mangrove liquors for both tests is higher than the wattle liquors, and one might therefore expect the mangrove leather to fix more tannin. However, we are now carrying out comparative tests for the value of acid in tan liquors and hope to discuss this point at a future date. The variable ratio between tannin and specific gravity is fully demonstrated in both tannages. The wattle tannins penetrated the hide quicker than the mangrove tannins.

The figures for the tanning process show a small irregularity due to the process of extracting the tannin from the bark. We were extracting tannin from the bark at irregular intervals and some liquors had a short time for exposure to fermentation. The amount of difficultly soluble tannins was low for these tan liquors, and these conditions might adversely affect the percentage of combined tannins.

FIRST TEST.

Days	Sections 2 and 5 Mangrove bark liquors			Sections 1 and 6 Wattle bark liquors	
	Tannin g. per liter	Barkometer degrees	Lime water cc.	Barkometer degrees	Lime water cc.
2	16.64	8.2	2.6	7.7	1.8
4	24.96	12.3	3.9	11.6	2.7
6	35.56	18.0	4.7	17.0	4.4
8	47.6	24.3	9.4	24.1	5.9
10	67.0	32.6	11.3	32.7	8.0
20	90.53	47.3	8.7	45.4	8.4
29	111.8	62.0	15.0	62.2	8.0

SECOND TEST.

Days	Sections 4 and 7 Mangrove bark liquors			Sections 3 and 8 Wattle bark liquors	
	Tannin g. per liter	Barkometer degrees	Lime water cc.	Barkometer degrees	Lime water cc.
2	17.86	8.7	3.8	9.3	2.8
5	26.8	13.3	5.6	13.9	4.2
6	39.86	18.7	8.2	17.6	5.3
8	47.31	23.0	9.0	22.4	5.4
10	63.63	31.3	11.2	32.8	5.8
19	88.75	44.8	12.8	44.8	7.8
28	117.06	60.0	15.3	62.1	9.6

The following are results obtained by weighing each section after it was taken out of the various tan liquors. The pelt weight is taken at 100 and the percentage increase is added to that figure. It will be noted that the increase is higher with the mangrove tannage, but the increase for both tannages is lower than the amount representing combined tannins, and therefore we can assume that as the hide takes up tannin water is expelled.

WEIGHT GAINED DURING TANNING PROCESS.

Sections Tannage	1. W.	5. M.	6. W.	2. M.	3. W.	7. M.	8. W.	4. M.
Pelt weight	100	100	100	100	100	100	100	100
1st Liquor	104.6	101.9	102	102.1	103.4	105.1	104.5	102.8
2nd Liquor	105.5	105.0	105.3	105.1	106.1	108.4	109.2	108.9
3rd Liquor	107.6	106.5	107.6	106.1	109.1	111.3	112.1	112.2
4th Liquor	110.1	109.2	110.5	108.1	110.7	113.3	113.4	114.1
5th Liquor	111.4	111.0	111.3	111.0	112.8	116.7	115.2	116.9
6th Liquor	112.5	113.0	111.7	113.4	113.1	117.2	116.3	117.5
7th Liquor	113.2	114.1	112.3	114.4	113.7	117.7	117.2	118.2
Wash-pit	——	——	——	——	108.4	109.8	108.3	109.9

Sections 1, 2, 5, and 6 were taken from the tan liquors and suspended in water for 2 hours, drained overnight, scoured on the grain, oiled, and then finished as sole-leather. Sections 3, 4, 7, and 8 were washed in water and allowed to dry. These sections did not receive any oil. The dry rolled sections were what tanners call "firm" but not hard. The mangrove leather was a bright clean red color. The dry unrolled mangrove-tanned sections were not inclined to a brittle grain, so that scouring is not a necessary factor in the finishing process.

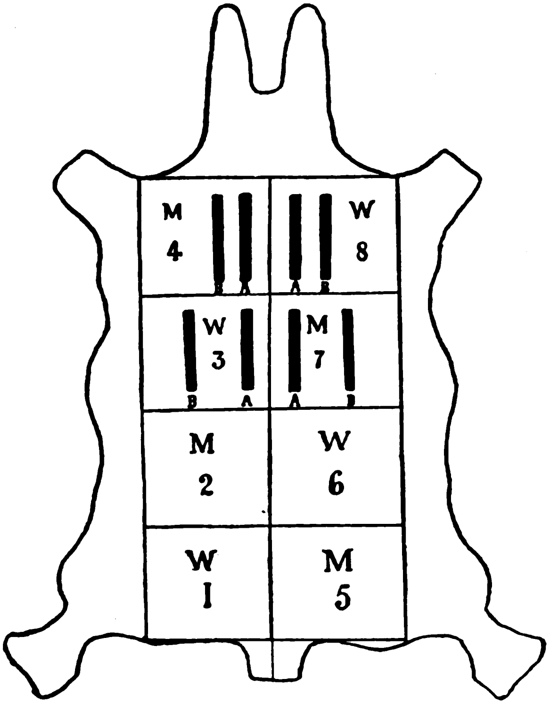

Diagram of Ox-Hide.

The analytical results are worked out on a leather free from fat. The sum of water, total solubles, combined tannin, and hide-substance is 100 per cent. The non-tannins are very low, suggesting that the total solubles include free tannin which was originally combined tannin. Total solubles were extracted from the leather shavings at a temperature of 45° C. The time for extraction was 3 hours. Previous experiments with pine and wattle barks show that the degree of tannage is low for these mangrove and wattle tests. This difference is partially explained by the fact that we used a thicker hide for this experiment. Another matter would be the age of the leather. For the pine bark experiment the leather was not analyzed until 10 months after it was removed from the tan liquors, but for this experiment the same work was all completed within one month. It has been proved (Report of the Committee of the Soc. of Arts on Leather for Bookbinding; *J. S. C. I.*, 1901, 819; 1902, 128) that the catechol tannins, both free and combined, are gradually changing in the air-dried leather. Probably this change adversely affects the solubility of these substances and the natural result would be a lower figure for total solubles. When leather is placed in water at 45° C. it apparently releases a certain amount of combined tannin, so that, omitting bloom and reds, a final and approximately constant figure might be obtained for mangrove tannins. We carried out a second extraction for Sections 4 and 8, and the usual standard process was repeated daily for four days. The results obtained brought the degree of tannage down to 32.7 for mangrove and 31.8 for wattle; after several days the mangrove (in water 18° C.) was still giving up a little coloring matter, and it seems probable that under these conditions we could have reached 30 as a final figure for both tannages.

The stability of the combination of hide-substance and tannin, as shown by the degree of tannage, varies to a considerable extent according to the process of extraction ,etc. We took four pieces out of each section, when sampling for analysis, and the samples from the two sections in each group were in the same water bath during the process of extraction; so that the results show differences between the two sections of any one group under approximately constant conditions. We have to compare results from leather shavings with results from leather ground in a mill (Leather Industries Laboratory Book), and if higher total solubles were obtained from the latter then it would appear as if these tannins produce a very unstable leather. However, we recognize that we must carry out more experiments in connection with this problem of extraction.

From a commercial standpoint the leather weights returns calculated on the pelt and green-salted weights are all in favor of mangrove.

	1st test				2nd test			
Section numbers	1.	5.	6.	2.	3.	7.	8.	4.
Tannage	W.	M.	W.	M.	W.	M.	W.	M.
Water	14.00	14.00	14.00	1.400	14.00	14.00	14.00	14.00
Total solubles	20.05	17.31	20.00	19.52	16.54	15.91	18.6	20.31
Non-tans	3.11	2.55	3.24	2.85	1.93	1.36	2.26	1.89
Tannin	16.94	14.76	16.76	16.67	14.61	14.55	16.34	18.42
Hide-substance	43.84	39.92	42.59	39.09	45.40	38.89	44.71	40.33
Combined tannin	22.11	28.77	23.41	27.39	24.06	31.20	22.69	25.36
Degree of tannage	50.43	72.07	54.97	70.07	53.00	80.23	50.75	62.88
$\frac{\text{Pelt weight} \times 100}{\text{Green weight}}$	116.9	119.9	126.1	122.6	118.7	126.0	129.9	126.8
$\frac{\text{Leather weight} \times 100}{\text{Green weight}}$	76.35	85.56	80.87	85.45	68.8	80.19	63.84	70.25
$\frac{\text{Leather weight} \times 100}{\text{Pelt weight}}$	65.31	71.35	64.15	69.73	57.91	63.60	49.12	55.39
Hide-substance in pelt	28.63	28.48	27.32	27.25	26.29	24.73	21.97	22.33
Fats	1.35	1.31	1.09	1.53	0.40	0.31	0.58	0.47
Ash	0.30	0.33	0.35	0.40	0.29	0.22	0.23	0.20

The water-absorption test was carried out by placing the unrolled sections in water for various periods as shown below. The leather weight, calculated free from water, is taken at 100, and the water absorbed is shown as a percentage on that figure. In both cases the mangrove absorbed less water than the wattle leather. The sum of the fixed tannin and total solubles is greater with the former than with the latter, and therefore there is less room for water in the mangrove leather, providing other conditions are equal for both leathers.

Sections	3. Wattle	7. Mangrove	8. Wattle	4. Mangrove
Air-dried leather	19.0	19.7	18.5	18.9
1 Minute	51.1	54.9	49.0	47.2
1 Minute	63.7	56.4	64.9	62.4
1 Minute	74.3	65.3	77.9	73.3
1 Minute	83.7	72.6	89.9	83.1
1 Minute	90.0	79.6	97.9	90.8
1 Minute	94.0	83.3	103.9	97.8
1 Minute	96.3	86.6	110.0	101.1
5 Minutes	97.1	88.7	114.7	105.1
20 Minutes	98.9	91.0	120.7	108.7
13 Hours	103.1	94.1	129.1	113.9
32 Hours	108.6	99.2	137.7	120.7

If t_1 is the percentage of water absorbed by a leather containing a small amount of water solubles, t_2 that absorbed by a leather with a large amount of solubles, and t_3 that absorbed by a rolled leather with a large amount of total solubles, then

$$t_1 = \frac{w}{r} 100. \quad t_2 = \frac{w - x}{r + y} 100. \quad t_3 = \frac{w - (x + m)}{r + y} 100$$

where w = weight of water absorbed,
r = weight of leather,
x = water displaced by the extra amount of solubles,
y = weight of the extra amount of solubles,
m = the decrease in the volume of air spaces after the leather has been rolled.

Another factor would be an increased amount of insoluble matter such as combined tannin, bloom and adulterants. Let t_4 be the percentage of water absorbed by a leather with a large amount of solubles and an excess of insoluble matter, then

$$t_4 = \frac{w-(x+l)}{r + y + u} 100$$

where l = water displaced by excess of insoluble matter,
u = weight of the excess of insoluble matter.

Leather, like wood, contracts or swells according to the moisture content, and this varies with the different tannages. The rate at which water penetrates the leather is related to the solubility of the substances deposited on the leather fibers. Leather adulterated with an easily soluble substance, like glucose, offers very little resistance to water penetration.

The tensile strength tests were carried out by Mr. H. T. Swain at the Mechanical Engineering Laboratory of the Sydney Technical College. Two pieces were cut from each section as shown on the diagram. Mangrove 4*a* and wattle 8*a* are placed together for comparative purposes, as they differ only in the barks used for the tanning process. The other groups are shown below, the results being all in favor of the wattle tannage.

The moisture in the leathers is slightly higher with the wattle, and it is not possible to get the four sections with constant percentage of water when they are exposed to changeable climatic conditions. However, the difference is below 1 per cent., and this amount will probably be reduced in future experiments.

Tensile Strength Test.

	Tannage Number	1st test		2nd test	
		Wattle 3A.	Mangrove 7A.	Wattle 3B.	Mangrove 7B.
	Moisture	13.79	12.82	13.79	12.82
Original dimensions	Breadth	1.5	1.54	1.5	1.51
	Thickness	0.25	0.239	0.25	0.240
	Area	0.375	0.368	0.375	0.363
Stress in pounds	Total	960	750	1200	920
	Per square inch	2560	2038	3200	2534
	Total elongation, %	35.6	31.9	33.4	33.4
	Time	12 min.	10 min.	—	11 min.

	Tannage Number	3rd test		4th test	
		Wattle 8A.	Mangrove 4A.	Wattle 8B.	Mangrove 4B.
	Moisture	13.2	12.6	13.2	12.6
Original dimensions	Breadth	1.51	1.49	1.53	1.51
	Thickness	0.229	0.239	0.255	0.239
	Area	0.346	0.345	0.390	0.360
Stress in pounds	Total	800	650	810	740
	Per square inch	2312	1884	2077	2055
	Total elongation, %	47.2	38.9	55.6	40.25
	Time	15 min.	10 min.	16 min.	13 min.

The leather received no special treatment for this work, and was absolutely free from oil, fat, etc., other than the natural fats in the original hide. The pieces tested were not cut out of the best part of the hide and therefore the results obtained have no value outside of this experiment.

Analyses show that these leathers differ after they are tanned, and therefore the results obtained may be influenced by this. The tensile strength of each section is at the maximum in the raw hide, where the physical condition is all that could be desired. A fibrous structure would be at its maximum tensile strength under conditions which allowed the weight to be evenly distributed between all the fibers. The other extreme would be under conditions where the whole of the weight was on a few fibers which break, and then the weight is thrown on another small portion which breaks also, and the result must be a low value for that particular test. It would not be possible to place all the weight on a few fibers until they break, if one were testing a strip of raw hide, where the elastic properties and the general structure are so finely balanced that a strain on any group of fibers causes them to stretch, and then the weight is partially taken up by other fibers, and in this way it is distributed over the whole number before any single fiber breaks. When the rawhide or pelt is placed in tannin solutions, the physical condition is changed. It loses to a certain extent its elastic properties. The semi-liquid intercellular substances combine with tannin to form a non-elastic solid. The fibers contract and under certain conditions they may reach a brittle state.

Procter states that the tensile strength decreases with increased amounts of fixed tannin, and the same could be said of those water-solubles which dry like tannin extracts to a hard brittle state. However, the variations in fixed tannin, etc., and their influence on these results is a problem which will require special research. If all other conditions were equal we would still expect a difference in tensile strength because the various tannins could combine with the hides in equal proportions by weight, and yet the resulting leathers would differ in their physical properties. The leather with the higher tensile strength will probably offer the greater resistance to friction. Balderston (J. Amer. Leather Chem. Assoc., 1916, 11, 429; see *J. S. C. I.*, 1916, 935) has described a machine for testing the wear-resistance of sole-leather, and his results show that the loss by friction is at the minimum with a straight chrome and the maximum with a hemlock tannage. Now this is just the position one would expect them to occupy in a series of tests for tensile strength. Hard leather offers a low resistance to friction, the tensile strength is not high, but the water resistance is generally good.

We do not claim to be working the best processes for preparing the pelt or tanning the leather, but we feel certain that this "one hide experimental process" is capable of giving results which should enable tanners to prove the value of a great number of factors such as various tanning materials, laying away in bark, acidity of liquors, strong liquors, time for tanning, etc.

DISCUSSION.

The Chairman asked what species of mangrove had been used in the experiments.

Mr. A. H. Dettman said that leather tanned with mangrove answered well for the soles of boots, as it took up less water, and so resisted damp better than when tanned with wattle. The dark color given by mangrove was commonly supposed to be caused by "loading," and there was a prejudice against color.

Mr. A. E. Stephen asked if there was any difference in the tensile strength of tanned and green hide.

Mr. R. W. Challinor drew attention to the great variation in total solubles from the proportion in the original liquor. He asked what had been done in testing the tensile strength after soaking at 45° C.

Mr. Coombs, in reply, said that *Rhizophora* predominated in the Queensland mangroves, but it was impracticable to keep the different kinds separate, and their experiments were made with the ordinary commercial mixed bark. The sections had been taken from the hide, and the tests made in such a way, alternately, to guard against any possible variation in the right and left halves of the hide, though he did not think there was any difference. Tensile strength was at its maximum when the hide was newly off the animal, but the hide must be tanned so as to preserve it from decay, even at the cost of loss of strength. He had made no experiments on soaking at 45° C.

CHEMISTRY AND ITS RELATION TO TANNING.*

By George J. Laemmle.

(Somewhat abridged.)

In working out a manufacturing cost recently, covering the production of a staple side leather for shoe repairs, the various steps were itemized and departmentalized, revealing the following summations:

Number of chemicals used	50
Chemical operations	31
Hand operations	183
Mechanical operations	31

This summation did not take into consideration the handling of the splits which would add interesting totals when one considers that a single lot of hides could have grains worked into one run of grain leather and yield gusset, wax, flexible, "dope" and gun-metal splits. Few tanneries confine themselves to one kind of grain leather and the proportion is, therefore, greater, since the hand and mechanical operations will remain the same,

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* *Leather Manufacturer,* April, 1917, pp. 113-6.

limited as they are by the total output of the tannery, whereas the number of chemicals and the chemical operations multiply in proportion to the number of kinds of leather produced.

Most tanners have profited during the last 18 months and many chemists have not. Some of them had to go into gunpowder plants. Shoe manufacturers were so anxious for leather that stock complaints were forgotten. "Pipey," "Grainy," "Soft," "Hard," "Flanky," "Tender" were temporarily shelved and it had to be pretty bad leather if it didn't get by. Fading? why it was out of the tannery and cut into shoes before it had a chance to fade. Many a warehouse has coughed up "leather" this past year that required a world war to fetch it out. This doesn't mean that certain tanneries who have produced high-grade leathers for years passed have changed their quality, but it is true that good tanners, and chemists, too, require normal times to demonstrate their value. If this boom should continue after the war, leather chemistry will receive a setback. The war with its easy selling conditions has kept many a hostile superintendent in his job.

A survey of the leather field to-day shows several well-developed lines. First, that there is little room in the tannery for a mere chemist. A chemist with engineering training or chemical engineer is required. Few tanneries will support more than one technical man on the staff and very few have even one. Tanneries are continually constructing, new machines are appearing on the market, drying and blower systems are being installed and the wear and tear on tannery equipment is well known. Tanneries are large users of liquids and have extensive electrical equipment, motors, generators, etc. Experts of all kinds call on the tanner and outline plans for increasing efficiency and too many of these are manifestly for their own profit. It is well to have a man on the home staff who has the training to judge which of these projects are fundamentally sound and which are not.

Secondly, there are few tanneries which have flexible organizations, where provision is made for the absence of a foreman here and there, and where a chemist is employed and utilized by the firm, it is a distinct asset if he is ready at all times to take the place of any foreman who is absent. It increases the familiarity of the chemist with the details of the process, also keeping his imagination confined to material lines. What is more important, in the event of trouble it helps in the location of it. Perhaps this last is the most important of all. It could well be said that along with this familiarity with the details of the processes the chemist should be successful in his own work and without it he cannot possibly succeed in his work. Just walking through the tannery will not give this result. This familiarity must be bred by some definite method. Training the chemist to relieve any foreman so that in the event of a sudden emergency he stands ready to take over the work of that department, and carry it on fully as well as the foreman, taking full responsibility for the leather during that period, means a flexible organization and is about the only way to give the chemist that familiarity with the process which is so necessary in his work. With such a course in mind a chemist with engineering training is much better suited for the tannery. Many such chemists have found success in tanneries not so much by their chemical knowledge as by draughting, electrical or mechanical work or in planning. It is certain that the power and maintenance and planning of tanneries are more backward at the present time than the chemical end; however, little can be said for the latter.

There are few successful leather laboratories attached directly to tannery organizations to-day. The sole-leather or bark-tanning section have the most of these, for the difference between tasting and testing is too apparent. The process is simple and even the old-time tanners admit the value of sending samples from time to time to a trades chemist for analysis. Therefore, it becomes simply a question of mathematics. How much is being paid to the leather trades chemist and how much would it cost to have our own man who would turn out the same work and more of it. The leather trades laboratories are well established and have found their place in acting as arbiter between the buyer and seller of tanning extracts.

The principal trouble with the chemist has been in the upper leather end and, in fact, all leathers except bark sole-leather and harness leather can be included in this classification. Here the chemical operations, both in number and kind are far more complex than in straight bark work and one would expect to find the greatest results in this field, for it includes many of the bark tanner's problems. Nearly all chrome tanners use extracts for bottoming or retanning and have all the sole-leather tanner's beamhouse and oil problems, but in more complicated form. But it is nevertheless true that it is here that the battle between the tannery staff and the chemist is brisk. The following are some of the reasons why in general it may be termed a battle rather than a sphere of co-operation.

First, there was a tendency to build a laboratory and then tell the chemist he was to stay there and have his work brought to him. Offhand this is straight enough. Under proper conditions it means efficiency. When you are sick you go to the doctor and when you are well you stay away. But there are cases where the doctor has to go to the patient. What is most important, there are cases that could go to the doctor and don't. Symptoms are important to the physician, and we are truthful about it, for our own lives may be at stake, but the physician cannot entirely rely upon our own statements as to the symptoms. He goes over the ground himself and finds things which only a trained observer will notice. Keeping the chemist tied to the laboratory was a poor policy because the problems were not brought to him properly. He could, therefore, do nothing unless he went over the ground himself. This was not allowed, for the superintendent and foremen objected on the ground that the chemist would know their processes and might then leave to capitalize his knowledge elsewhere. This argument proved to be enough in many cases. In looking over the payrolls of any tannery it seems ridiculous enough, for many foremen in tanneries are drifters. Most of the processes prevailing to-day were developed by the superintendents and they have always looked upon these as their own property. Therefore, when the owners engage a chemist they may be doing so on a purely business basis for more efficiency, but it is looked upon by the organization as a move to control the salaries.

So we find leather chemists going into the tannery as workmen and foremen and keeping quiet about their training until they are established. These men have made the most progress, and in time they will accomplish the revolution. To employ a chemist in the laboratory successfully it is necessary to have a chemist in the plant in some executive capacity—superintendent or assistant superintendent. Then the problems are observed properly and are brought intelligently to the laboratory. Taking the sample is the principal part of any analytical process. Knowing the scope of chemistry is another important point. Nowadays we find tannery owners, foremen and superintendents bringing propositions to the laboratory that scientists the world over are grappling with unsuccessfully, and because the chemist is unable to solve it in the time that it takes to get a haircut they throw up their hands and say they are cured, whereas there are hundreds of things that they are passing by which could be solved.

Pratt Institute has specialized in training leather chemists and places more of them in the field than any other institution. The course is showing results partly because the large proportion of students are sons of tanners or owners. They go into the tannery with freedom and do not meet with the difficulties mentioned above. The speed of their progress as against that of a chemist without influence is bona fide evidence that here we have a form of solution. By the work of these men, unhampered because of their relationship, leather chemistry is making progress and eventually the change will be accomplished, namely, every tanning superintendent of the future will be a man of chemical training.

There are in this country some upper leather tanners who set the pace for the entire field. Everyone in the trade knows who they are. Look over their organizations and you will find that the superintendents who have been responsible for the uniformity of production, low manufacturing cost, and high quality leathers are men of chemical training. True, their training dates back ten or twenty years, or even longer and they have since acquired more practical experience than any other practical men in the trade. They have established a precedent, however. You may agree with this summary or not, but these are the leathers you compete with to-day. This is a good indication of the future for the leather chemist, for, after all, the shoe manufacturer is impartial as to the method; he asks for price and quality and principally uniformity, and he takes it where he finds it.

There is more in the problem than just the chemist. It really means the policy of tanning, and the chemist is just a typical point. Starting out with that, it is only another step to organizing the purchasing and mechanical departments, plan of building, etc., all of which are generally situated as chemistry is in the tanner's opinion.

Summing up, we have a large number of tanners who never had a chemist and, at present, do not think they will ever want one. The good business produced by the war has convinced these men that they are right. In some instances chemists have tried to work and have been hindered by the tannery organization, and sometimes the chemist was installed not for the purpose of assisting the tanner but to break his grip.

We have the leather trades laboratories which have reached the position of arbiters between buyer and seller, principally in tanning extracts. We have that group of young leather chemists, who, seeing the situation in the laboratory, have gone into the tannery on the same plane as the common workman, applying their knowledge and biding their time, awaiting the outcome in which they have faith. We have that other group of leather chemists who entered tanneries in which they had privileges by reason of being related to the owner. We also have that small but powerful group of tanners whose processes have for years been in the hands of technical men and whose progress has set the mark for the entire industry; in fact, they have had such a long start that it is doubtful if they will ever be caught.

Tanning is one of the departments of chemistry just as the making of paints, soaps, steel, chemicals, or any other branch of industry in which chemistry is applied. You may have heard of a chemist in a tannery who was a laughable failure and you may be sure that this chemist was given every fair opportunity and co-operation, but there is nothing wrong with chemistry even though there may have been something radically wrong with the man who professed to be a chemist. The college diploma does not make all men equal in any other profession and the same thing applies in chemistry. There are grades of chemists, good and poor, as in bookkeepers, foremen and even superintendents. It is questionable whether there have been as many failures among chemists as there have been among foremen and superintendents, and whether chemists have ruined the amount of leather that some men in the trade, highly thought of to-day, have spoiled.

The Standard Oil Company is a successful corporation, we admit, but from another standpoint than the one usually considered. Their by-products have been ever increasing by reason of chemical research and an insight into their policy is gleaned from a statement made by one of their chief executives three years ago, that in employing young men to enter any of their plants, they required two things, character and technical training. German efficiency as shown in this war has impressed the entire world, and the old hit-and-miss way won't do for the future. Assuming this viewpoint for the purpose of discussion, we will consider under the following headings the various ways in which a chemist may prove of value in a tannery.

Employment.—The first suggestion is to employ two chemists, one to work through the plant and the other to work in the laboratory and to have all the problems go to the laboratory through the plant chemist. It is unnecessary to have a plant chemist, of course, if there is at present among the foremen or the superintendents a man who is technically trained and who understands the shaping of the problems and the manner of sampling, which is essential. If the plant will not carry two chemists, though one of them is productive under this plan, it would be more profitable to employ one for the plant as a foreman or assistant superintendent, than to have a laboratory.

Purchasing of Materials.—Every item purchased by the tannery under the heading of chemicals, oils, dyestuffs, etc., should be tested in the laboratory. This is a line of work where no conflict occurs with the staff and throws light on the purchasing. It widens the field of purchase and gives the buyer more confidence in considering new materials and new firms to deal with. Also it stops a lot of buying that might cause trouble. A salesman in the past would approach the buyer who, in many instances, was also the superintendent, and seek an order for logwood crystals, a new brand. He would be told that the tannery always used Blank's logwood and as long as it gave good results and the leather was coming right no changes would be made. Price was not the important consideration. Not knowing the nature of logwood, its origin, etc., the superintendent feared to change. There was no telling what danger might lurk in changing, and he would rather stand pat if the leather was "coming good."

Many superintendents bought on personal friendship, believing that Smith would not sell them anything that might "get them in wrong." Before the war, leather chemists in some cases found the analysis of tannery materials almost useless for these reasons. Then along came the war and the tannery superintendent who would not use any other oil but So-and-So's, or only this chrome or that logwood, had to take what he could get or shut up shop, and they haven't shut up many leather shops the past year or two. This proved that the chemist was right, but then another argument came, "What's the use of testing anything, when you've got to be glad to get it at all?"

So there we stand to-day. When the war ends the chemical market will open up first of all. Already some of the false "corners" are crumbling. Many of the rises and "shortages" were only sympathetic. Later the margins in leather making will be closer than they are now and manufacturing cost will be more of a factor. Then, when there is a chance to economize by using one chemical instead of another, the superintendent cannot say that he could not make a change. It seems that the testing of materials should have been even more urgent on this high market, but it was neglected to a great extent. It would seem to be valuable information to have when the market is normal again to know which firms looked after the customer's interest and which did not. It is a safe prediction that the further we advance in the future, the more will we find all sorts of materials being offered on chemical analysis.

To-day tanning extracts are offered entirely on analysis. Coal is bought by large users (electric light companies and others) on its B. t. u. output. Milk is sold and regulated on butter fat content. This latter regulation controlled not only the sale of milk, but immediately reached back into the industry and even changed the breeding methods. Sulphuric acid is almost universally sold on percentage basis. Such chemicals as are broadly used in all industries are already on this basis, and we will find as we go along that all of the tannery materials will gradually fall into this classification. Removing the personal element out of the purchasing also removes a lot of doubt and saves a lot of selling expense. On this line of work alone, every tannery could afford its own laboratory. When this is done we will find less of the stock "cure-alls" being offered to tanners.

In testing materials it follows that the chemist informs himself of the method of manufacture and the nature of impurities that might be expected from the process of making, even where no adulteration is practiced. With this in mind, plus a familiarity with all the details of the process of leather making, there is created a reserve fund of knowledge that is useful in the event of trouble in the tannery.

Raw Stock Problems.—The hide cellar is generally passed over as a field for the chemist, but there is plenty to do there. So much raw stock is imported nowadays that "Sea Damage" in its manifold forms is now a factor. The curing of hides is a process of dehydration either drying or brining, and chemical observation here has value. We are reading to-day of the wonderful progress made in the vacuum drying of fruits and vegetables and it would not be surprising to see something of this sort develop in the hide industry. The prevention of salt stain has been worked out quite well and recently attention has been called to the practice of adulterating in raw stock or, in other words, adding false weights by means of alum loading and other means. The hoof-and-mouth disease epidemic of only recent date is still fresh in the tanner's mind, and this brought with it chemical problems, because of the high cost of bichloride of mercury solutions and salt solutions. Every once in a while an anthrax scare brings in similar work.

INSPECTION TRIP OF TANNERY STUDENTS FROM PRATT INSTITUTE, 1917.*

On Sunday evening, April 1, the students from the course in Tanning and Applied Leather Chemistry left New York City over the New York Central on the annual tour of inspection. The first plant visited was that of G. F. Zeller & Co., Buffalo, where the party arrived early Monday morning. Mr. Henry Zeller received the boys in a very cordial manner and after meeting Mr. Edward Zeller and Mr. William Z. Beier, a former graduate of the tanning course, the party proceeded through the factory. During the inspection the boys were shown the various processes employed in making harness and sole-leather. While at the Zeller plant, Mr. A. W. Hoppenstedt came over from the Hoppenstedt Laboratories and invited the party to go through his place. The invitation was gladly accepted and through the courtesy of the G. F. Zeller Co. automobiles were provided to take the boys across the city. After visiting the A. W. Hoppenstedt Laboratories the afternoon was left free. Most of the students took advantage of the opportunity to visit Niagara Falls.

At 7.45 Monday evening the party left for Olean over the Pennsylvania, where they arrived at 9.58. Arrangements for the night had previously been made with the Olean House. Tuesday morning was spent in the side-leather tannery of the Northwestern Leather Company at Portville, where Mr. Bert Cox and Mr. Murdock kindly explained the different processes in a very interesting manner.

On returning to the hotel the boys were escorted to a private dining-room, where through the courtesy of the Olean Tanners an elaborate dinner had been provided. After the dinner Dr. Rogers extended the thanks of the instructors and students for the kindness and courtesy shown to them. The arrangements for the dinner were in the hands of Mr. Bert Cox, Superintendent of the Northwestern Leather Company, a graduate of the tanning course in the Class of 1915. Twelve representatives of local tanneries attended the dinner and Mr. Ray of the Union Tanning Company extended his best wishes for the success of the tanning school.

On Tuesday afternoon the party visited the sole-leather plant

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* *Tanners' Institute News*, Bulletin No. 33.

of the Cattaraugus Tanning Company, where they were escorted through the factory by Mr. Macaulay, Mr. Gayla, Mr. Sprague and Mr. Newman, the last-mentioned being a graduate of the Applied Chemistry and Applied Leather Chemistry courses in the Class of 1914. Besides the many interesting points shown at this plant the boys had an opportunity to observe the construction work there under way, as new pits were being installed in the beam-house and other repairs were being made.

Tuesday evening found the party again on the train bound for Mercersburg, where they arrived at 10.30 Wednesday morning. Here the russet and in-sole leather plant of W. D. Byron & Sons was visited. At the tannery the party was met by Mr. Henry Byron and Major William Byron. They were then shown through the plant by Mr. William Byron, Jr., a graduate of the Tanning course in the Class of 1916, Mr. Hundhausen, the superintendent, Mr. H. C. Hundhausen, a graduate of the tanning course in the Class of 1915, and Mr. Fred Byron. In going through the factory the boys were shown many novel mechanical appliances which had been devised by Mr. Henry Byron and which furnished considerable food for thought. The new leach-house which has just been completed was also a fine illustration of construction work.

On finishing the tour of inspection the party proceeded to the Mansion House where a bountiful spread had been provided through the courtesy of the W. D. Byron & Sons Co. Words of welcome and good advice were given to the boys by both Major William Byron and Mr. Henry Byron. As the party left the Mansion House they were escorted to seven automobiles in waiting and taken on a 40-mile drive to the battlefield of Gettysburg. There a guide was secured who gave a complete description of this historical event, going from place to place until the 25 square miles had been covered. Leaving Gettysburg the automobile party made a hasty return trip to Chambersburg where another sumptuous dinner awaited them. The day was so enjoyable and the hospitality so great that it will long remain as one of the bright spots in the memory of all.

From Chambersburg the party proceeded to Philadelphia, where they arrived at 11.40. Here automobiles were waiting to take them to the Continental Hotel, which served as headquarters during the stay in the Quaker City. Thursday morning found the boys at the Drueding Brothers Tannery where they were received and shown through the plant by Mr. Caspar Drueding. Here the manufacture of hat leather and chamois was seen. In order to answer any question that might be asked, Mr. Drueding had prepared a printed form giving in detail every step in the manufacturing process from the raw stock to the finished product. This foresight on the part of Mr. Drueding saved much time and confusion, for as the party entered any department all that was necessary was to refer to the printed circular and find the story in a nutshell. After visiting the plant a luncheon was provided through the courtesy of Mr. Drueding. During the luncheon Mr. Drueding offered a prize of a $10 gold piece to the student who would send in the best report of his visit. In the report the processes are to be considered first, the arrangement of the plant second and the literary ability last.

In the afternoon of this day a visit was made to D. Strauss & Sons Co., wool-pullers. Here they were met by Mr. Sydney Davis, a former instructor at Pratt Institute, who in a very interesting way showed the party through the plant. The remainder of Thursday afternoon was taken up by visiting various points of interest in good old historic Philadelphia.

Friday morning through the courtesy of Mr. Chute the plant of Duncan Hood & Co. was visited, where Mr. Fred Rollins, a former student of the tanning course, explained the various processes employed in the manufacture of glazed kid leather. This plant is one of the largest in the country and the process employed is thoroughly up-to-date. On Friday afternoon the party returned to Brooklyn, all voting that the week had been spent in a most enjoyable and instructive manner.

REPORT OF 1916–1917 COMMITTEE ON COMPARATIVE ANALYSIS OF TANNING MATERIALS.

Roy H. Wisdom, Chairman.

The instructions to the Chairman for this year's work were simply to check up the various laboratories. The Chairman therefore sent out samples with the idea of covering every detail of the method. It is rather significant that in every case but one, 21 out of 23 analysts used the slow cooling method.

The question has been raised in the past as to allowable differences in analysis on various materials. A study of the figures showing the average deviation will give a good idea as to what may be expected. On extracts the following results were obtained on the tannin figure:

	Average deviation
Chestnut	0.25
Oak bark blend	0.36
Hemlock	0.80
Myrobalan	0.23
Sulphite-cellulose	0.65
Quebracho crystals, unclarified	0.60

The variation shown on the hemlock is hardly fair, as the extract was treated to produce a maximum of insolubles. The variation on the sulphite-cellulose extract was due principally to the differences on the non-tannin figure.

On raw and spent materials the variation was as follows:

	Average variation	
Chestnut wood	0.28	"water as found" basis
Sumac	0.62	"water as found" basis
Spent tan	0.17	"water as found" basis

On the tannery liquor the average variation was 0.13. The average variation on the acid was 0.06. In this connection the Elk Tanning Co. Laboratory submits the following table showing the variation in tannin due to different amounts of hide powder.

TANNERY LIQUOR—108 Grams per Liter.

			Grams hide powder used	
			Wet	Dry
Total solids		6.65		
Soluble solids		6.37		
Insolubles		0.28		
Non-tannins—	1	3.80	40	10.6
	2	3.90	30	7.95
	3	3.93	27	7.15
	4	4.07	20	5.3
Tannin—	1	2.57		
	2	2.47		
	3	2.44		
	4	2.30		

It is a source of considerable satisfaction that on the extracts with the exception of the hemlock—a freak extract in every way—the tannin limits per 100 cc. were closely adhered to in the majority of cases.

On the chestnut wood but six analysts came within the limits. Notwithstanding the wide difference in amounts extracted but two analysts' results were omitted from the average.

On the spent tan the amounts taken varied from 10 to 100 g. per 1,000 cc. with but one analyst's results omitted from the average.

The Chairman wishes to express his thanks to all those who so kindly collaborated.

The results follow:

CHESTNUT EXTRACT.

No.	Date of Analysis	Laboratory	Analyst	Total Solids	Soluble Solids	Insolubles	Non-Tannin	Tannin	Tannin per 100 cc. solution	Grams per 1000	Method of cooling	Deviation from average				
												T. S.	S. S.	Ins.	N. T.	T.
1	11- 8-16	Ashland Leather Co.	R. E. Porter...	41.35	39.95	1.40	14.10	25.85	0.415	16.11	Rapid	0.05	0.17	0.12	0.24	0.10
2	11- 9-16	Cattaraugus Tanning Co.	C. M. Hulings..	41.45	39.54	1.91	13.77	25.77	0.412	16.	Slow	0.15	0.24	0.39	0.09	0.18
3	11-13-16	Champion Fibre Co......	J. C. Dickson..	41.23	39.79	1.44	13.85	25.94	0.418	16.1	Slow	0.07	0.01	0.08	0.01	0.01
4	11-24-16	Du Bois Laboratory Co...	R. J. Bailey	41.13	39.64	1.49	13.95	25.69	0.4118	16.03	Slow	0.17	0.14	0.03	0.09	0.26
5	12- 8-16	Elk Tanning Co.......	E. R. Lobaugh.. J. Earle McNutt	41.27	39.63	1.64	14.12	25.51	0.3825	15.	Slow	0.03	0.15	0.12	0.26	0.44
6	11-10-16	England, Walton & Co	C. R. Oberfell.. C. W. Reilly...	41.00	39.55	1.45	13.89	25.66	0.4108	16.01	Slow	0.30	0.23	0.07	0.03	0.29
7	11- 7-16	Graton & Knight Mfg. Co.	V. J. Mlejnek ..	41.19	39.69	1.50	13.97	25.72	0.4147	16.12	Slow	0.11	0.09	0.02	0.11	0.23
8	11-10-16	Hoppenstedt, A. W. Lab..	N. F. Chapin...	41.05	39.62	1.43	13.42	26.20	0.3957	15.1	Slow	0.25	0.16	0.09	0.44	0.25
9	11-16-16	Kistler, Lesh & Co.	J. M. Seltzer ...	41.17	39.56	1.61	13.78	25.78	0.415	16.09	Slow	0.13	0.22	0.09	0.08	0.17
10	11-17-16	Kistler, Lesh & Co.. ...	F. F. Marshall .	41.24	39.66	1.58	13.77	25.89	0.415	16.07	Slow	0.06	0.12	0.06	0.09	0.06
11	11- 7-16	Leather & Paper Lab'y	J. S. Rogers.... R. W. Frey	40.94	39.73	1.21	14.26	25.47	0.4127	16.21	Slow	0.36	0.05	0.31	0.40	0.48
12	11- 7-16	Mosser, J. K. Co.........	T. J. Mosser....	41.09	39.63	1.46	13.57	26.06	0.3916	15.03	Slow	0.21	0.15	0.06	0.29	0.11
13	11-14-16	Mosser, William F. Co. ..	Oskar Riethof..	41.28	39.76	1.52	13.57	26.19	0.418	16.	Rapid	0.02	0.02	0.00	0.29	0.24
14	11- 5-16	Nichols Laboratory......	M. F. Nichols..	41.51	39.90	1.61	14.36	25.54	0.409	16.	Slow	0.21	0.12	0.09	0.50	0.41
15	11-21-16	Pfister & Vogel Lea. Co..	A. C. Orthmann	41.88	39.81	2.07	[1]15.20	[1]24.61	0.3966	16.12	Slow	0.58	0.03	0.55	[1]1.34	[1]1.34
16	11-25-16	Smoot, C. C. & Sons Co.	C. C. Smoot, III L. E. Stacy	41.17	39.71	1.46	13.43	26.28	0.4068	15.48	Slow	0.13	0.07	0.06	0.43	0.33
17	11- 4-16	Stamford Mfg. Co......	R. H. Wisdom .	41.16	39.70	1.46	13.95	25.75	0.412	16.	Slow	0.14	0.08	0.06	0.09	0.20
18	11-14-16	Yocum, Jno. H..........	J. H. Yocum ...	41.07	39.76	1.31	13.35	26.41	0.390	14.75	Slow	0.23	0.02	0.21	0.51	0.46
19	11- 7-16	Yocum, Jno. H..........	C. M. Kernahan	41.24	39.97	1.27	13.50	26.47	0.391	14.77	Slow	0.06	0.19	0.25	0.36	0.52
20	11-15-16	Yocum, Faust, Ltd.	T. A. Faust	41.31	39.85	1.46	13.94	25.91	0.415	16.04	Slow	0.01	0.07	0.06	0.08	0.04
21	2- 8-17	Young, J. S. Co.	J. Alexander...	41.60	40.08	1.52	13.82	26.26	0.420	16.	......	0.30	0.30	0.00	0.04	0.31
22	1- 3-17	Young, J. S. Co.	B. A. Gish	41.98	40.44	1.54	14.12	26.32	0.395	15.	Slow	0.68	0.66	0.02	0.26	0.37
23		Young, J. S. Co.	H. Shaffer	41.60	40.03	1.57	13.88	26.15	0.392	15.	Slow	0.30	0.25	0.05	0.02	0.20
		Average		41.30	39.78	1.52	13.86	25.95				0.20	0.15	0.12	0.20	0.25
		Highest		41.98	40.44	2.07	14.36	26.47								
		Lowest		40.94	39.54	1.21	13.35	25.47								
		Greatest Difference......		1.04	0.90	0.86	1.01	1.00								

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[1] Over 1 per cent. deviation omitted from average.

OAK BARK BLEND EXTRACT.

No.	Date of Analysis	Laboratory	Analyst	Total Solids	Soluble Solids	Insol-ubles	Non-tannin	Tannin	Tannin per 100 cc. solution	Grams per 1000	Method of cooling	Deviation from average				
												T.S.	S.S.	Ins.	N.T.	T.
1	12- 8-16	Ashland Leather Co.	R. E. Porter...	40.75	37.50	3.25	13.45	24.05	.386	16.06	Rapid	.37	.18	.55	.23	.14
2	11- 9-16	Cattaraugus Tanning Co.	C. M. Hulings.	40.24	37.05	3.19	13.75	23.30	.387	16.6	Slow	.14	.63	.49	.07	.61
3	11-13-16	Champion Fibre Co.	J. C. Dickson..	40.41	37.13	3.28	14.57	[1]22.56	.39	17.25	''	.03	.55	.58	.89	[1]1.35
4	11-24-16	DuBois Laboratory Co...	R. J. Bailey....	40.15	37.39	2.76	12.98	24.41	.3931	16.1	''	.23	.29	.06	.70	.50
5	12- 8-16	Elk Tanning Co.	E. R. Lobaugh. J. Earl McNutt	40.15	37.69	2.46	13.41	24.28	.4011	16.5	''	.23	.01	.24	.27	.37
6	11-10-16	England, Walton & Co.	C. R. Oberfell. C. W. Reilly...	40.11	36.87	3.24	13.96	22.91	.3895	17.	''	.27	.81	.54	.28	1.00
7	11- 7-16	Graton & Knight Mfg. Co.	V. J. Mlejnek..	40.15	37.16	2.99	[1]15.20	[1]21.96	.3656	16.65	''	.23	.52	.29	[1]1.52	[1]1.95
8	11-15-16	Hoppenstedt, A. W. Lab'y	N. F. Chapin..	40.24	37.52	2.72	13.08	24.44	.3684	15.07	''	.14	.16	.02	.60	.53
9	11-16-16	Kistler, Lesh & Co.	J. M. Seltzer...	40.22	37.03	3.19	13.41	23.62	.382	16.1	''	.16	.65	.49	.27	.29
10	11-17-16	Kistler, Lesh & Co.	F. F. Marshall.	40.25	37.06	3.19	13.18	23.88	.385	16.13	''	.13	.62	.49	.50	.03
11	11- 7-16	Leather & Paper Lab'y	J. S. Rogers... R. W. Frey....	40.03	36.77	3.26	[1]12.55	24.22	.4077	16.83	''	.35	.91	.56	[1]1.13	.31
12	11- 7-16	Mosser, J. K. Co.	Thos. J. Mosser	40.12	38.15	1.97	14.06	24.09	.3613	15.	''	.26	.47	.73	.38	.18
13	11-14-16	Mosser, William F. Co. .	Oskar Riethof.	40.40	37.51	2.89	[1]12.36	[1]25.15	.4	16.	Rapid	.02	.17	.19	[1]1.32	[1]1.24
14	11- 5-16	Nichols Laboratory	M. F. Nichols.	40.61	38.06	2.55	14.04	24.02	.385	16.	Slow	.23	.38	.15	.36	.11
15	11-21-16	Pfister & Vogel Lea. Co.	A. C. Orthmann	40.86	36.76	[1]4.10	[1]15.51	[1]21.25	.3659	17.22	''	.48	.92	[1]1.40	[1]1.83	[1]1.66
16	11- 4-16	Smoot, C. C. & Sons Co.	C. C. Smoot, III L. E. Stacy....	40.33	38.32	2.01	13.62	24.70	.3741	14.67	''	.05	.64	.69	.06	.79
17	11- 4-16	Stamford Mfg. Co.......	Roy H. Wisdom	40.13	37.81	2.32	13.86	23.95	.383	16.	''	.25	.13	.38	.18	.04
18	11-14-16	Yocum, Jno. H.	Jno. H. Yocum	40.27	37.49	2.78	13.68	23.81	.384	16.14	''	.11	.19	.08	.00	.10
19	11- 7-16	Yocum, Jno. H.	C. M. Kernahan	40.30	37.46	2.84	13.63	23.83	.384	16.12	''	.08	.22	.14	.05	.08
20	11-15-16	Yocum, Faust, Ltd......	Thos. A. Faust.	40.26	37.64	2.62	14.08	23.56	.374	15.89	''	.12	.04	.08	.40	.35
21	1-29-17	Young, J. S. Co.........	J. Alexander...	40.70	37.70	3.00	13.65	24.05	.385	16.	''	.32	.02	.30	.03	.14
22	1-3&15-17	Young, J. S. Co.	B. A. Gish.....	41.10	37.83	3.27	13.83	24.00	.36	15.	''	.72	.15	.57	.15	.09
23	—	Young, J. S. Co.	H. Shaffer.....	40.95	38.13	2.82	[1]15.03	23.10	.346	15.	''	.57	.45	.12	[1]1.35	.81
		Average		40.38	37.68	2.70	13.68	23.91				.24	.40	.35	.30	.36
		Highest		41.10	38.32	3.28	14.57	24.70								
		Lowest		40.03	36.76	1.97	12.98	22.91								
		Greatest Difference		1.07	1.56	1.31	1.59	1.79								

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[1] Over 1% deviation omitted from average.

HEMLOCK EXTRACT.

No.	Date of Analysis	Laboratory	Analyst	Total solids	Soluble solids	Insolubles	Non-Tannin	Tannin	Tannin per 100 cc. solution	Grams per 1000	Method of cooling	Deviation from average T. S.	S. S.	Ins.	N. T.	T.
1	2-21-17	Ashland Leather Co....	R. E. Porter ...	45.50	33.80	11.70	14.50	19.30	0·3095	16.03	Rapid	0·05	0·09	0·11	0·25	0·56
2	11- 9-16	Cattaraugus Tan'g Co...	C. M. Hulings..	44.67	33.38	11.29	15.70	17.68	0·283	16.	Slow	0·78	0·33	0·52	0·95	1·06
3	11-13-16	Champion Fibre Co.....	J. C. Dickson...	45.54	33.64	11.90	14.57	19.07	0·408	21.28	Slow	0·09	0·07	0·09	0·18	0·33
4	11-24-16	Du Bois Laborat'y Co...	R. J. Bailey	[1]44.33	34.72	[2]09.61	14.56	20.15	0·331	16.43	Slow	[1]1·12	1·01	[2]2·20	0·19	1·41
5		Elk Tanning Co......	E. R. Lobaugh. J. Earle McNutt													
6	11-10-16	England, Walton & Co.	C. R. Oberfell.. C. W. Reilly...	44.80	32.06	12.74	14.83	17.23	0·3515	21.36	Slow	0·65	1·65	0·93	0·08	1·51
7	11- 7-16	Graton & Knight M. Co...	V. J. Mlejnek ..	45.46	33.19	12.27	15.04	18.15	0·3796	18.67	Slow	0·01	0·52	0·46	0·29	0·59
8	11-16-16	Hop'enstedt, A. W. Lab.	N. F. Chapin...	45.56	35.07	10.49	14.78	20.29	0·3046	15.01	Slow	0·11	1·36	1·32	0·03	1·55
9	11-22-16	Kistler, Lesh & Co......	J. M. Seltzer ...	45.68	32.44	13.24	14.78	17.66	0·393	22.24	Slow	0·23	1·27	1·43	0·03	1·08
10	11-17-16	Kistler, Lesh & Co......	F. F. Marshall .	45.46	32.63	12.83	14.78	17.85	0·401	22.3	Slow	0·01	1·08	1·02	0·03	0·89
11	11- 7-16	Leather & Paper Lab'y	J. S. Rogers.... R. W. Frey	45.24	35.23	[2]10.01	14.55	[2]20.68	0·3316	16.04	Slow	0·21	1·52	[2]1·80	0·20	[2]1·94
12	12-16-16	Mosser, J. K. Co.	T. J. Mosser....													
13	12- 4-16	Mosser, Wm. F. Co.	Oskar Riethof..	45.59	32.34	13.25	13.74	18.60	0·4	21.	Rapid	0·14	1·37	1·44	1·01	0·14
14	11- 5-16	Nichols Laboratory.....	M. F. Nichols ..	45.21	34.76	10.45	13.98	[2]20.78	0·332	16.	Slow	0·24	1·05	1·36	0·77	[2]2·04
15	12-19-16	Pfister & Vogel, L. Co...	A. C. Orthmann	46.20	34.47	11.73	14.93	19.54	0·3209	16.43	Slow	0·75	0·76	0·08	0·18	0·80
16	11-18-16	Smoot, C. C. & Sons Co.	C. C. Smoot, III L. E. Stacy	44.89	33.46	11.43	[2]07.90	[2]25.56	0·4617	18.05	Slow	0·56	0·25	0·38	[2]6·85	[2]6·82
17	11- 8-16	Stamford Mfg. Co.......	R. H. Wisdom .	45.47	34.46	11.01	15.06	19.40	0·388	20.	Slow	0·02	0·75	0·80	0·31	0·66
18	11-14-16	Yocum, Jno. H.........	J. H. Yocum ...	45.15	33.69	11.46	14.85	18.84	0·409	21.69	Slow	0·30	0·02	0·35	0·10	0·10
19	11- 7-16	Yocum, Jno. H.	C. M. Kernahan	45.55	33.90	11.65	15.32	18.58	0·403	21.7	Slow	0·10	0·19	0·16	0·57	0·16
20	11-15-16	Yocum, Faust, Ltd......	T. A. Faust	45.29	33.98	11.31	16.00	17.98	0·288	16.02	Slow	0·16	0·27	0·50	1·25	0·76
21	2- 9-17	Young, J. S. Co.........	J. Alexander ...	46.12	32.23	[2]13.89	14.08	18.15	0·363	20.	Slow	0·67	1·48	[2]2·08	0·67	0·59
22	1-3&15-17	Young, J. S. Co.........	B. A. Gish	[1]46.81	34.77	12.04	14.69	20.08	0·301	15.	Slow	[1]1·36	1·06	0·23	0·06	1·34
23	....	Young, J. S. Co.........	H. Shaffer	46.20	[2]40.40	[2]05.80	14.19	[2]26.21	0·393	15.	Slow	0·75	[2]6·69	[2]6·01	0·56	[2]7·47
		Average		45.45	33.71	11.81	14.75	18.74				0·31	0·80	0·66	0·39	0·80
		Highest		46.20	35.07	13.25	16.00	20.29								
		Lowest		44.67	32.23	10.45	13.74	17.23								
		Greatest difference		01.53	02.84	02.80	02.26	03.06								

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[1] Over 1 % deviation omitted from average. [2] Over 1¼ % deviation omitted from average.

MYROBALAN EXTRACT.

No.	Date of Analysis	Laboratory	Analyst	Total solids	Soluble solids	Insolubles	Non-tannin	Tannin	Tannin per 100 cc. solution	Grams per 1000	Method of cooling	Deviation from average				
												T. S.	S. S.	Ins.	N. T.	T.
1	12- 8-16	Ashland Leather Co.	R. E. Porter...	42.45	40.60	1.85	16.00	24.60	.399	16.22	Rapid	.29	.02	.27	.05	.02
2	11- 9-16	Cattaraugus Tanning Co.	C. M. Hulings.	42.19	40.83	1.36	15.73	25.10	.402	16.	Slow	.03	.25	.22	.22	.52
3	11-13-16	Champion Fibre Co.	J. C. Dickson ..	42.32	40.22	2.10	16.03	24.19	.392	16.2	Slow	.16	.36	.52	.08	.39
4	11-24-16	DuBois Laboratory Co...	R. J. Bailey....	42.11	40.93	1.18	15.85	25.08	.403	16.06	Slow	.05	.35	.40	.10	.50
5	12- 8-16	Elk Tanning Co.......	E. R. Lobaugh. J. Earle McNutt	42.20	40.75	1.45	16.06	24.69	.407	16.5	Slow	.04	.17	.13	.11	.11
6	11-10-16	England, Walton & Co.	C. R. Oberfell.. C. W. Reilly...	42.22	40.64	1.58	15.83	24.81	.398	16.04	Slow	.06	.06	.00	.12	.23
7	11- 7-16	Graton & Knight Mfg.Co.	V. J. Mlejnek..	41.96	40.39	1.57	16.15	24.24	.389	16.05	Slow	.20	.19	.01	.20	.34
8	11-20-16	Hoppenstedt, A.W. Lab'y	N. F. Chapin ..	41.68	40.09	1.59	15.79	24.30	.367	15.11	Slow	.48	.49	.01	.16	.28
9	11-16 16	Kistler, Lesh & Co......	J. M. Seltzer...	42.09	40.39	1.70	15.97	24.42	.395	16.17	Slow	.07	.19	.12	.02	.16
10	11-17-16	Kistler, Lesh & Co......	F. F. Marshall.	42.07	40.46	1.61	15.89	24.57	.396	16.11	Slow	.09	.12	.03	.06	.01
11	11- 7-16	Leather & Paper Lab'y	J. S. Rogers .. R. W. Frey....	42.04	40.66	1.38	15.96	24.70	.407	16.46	Slow	.12	.08	.20	.01	.12
12	11- 7-16	Mosser, J. K. Co.	Thos. J. Mosser	41.83	39.87	1.96	15.56	24.31	.365	15.	Slow	.33	.71	.38	.39	.27
13	11-16-16	Mosser, William F. Co. .	Oskar Riethof .	42.13	41.28	.85	15.61	[1]25.67	.4	16.	Rapid	.03	.70	.73	.34	[1]1.09
14	11- 5-16	Nichols Laboratory	M. F. Nichols .	41.97	40.77	1.20	16.23	24.54	.396	16.	Slow	.19	.19	.38	.28	.04
15	11-24-16	Pfister & Vogel Lea. Co.	A. C. Orthmann	43.00	40.67	2.33	16.34	24.33	.394	16.18	Slow	.84	.09	.75	.39	.25
16	2-17-17	Smoot, C. C. & Sons Co.	C. C. Smoot, III L. E. Stacy....	41.98	40.79	1.19	15.99	24.80	.377	15.19	Slow	.18	.21	.39	.04	.22
17	10-18-16	Stamford Mfg. Co.......	Roy H. Wisdom	41.97	40.65	1.32	16.11	24.54	.393	16.	Slow	.19	.07	.26	.16	.04
18	11-14-16	Yocum, Jno. H..........	Jno. H. Yocum	41.99	40.45	1.54	15.58	24.87	.401	16.14	Slow	.17	.13	.04	.37	.29
19	11- 7-16	Yocum, Jno. H..........	C. H. Kernahan	42.33	40.83	1.50	15.83	25.00	.406	16.24	Slow	.17	.25	.08	.12	.42
20	11-16-16	Yocum, Faust, Ltd.	Thos. A. Faust.	42.14	40.28	1.86	15.85	24.43	.388	15.87	Slow	.02	.30	.28	.10	.15
21	2- 9-17	Young, J. S. Co.	J. Alexander...	42.38	40.74	1.64	[1]17.99	[1]22.75	.364	16.	Slow	.22	.16	.06	[1]2.04	[1]1.83
22	1- 9-17	Young, J. S. Co.	B. A. Gish.....	42.31	40.75	1.56	16.54	24.21	.363	15.	Slow	.15	.17	.02	.59	.37
23	—	Young, J. S. Co.	H. Shaffer.....	42.31	40.36	1.95	15.94	24.42	.366	15.	Slow	.15	.22	.37	.01	.16
		Average		42.16	40.58	1.58	15.95	24.58				.18	.24	.25	.18	.23
		Highest		43.00	41.28	2.33	16.54	25.10								
		Lowest		41.68	39.87	.85	15.56	24.19								
		Greatest difference ..		1.32	1.41	1.48	.98	.91								

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[1] Over 1% deviation omitted from average.

SULPHITE-CELLULOSE EXTRACT.

No.	Date of Analysis	Laboratory	Analyst	Total solids	Soluble solids	Insolubles	Non-Tannin	Tannin	Tannin per 100 cc. solution	Grams per 1000	Method of cooling	Deviation from average				
												T. S.	S. S.	Ins.	N. T.	T.
1	11-10-16	Ashland Leather Co....	R. E. Porter...	[1]52.70	52.58	0.12	27.60	24.98	0.404	16.03	Rapid	0.67	0.70	0.07	1.05	0.35
2	11- 9-16	Cattaraugus Tan. Co...	C. M. Hulings .	52.18	52.18	0.00	26.55	25.63	0.41	16.	Slow	0.15	0.30	0.19	0.00	0.30
3	11-13-16	Champion Fibre Co....	J. C. Dickson ..	51.78	51.64	0.14	26.61	25.03	0.404	16.15	Slow	0.25	0.24	0.05	0.06	0.30
4	11-24-16	Du Bois Lab. Co.......	R. J. Bailey....	51.97	51.91	0.06	26.71	25.20	0.405	16.09	Slow	0.06	0.03	0.13	0.16	0.13
5	12- 8-16	Elk Tanning Co.	E. R. Lobaugh. J. E. McNutt ..	51.33	51.33	0.00	25.57	25.76	0.422	16.	Slow	0.70	0.55	0.19	0.98	0.43
6	11-10-16	England, Walton & Co.	C. R. Oberfell.. C. W. Reilly...	51.87	51.61	0.26	27.00	24.61	0.399	16.16	Slow	0.16	0.27	0.07	0.45	0.72
7	11- 7-16	Graton & Knight M. Co.	V. J. Mlejnek..	51.72	52.18		[2]28.26	[2]22.76	0.389	16.72	Slow	0.31	0.30		[2]2.41	[2]2.57
8	11-13-16	Hoppenstedt, A. W., L.	N. F. Chapin ..	51.99	52.02		[2]28 53	[2]23.46	0.376	16.03	Slow	0.04	0.14		[2]1.98	[2]1.87
9	11-24-16	Kistler, Lesh & Co.....	J. M. Seltzer...	52·15	51.79	0.36	26.35	25.44	0.411	16.15	Slow	0.12	0.09	0.17	0.20	0.11
10	11-17-16	Kistler, Lesh & Co.....	F. F. Marshall.	52.34	51.83	0.51	26.56	25.27	0.408	16.16	Slow	0.31	0.05	0.32	0.01	0.06
11	11- 7-16	Leather & Paper Lab'y	J. S. Rogers ... R. W. Frey....	51.14	51.04	0.10	26.00	25.04	0.405	16.17	Rapid	0.89	0.84	0.09	0.55	0.29
12	11- 7-16	Mosser, J. K. Co.......	T. J. Mosser ...	[1]50.92	[2]50.35	0.57	[2]23.89	26.46	0.397	15.	Slow	[1]1.11	[2]1.53	0.38	[2]2.66	1.13
13	11-16-16	Mosser, Wm. F. Co. ...	O. Riethof.....	52.40	52.02	0.38	25.32	26.70	0.412	15.5	Slow	0.37	0.14	0.19	1.23	1.37
14	11- 5-16	Nichols Laboratory....	M. F. Nichols.	51.87	51.73	0.14	26.76	24.97	0.406	16.	Slow	0.16	0.15	0.05	0.21	0.36
15	11-21-16	Pfister & Vogel L. Co...	A. C. Orthmann	52.78	52.49	0.29	[2]30.32	[2]22.17	0.358	16.16	Slow	0.75	0.61	0.10	[2]3.77	[2]3.16
16	11-18-17	Smoot, C. C. & Sons Co.	C. C. Smoot, III L. E. Stacy....	51.55	51.18	0.37	26.22	24.96	0.364	14.38	Slow	0.48	0.70	0.18	0.33	0.37
17	10-14-16	Stamford Mfg. Co......	R. H. Wisdom.	51.69	51.69	0.00	25.83	25.86	0.414	16.	Rapid	0.34	0.19	0.19	0.72	0.53
18	11-14-16	Yocum, J. H....	J. H. Yocum...	51.87	51.76	0.11	27.76	24.00	0.363	15.13	Slow	0.16	0.12	0.08	1.21	1.33
19	11- 7-16	Yocum, J. H...........	C. M. Kernahan	52.04	51.73	0.31	27.67	24.06	0.365	15.16	Slow	0.01	0.15	0.12	1.12	1 .27
20	11-16 16	Yocum, Faust, Ltd.....	T. A. Faust....	51.68	51.68	0.00	27.33	24.35	0.39	16	Slow	0.35	0.20	0.19	0.78	0.98
21		Young, J. S. Co........	J. Alexander...													
22	1-15-17	Young, J. S. Co........	B. A. Gish	52.59	52.60		26.26	26.34	0.395	15	Slow	0.56	0.72		0.29	1.01
23		Young, J. S. Co........	H. Shaffer.....	52.93	52.48	0.45	25.81	26.67	0.4	15	Slow	0.90	0.60	0.26	0.74	1.34
		Average...............		52.03	51.88	0.19	26.55	25.33				0.37	0.34	0.16	0.95	0.65
		Highest...............		52.93	52.60	0.57	27.76	26.70								
		Lowest		51.14	51.04	0.00	25.32	24.00								
		Greatest Difference....		1.79	1.56	0.57	2.44	2.70								

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[1] Over 1% deviation omitted from average. [2] Over 1½% deviation omitted from average.

QUEBRACHO EXTRACT.

No.	Date of Analysis	Laboratory	Analyst	Total solids	Soluble solids	Insolubles	Non-tannin	Tannin	Tannin per 100 cc. solution	Grams per 1000	Method of cooling	Deviation from average				
												T. S.	S. S.	Ins.	N.T.	T.
1	2-21-17	Ashland Leather Co.	R. E. Porter...	99.10	[2]94.10	[2]5.00	11.20	82.90	0.415	5	Rapid	0.29	[2]2.46	[2]2.00	0.97	1.06
2	11- 9-16	Cattaraugus Tanning Co.	C. M. Hulings.	99.12	92.69	6.43	9.82	82.87	0.414	5	Slow	0.31	1.05	0.57	0.41	1.03
3	11-13-16	Champion Fibre Co.	J. C. Dickson..	98.27	92.73	5.54	10.30	82.43	0.412	5	Slow	0.54	1.09	1.46	0.07	0.59
4	11-24-16	DuBois Laboratory Co. ..	R. J. Bailey ...	98.54	92.35	6.19	10.36	81.99	0.412	5.03	Slow	0.27	0.71	0.81	0.13	0.15
5	2- 3-17	Elk Tanning Co.......	E. R. Lobaugh J. Earle McNutt	99.57	91.55	8.02	9.78	81.77	0.409	5	Slow	0.76	0.09	1.02	0.45	0.07
6	11-10-16	England, Walton & Co.	C. R. Oberfell . C. W. Reilly...	98.15	91.27	6.88	10.31	80.96	0.406	5.02	Slow	0.66	0.37	0.12	0.08	0.88
7	11- 7-16	Graton & Knight Mfg. Co.	V. J. Mlejnek .	99.06	92.02	7.04	10.32	81.70	0.412	5.05	Slow	0.25	0.38	0.04	0.09	0.14
8	11-10-16	Hoppenstedt, A. W. Lab'y	N. F. Chapin ..	98.83	91.32	7.51	10.19	81.13	0.405	4.99	Slow	0.02	0.32	0.51	0.04	0.71
9	11-16-16	Kistler, Lesh & Co.	J. M. Seltzer...	98.84	90.52	8.32	9.91	80.61	0.403	5	Slow	0.03	1.02	1.32	0.32	1.23
10	11-17-16	Kistler, Lesh & Co.	F. F. Marshall.	99.06	90.94	8.12	9.80	81.14	0.406	5	Slow	0.25	0.70	1.12	0.43	0.70
11	11- 7-16	Leather & Paper Lab'y	J. S. Rogers ... R. W. Frey....	98.30	92.37	5.93	10.23	82.14	0.411	5	Slow	0.51	0.73	1.07	0.00	0.30
12	11- 7-16	Mosser, J. K. Co.	Thos. J. Mosser	98.14	90.48	7.66	10.13	80.35	0.455	5.67	Slow	0.67	1.16	0.66	0.10	1.49
13	11-16-16	Mosser, William F. Co...	Oskar Riethof .	98.87	92.23	6.64	9.46	82.77	0.41	5	Rapid	0.06	0.59	0.36	0.77	0.93
14	11- 5-16	Nichols Laboratory	M. F. Nichols .	99.60	[2]93.60	6.00	11.25	82.35	0.412	5	Slow	0.79	[2]1.96	1.00	1.02	0.51
15	11-24-16	Pfister & Vogel Lea. Co.	A. C. Orthmann	[1]100.00	93.22	6.78	10.15	83.07	0.415	5	Slow	[1]1.19	1.58	0.22	0.08	1.23
16	2-10-17	Smoot, C. C. & Sons Co.	C. C. Smoot, III L. E. Stacy....	98.86	91.78	7.08	9.74	82.04	0.411	5.01	Slow	0.05	0.14	0.08	0.49	0.20
17	10-18-16	Standard Mfg. Co.	Roy H. Wisdom	98.24	92.04	6.20	10.47	81.57	0.408	5	Slow	0.57	0.40	0.80	0.24	0.27
18	11-14-16	Yocum, Jno. H.	Jno. H. Yocum	98.61	90.77	7.84	9.17	81.60	0.408	5	Slow	0.20	0.87	0.84	1.06	0.24
19	11- 7-16	Yocum, Jno. H.	C. M. Kernahan	99.08	91.32	7.76	9.81	81.51	0.408	5	Slow	0.27	0.32	0.76	0.42	0.33
20	11-17-16	Yocum, Faust, Ltd.	Thos. A. Faust.	99.10	90.91	8.19	11.65	[2]79.26	0.396	5	Slow	0.29	0.73	1.19	1.42	[2]2.58
21	12-12-17	Young, J. S. Co.	J. Alexander...	[1]100.00	89.96	[2]10.04	10.25	[2]79.71	0.398	5	Slow	[1]1.19	1.68	[2]3.04	0.02	[2]2.13
22	1-22-17	Young, J. S. Co.	B. A. Gish.....	[1]101.17	92.33	[2]8.84	10.48	81.85	0.388	4.75	Slow	[1]1.36	0.69	[2]1.84	0.25	1.01
23	—	Young, J. S. Co.	H. Shaffer.....	[1]103.43	[2]97.52	5.91	10.34	[2]87.18	0.414	4.75	Slow	[1]4.62	[2]5.88	1.09	0.11	[2]5.34
		Average		98.81	91.64	7.00	10.23	81.84				0.36	0.73	0.75	0.35	0.60
		Highest		99.60	93.22	8.32	11.65	83.07								
		Lowest		98.14	89.96	5.54	9.17	80.35								
		Greatest difference..		1.46	3.26	2.78	2.48	2.72								

[1] Over 1% deviation omitted from average. [2] Over 1½% deviation omitted from average.

CHESTNUT WOOD.

No.	Date of analysis	Laboratory	Analyst	Water as found	Total solids	Soluble solids	Insol-ubles	Non-tannin	Tannin	Tannin dry basis	Tannin per 100 solution	Grams per 1000	Type Ex-tractor	Deviation from average						
														Wa-ter	T. S.	S.S.	Ins.	N. T.	Tan.	Tan dry
1	12-23-16	Ashland	Porter	24.06	9.15	8.40	0.75	2.35	6.05	7.96	0.242	40	Glass Soxhlet	0.41	0.97	0.82	0.05	0.60	0.12	0.08
2	11- 9-16	Cat'r'g's Co. ...	Hulings	22.87	10.28	8.90	1.33	2.74	6.16	7.99	0.37	60	Teas	0.78	0.16	0.32	0.53	0.21	0.01	0.05
3	11-13-16	Champion	Dickson	23.46	10.11	9.35	0.76	2.83	6.52	8.05	0.391	60	Teas	0.19	0.01	0.13	0.04	0.12	0.35	0.01
4	3-15-17	DuBois	Bailey	17.35	11.34	10.85	0.49	2.58	[1]8.27	[1]10.00	0.201	25	Teas	6.30	1.22	1.63	0.31	0.37	[1]2.10	[1]1.96
5	2-10-17	Elk T. Co.	Lobaugh . McNutt ..	28.03	9.74	8.65	1.09	2.58	6.07	7.14	0.303	50	Teas	4.38	0.38	0.57	0.29	0.37	0.10	0.90
6	11- 3-16	England Wal. .	Oberfell .. Reilly	24.19	11.18	10.21	0.97	3.79	6.42	8.47	0.398	62	Teas	0.54	1.06	0.99	0.17	0.84	0.25	0.43
7	11- 7-16	G. & K. M. Co.	Mlejnek	23.28	11.17	9.81	1.36	3.53	6.28	8.20	0.358	57	Teas	0.37	1.05	0.59	0.56	0.58	0.11	0.16
8	11-24-16	Hoppenstedt ..	Chapin	23.20	9.73	9.24	0.49	3.01	6.23	8.12	0.374	60	Teas	0.45	0.39	0.02	0.31	0.06	0.06	0.08
9	11-22-16	Kistler, L'h Co.	Seltzer	25.58	10.10	9.16	0.94	3.03	6.13	8.22	0.381	63	Teas	1.93	0.02	0.06	0.14	0.08	0.04	0.18
10	12- 7-16	Kistler, L'h Co.	Marshall ...	25.33	10.30	9.34	0.96	3.14	6.20	8.30	0.393	64	Teas	1.68	0.18	0.12	0.16	0.19	0.03	0.26
11	11-24-16	Lea. & Paper ..	Rogers ... Frey	26.52	9.15	8.58	0.57	2.81	5.77	7.85	0.298	51.6	Teas	2.87	0.97	0.64	0.23	0.14	0.40	0.19
12	11-10-16	Mosser, J. K. .	Mosser	26.50	9.72	8.53	1.19	2.57	5.96	8.10	0.324	40	Teas	2.85	0.40	0.69	0.39	0.38	0.21	0.06
13	11-10-16	Mosser, W. F. .	Riethof	26.41	9.19	8.45	0.74	2.49	5.96	8.09	0.396	50	Teas	2.76	0.93	0.23	0.06	0.46	0.21	0.05
14	11- 5-16	Nichols	Nichols	19.50	9.16	8.37	0.79	2.52	5.85	7.28	0.292	50	Teas	4.15	0.96	0.85	0.01	0.43	0.32	0.76
15	12- 8-16	P. & V. L. Co. .	Orthmann ..	26.00	10.68	9.69	0.99	2.96	6.73	9.09	0.404	60	Soxhlet	2.35	0.56	0.47	0.19	0.01	0.56	1.05
16	2-16-17	Smoot & Son ..	Stacy .... Smoot	24.85	10.14	9.34	0.80	3.34	6.00	7.99	0.32	53	Teas	1.20	0.02	0.12	0.00	0.39	0.17	0.05
17	10-25-16	S. Mfg. Co.	Wisdom	25.13	10.60	9.56	1.04	3.42	6.14	8.20	0.368	60	Reed.	1.48	0.48	0.34	0.24	0.47	0.03	0.16
18	11-14-16	Yocum, J. H. ..	Yocum	22.70	11.27	10.60	0.67	3.68	6.92	8.95	0.208	30	Teas	0.95	1.15	1.38	0.13	0.73	0.75	0.91
19	11- 7-16	Yocum, J. H. ..	Kernahan ..	21.00	10.64	10.12	0.52	3.32	6.80	8.61	0.204	30	Teas	2.65	0.52	0.90	0.28	0.37	0.63	0.57
20	11-10-16	Yocum, Faust ..	Faust	25.11	9.57	8.81	0.76	3.11	5.70	7.61	0.228	40	Teas	1.46	0.55	0.41	0.04	0.16	0.47	0.43
21		Young Co.	Alexander ..																	
22	1-22-17	Young Co.	Gish	18.76	9.33	9.06	0.27	2.67	6.39	7.85	0.156	24.37	Imp. Soxhlet	4.89	0.79	0.16	0.53	0.28	0.22	0.19
23	—	Young Co.	Shaffer	20.39	[1]8.05	7.75	0.30	2.37	5.38	6.76	0.169	25	Soxhlet	3.26	[1]2.07	1.47	0.50	0.58	0.79	1.28
		Average		23.65	10.12	9.22	0.80	2.95	6.17	8.04				2.18	0.61	0.59	0.23	0.36	0.28	0.37
		Highest		28.03	11.34	10.85	1.36	3.79	6.92	9.09										
		Lowest		17.35	9.15	8.37	0.27	2.35	5.38	6.76										
		Greatest difference		10.68	2.19	2.48	1.09	1.44	1.54	2.33										

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[1] Over 1¾ % deviation omitted from average except on "Water as found".

A few analysts returned all results on dry basis and one on basis of small percentage of water. For comparison, these have been calculated to the "was found" basis.

SUMAC.

No.	Date of Analysis	Laboratory	Analysts	Water as found	Total solids	Soluble solids	Insolubles	Non-Tannin	Tannin	Tannin Dry Basis	Tannin per 100 solution	Grams per 1000	Type Extractor	Deviation from average						
														Water	T. S.	S. S.	Ins.	N. T.	Tan.	Tan dry
1	2-21-17	Ashland	Porter	7.22	44.10	42.00	2.10	17.65	24.35	26.22	0.365	15	Glass Soxhlet	0.60	.28	1.20	0.17	0.27	0.68	0.88
2	11- 9-16	Cattaraugus ..	Hulings	7.99	47.35	44.19	3.16	19.31	24.38	26.50	0.366	15	Teas	0.17	1.97	0.99	0.89	1.89	0.65	0.60
3	11-13-16	Champion ...	Dickson	8.15	[1]41.74	[1]40.41	1.33	16.58	23.83	25.17	0.382	16	Teas	0.33	[1]3.64	[1]2.89	0.94	1.34	1.20	1.93
4	3-15-17	Du Bois	Bailey	7.88	45.59	43.12	2.47	17.43	25.69	27.88	0.385	15	Teas	0.06	.21	0.08	0.20	0.49	0.66	0.78
5	2- 3-17	Elk T. Co. ...	Lobaugh . McNutt ..	7.86	46.32	43.07	3.25	18.34	24.73	26.85	0.396	16	Modfied Reed	0.04	.94	0.13	0.98	0.42	0.30	0.25
6	11- 3-16	England Wal.	Oberfell . Reilly	8.08	44.95	42.80	2.15	10.23	24.57	26.73	0.4	16.28	Teas	0.26	.43	0.40	0.12	0.31	0.46	0.37
7	11- 7-16	G. & K. M. Co.	Mlejnek	8.46	45.11	42.98	2.13	18.11	24.87	27.17	0.373	15	Teas	0.64	.27	0.78	0.14	0.19	0.16	0.07
8		Hop'enstedt ..	Chapin																	
9	11-14-16	Kistler, Lesh.	Seltzer	7.98	45.36	43.40	1.96	18.06	25.34	27.54	0.38	15	Teas	0.16	.02	0.20	0.31	0.14	0.31	0.44
10	11-14-16	Kistler, Lesh.	Marshall ...	7.92	45.38	43.69	1.69	17.98	25.71	27.90	0.373	14 5	Teas	0.10	.00	0.49	0.58	0.06	0.68	0.80
11	11-24-16	Lea. & Pap. ..	Rogers ... Frey	7.75	43.93	42.76	1.17	17.62	25.14	27.25	0.377	15	Teas	0.07	1.45	0.44	0.10	0.30	0.11	0.15
12	11- 7-16	Mosser, J. K .	Mosser	7.73	45.42	42.73	2.69	17.19	25.54	27.51	0.358	13	Teas	0.09	.04	0.47	1.42	0.73	0.51	0.41
13	12- 8-16	Mosser, W. F.	Riethof.....	7.79	44.15	42.70	1.45	17.44	25.26	27.39	0.41	16	Teas	0.03	1.23	0.50	0.82	0.48	0.23	0,29
14	11- 5-16	Nichols	Nichols.....	8.00	[1]47.90	44.70	3.20	18.82	25.88	27.96	0.259	10	Teas	0.18	[1]2.52	1.50	0.93	0.90	0.85	0.86
15	12- 8-16	P. & V. L. Co.	Orthmann ..	7.52	[1]50.05	[1]45.32	[1]4.73	[1]21.98	23.34	25.24	0.373	16	Teas	0.30	[1]4.67	[1]2.12	[1]2.46	[1]4.06	1.69	1.96
16	2-24-17	Smoot & Son.	Stacy .... Smoot....	8.07	44.33	42.84	1.49	17.27	25.57	27.82	0.408	16	Teas	0.25	1.05	0.36	0.78	0.65	0.54	0.72
17	10-18-16	S. Mfg. Co. ..	Wisdom	7.83	46.69	43.67	3.02	18·80	24.87	26.98	0.373	15	Reed.	0.01	1.31	0.47	0.75	0.88	0.16	0.12
18	11-14-16	Yocum, J. H. .	Yocum	7.70	45 22	43.07	2.15	17.34	25.73	27.88	0.36	14	Glass sim. to Teas	0.12	.16	0.13	0.12	0.58	0.70	0.78
19	11- 7-16	Yocum, J. H. .	Kernahan ..	7.80	45.29	42.94	2.35	17.22	25.72	27.90	0.36	14	Teas	0.02	.09	0.26	0.08	0.70	0.69	0.80
20	11-20-16	Yocum, Faust	Faust	8.20	44.27	41.76	2.51	17.68	24.08	26.23	0.337	14	Teas Glass	0.38	1.11	1.44	0.24	0.24	0.95	0.87
21		Young Co. ...	Alexander ..																	
22	1- 9-17	Young Co. ...	Gish	6.99	46.41	43.95	2.46	19.17	24.78	26.64	0.186	7.5	Imp. Soxhlet	0.83	1.03	.75	0.19	1.25	0.25	0.46
23		Young Co. ...	Shaffer	7.37	46.96	44.36	2.60	18.13	26.23	28.32	0.212	7.5	Soxhlet	0.45	1.58	1.16	0.33	0.21	1.23	1.22
		Average......		7.82	45.38	43.20	2.27	17.92	25.03	27.10				0.24	.73	0.62	0.50	0.60	0.62	0.70
		Highest......		8.46	47.35	44.70	3.25	19.81	26.23	28.32										
		Lowest.......		6.99	43.93	41.76	1.17	16.58	23.34	25.17										
		Greatest Difference		1.47	3.42	2.94	2.08	3.23	2.89	3.15										

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[1] Over 2% deviation omitted from average.

One laboratory returned all results on dry basis. For comparison these have been calculated to "water as found" basis.

SPENT TAN.

No.	Date of analysis	Laborntory	Analyst	Water as found	Total solids	Soluble solids	Insolubles	Non-tannin	Tannin	Tannin dry basis	Tannin per 100 solution	Grams per 1000	Type extractor	Deviation from average						
														Water	T. S.	S. S.	Ins.	N. T.	Tan	Tan dry
1	12-23-16	Ashland.......	Porter	1.30	3.95	3.10	0.85	1.85	1.25	1.27	0.066	50	Teas	0.80	0.18	0.61	0.42	0.17	0.45	0.47
2	11- 9-16	Cattaraugus Co.	Hulings ..	1.89	4.42	3.84	0.58	2.06	1.78	1.81	0.089	50	Teas	0.21	0.29	0.13	0.15	0.04	0.08	0.07
3	11-13-16	Champion	Dickson ..	2.10	3.17	3.03	0.14	1.55	1.48	1.51	0.148	100	Teas	0.00	0.96	0.68	0.29	0.47	0.22	0.23
4	3-15-17	DuBois	Bailey	2.15	3.40	3.16	0.24	1.64	1.52	1.55	0.106	70	Teas	0.05	0.73	0.55	0.19	0.38	0.18	0.19
5	2- 3-17	Elk T. Co......	Lobaugh McNutt.	1.63	4.65	4.22	0.43	2.35	1.87	1.90	0.112	60	Teas	0.47	0.52	0.51	0.00	0.33	0.17	0.16
6	11- 3-16	England, Wal..	Oberfell Reilly ..	1.99	4.02	3.59	0.43	2.11	1.48	1.51	0.148	100	Teas	0.11	0.11	0.12	0.00	0.09	0.22	0.23
7	11- 7-16	G. & K. M. Co.	Mlejnek ..	2.12	4.19	3.76	0.43	1.94	1.82	1.86	0.164	90	Teas	0.02	0.06	0.05	0.00	0.08	0.12	0.12
8	11-23-16	Hoppenstedt ..	Chapin ...	1.51	4.13	3.85	0.28	2.06	1.79	1.82	0.107	60	Teas	0.59	0.00	0.14	0.15	0.04	0.09	0.08
9	11-17-16	Kistler L'h Co.	Seltzer....	1.78	4.69	4.19	0.50	2.56	1.63	1.66	0.098	60	Teas	0.32	0.56	0.48	0.07	0.54	0.07	0.08
01	11-17-16	Kistler L'h Co.	Marshall..	2.02	4.23	3.85	0.38	2.13	1.72	1.76	0.103	60	Teas	0.08	0.10	0.14	0.05	0.11	0.02	0.02
11	11-24-16	Lea. & Paper..	Rogers . Frey....	2.27	4.29	3.82	0.47	2.12	1.70	1.74	0.102	60	Teas	0.17	0.16	0.11	0.04	0.10	0.00	0.00
12	11-10-16	Mosser, J. K. ..	Mosser....	0.00	4.85	4.15	0.70	2.31	1.84	1.84	0.092	50	Teas	2.10	0.72	0.44	0.27	0.29	0.14	0.10
13	11-10-16	Mosser, W. F...	Riethof ...	2.30	3.94	3.76	0.18	1.94	1.82	1.86	0.127	70	Teas	0.20	0.19	0.05	0.25	0.08	0.12	0.12
14	11- 5-16	Nichols	Nichols...	4.00	3.75	3.43	0.32	1.93	1.50	1.58	0.132	70 in 800 cc.	Teas	1.90	0.38	0.28	0.11	0.09	0.20	0.16
15	12-19-16	P. & V. L. Co..	Orthmann	2.37	4.77	4.22	0.55	1.94	2.28	2.33	0.137	60	Soxhlet	0.27	0.64	0.51	0.12	0.08	0.58	0.59
16	2-10-17	Smoot & Son ..	Stacy ... Smoot ..	3.75	4.85	4.05	0.80	2.18	1.87	1.95	0.112	60	Teas	1.65	0.72	0.34	0.37	0.16	0.17	0.21
17	10-25-16	S. Mfg. Co.....	Wisdom ..	2.33	3.52	3.28	0.24	1.90	1.38	1.41	0.069	50	Reed	0.23	0.61	0.43	0.19	0.12	0.32	0.33
18	11-14-16	Yocum, J. H. ..	Yocum ...							1.76	0.088	50	Teas							
19	11-15-16	Yocum, J. H. ..	Kernahan.							1.77	0.089	50	Teas							
20	11-15-16	Yocum, Faust .	Faust	2.57	[1]5.76	[1]5.07	0.69	[1]3.27	1.80	1.85	0.072	40	Teas	0.47	[1]1.66	[1]1.36	0.26	[1]1.25	0.10	0.11
21		Young Co.	Alexander										Imp.							
22	1-17-17	Young Co.	Gish......	1.88	4.05	3.82	0.23	2.10	1.72	1.75	0.017	10	Soxhlet	0.22	0.08	0.11	0.20	0.08	0.02	0.01
23	—	Young Co.	Shaffer ...	2.00	3 60	3.46	0.14	1.63	1.83	1.86	0.093	50	Soxhlet	0.10	0.53	0.25	0.29	0.39	0.13	0.12
		Average.....		2.10	4.13	3.71	0.43	2.02	1.70	1.74				0.50	0.40	0.31	0.17	0.19	0.17	0.17
		Highest.....		4.00	4.85	4.22	0.85	2.56	2.28	2.33										
		Lowest......		0.00	3.17	3.03	0.14	1.55	1.25	1.27										
		Greatest difference		4.00	1.68	1.19	0.71	1.01	1.03	1.06										

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[1] Over 1 % deviation omitted from average except on "water as found".

A few analysts returned all results on dry basis. Where possible these have been calculated, for comparison, to the "water as found" basis.

TANNERY LIQUOR.

No.	Date of Analysis	Laboratory	Analyst	Bark at 70.	Total solids	Soluble solids	Insol-ubles	Non-Tannin	Tannin	T. S. per 100 cc.	Amount liquor per 1000	Acid	Deviation from average					
													T. S.	S. S.	Ins.	N. T.	Tan.	Acid
1	11- 8-16	Ashland	Porter	27	6.85	6.58	0.27	4.04	2.54	0.703	100 cc.	0.44	0.17	0.14	0.03	0.19	0.06	0.10
2	11- 9-16	Cattaraugus	Hulings	29	6.63	6.39	0.24	4.00	2.39	0.716	105	0.59	0.05	0.05	0.00	0.15	0.21	0.05
3	11-13-16	Champion	Dickson	27.9	6.66	6.40	0.26	3.72	2.68	1.71	250 cc.		0.02	0.04	0.02	0.13	0.08	
4	12-16-16	Du Bois	Bailey	28.2	6.62	6.29	0.33	3.82	2.47	1.01	150 cc.	0.57	0.06	0.15	0.09	0.03	0.13	0.03
5	2- 3-17	Elk Tan. Co.	Lobaugh McNntt	26.75	6.65	6.37	0.28	3.93	2.44	0.719	108g.		0.03	0.07	0.04	0.08	0.16	
6	11-14-16	England, Wal.	Oberfell Reilly	26.9	6.62	6.40	0.22	3.79	2.61	0.712	107.5g.	0.70	0.06	0.04	0.02	0.06	0.01	0.16
7	11- 7-16	Grat'n & K. Mfg. Co.	Mlejnek	27.8	6.59	6.35	0.24	3.73	2.62	0.677	100 cc.	0.51	0.09	0.09	0.00	0.12	0.02	0.03
8	11-14-16	Hop'enstedt, A. W. Lab.	Chapin	27.5	6.72	6.46	0.26	3.91	2.55	0.517	75 cc.		0.04	0.02	0.02	0.06	0.05	
9	11-16-16	Kistler, Lesh	Seltzer	28	6.60	6.35	0.25	3.82	2.53	0.678	100 cc.	0.53	0.08	0.09	0.01	0.03	0.07	0.01
10	11-17-16	Kistler, Lesh	Marshall	28	6.61	6.35	0.26	3.86	2.49	0.68	100 cc.	0.54	0.07	0.09	0.02	0.01	0.11	0.00
11	11- 7-16	Leather & Pap.	Rogers Frey	27	6.65	6.46	0.19	4.14	2.32	0.708	108	0.53	0.03	0.02	0.05	0.29	0.28	0.01
12	11-12-16	Mosser, J. K.	Mosser	27	6.75	6.54	0.21	[1]3.16	[1]3.38	0.693	100 cc.		0.07	0.10	0.03	[1]0.69	[1].78	
13	11-11-16	Mosser, W. F.	Riethof	27	6.61	6.47	0.14	3.84	2.63	0.679	100 cc.	0.52	0.07	0.03	0.10	0.01	0.03	0.02
14	11- 5-16	Nichols	Nichols	25	6.68	6.47	0.21	3.92	2.55	0.685	100 cc.	0.50	0.00	0.03	0.03	0.07	0.05	0.02
15	12- 7-16	P. & V. L. Co.	Orthmann	27.5	6.85	6.65	0.20	3.96	2.69	0.704	100 cc.	0.71	0.17	0.21	0.04	0.11	0.09	0.17
16	11-18-16	Smoot & Son	Stacy Smoot		6.86	6.71	0.15	3.93	2.78	0.704	100 cc.		0.18	0.27	0.09	0.08	0.18	
17	10-21-16	Stamford Mfg. Co.	Wisdom	26.5	6.60	6.40	0.20	3.84	2.56	0.677	100 cc.	0.52	0.08	0.04	0.04	0.01	0.04	0.02
18	11-14-16	Yocum, J. H.	Yocum	26.5	6.65	6.33	0.32	4.00	2.33	1.023	150 cc.	0.42	0.03	0.11	0.08	0.15	0.27	0.12
19	11- 7-16	Yocum, J. H.	Kernahan	26	6.72	6.35	0.37	3.97	2.38	1.021	150 cc.	0.44	0.04	0.09	0.13	0.12	0.22	0.10
20	11-15:16	Yocum-Faust Ltd.	Faust	27	6.73	6.46	0.27	3.99	2.47	1.04	154g.		0.05	0.02	0.03	0.14	0.13	
21		Young Co.	Alexander															
22	1-17-17	Young Co.	Gish	27.5	6.71	6.51	0.20	3.68	2.83	0.436	65g.		0.03	0.07	0.04	0.17	0.23	
23		Young Co.	Shaffer	27	6.70	6.55	0.15	3.67	2.88	0.435	65g.		0.02	0.11	0.09	0.18	0.28	
		Average		27¼	6.68	6.44	0.24	3.85	2.60			0.54	0.07	0.09	0.05	0.10	0.13	0.06
		Highest		29	6.86	6.71	0.37	4.14	2.88									
		Lowest		25	6.59	6.29	0.14	3.67	2.32									
		Greatest difference		4	.27	.42	0.13	.47	.56									

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[1] Over ½% deviation omitted from average.

SOLUBILITY OF HIDE IN SALT SOLUTIONS.

Committee Report, 1917.

By L. Balderston, Chairman.

The work assigned to this Committee included, beside the subject indicated by the above title, the effect of alkalies in the soaking of dried hides. No work has been done on the latter topic.

The Chairman drew up a plan of work and submitted it to F. H. Small for suggestions. A revised plan was submitted to him, and his further suggestions were in part incorporated in the directions as sent out.

Among the members who were asked to collaborate was Oskar Riethof. He declined, but was so kind as to point out that some light might be thrown on the subject by researches of Haenlein, von Schroeder and Paessler. The Chairman examined the volumes of *Collegium* and found only one article in which reference is made to the solubility of hide substance in salt solution. This is a paper by von Schroeder and Paessler, which appeared in Dingler's *Polytechnic Journal* in 1893, and was reprinted in *Collegium,* Nos. 179, 180, 181 and 182, Oct. and Nov., 1905.

The paper describes an extensive research on the analysis of white hide. Many kinds of hides beside those of cattle and sheep were examined. The passage bearing on the topic of the present paper is as follows: "According to Rollet's and Reimer's researches (Dingl. *poly. J.,* 1858 and 1872) the corium is not a single chemical substance, but consists of the connective tissue filaments or fibrils (hide-fiber) and the cementing intercellular substance which Reimer calls coriin. The latter is soluble in lime and baryta water and in a 10 per cent. solution of common salt, while in a salt solution of higher or lower concentration it is insoluble. These properties were used by Reimer for isolating it."

In the paper by G. J. Rosenthal published in the JOURNAL for September last the results of studies by Dr. W. J. Gies and his students on the substances in hide are given. Instead of regarding all the interfibrillar material together, Gies separates it into a number of different substances. Albumin and globulin he dissolves out with 10 per cent. salt solution at blood heat from the fresh skin, finding nearly 7 per cent. in dogskin, and 4.3 per cent.

in calfskin. It seems likely that the nitrogenous material which comes out of wet-salted hides the first day in the soaks belongs to these classes, and has been rendered soluble by contact with salt. The proportion of material dissolved out from calfskin by salt solution in Rosenthal's experiments increases with longer time in lime, and after bating has risen to nearly 15 per cent.

Part of the interfibrillar material, according to Gies, consists of mucins or mucoid substances, which are soluble in dilute alkalies, including lime water. The percentage in fresh skin is in the neighborhood of 1 per cent. Other constituents of the skin are rendered soluble by hydrolysis, digestion, or decay.

Three members expressed willingness to collaborate, but results have been received from only one. Directions were sent out for two experiments. The first aimed to compare the hide-dissolving effect of water on wet-salted hide which had been soaked with that of several strengths of salt solution at two temperatures, using both sterilized and unsterilized pieces of hide. A second, included at the suggestion of W. K. Alsop, compared the effect of water with 5 per cent. salt solution, day by day, the pieces of wet-salted hide not having been previously soaked.

DIRECTIONS.

Cut a strip about 6 inches wide from the belly of a "wet-salted" hide. Shave off the hair and remove any adhering flesh and fat. Divide the strip into five nearly equal parts by cutting square across. From each of these cut at least 20 pieces about 1 by 2 inches, keeping the five lots of pieces separate. From each of the 100 pieces cut a strip about 3 millimeters wide for an analysis sample. Put these in a closed vessel and analyze them as soon as possible by the methods suggested below. Make up 20 lots of the pieces of hide, taking one piece for each lot from each of the five piles, so as to secure as good distribution as possible for the pieces of each lot. Fasten each lot of five pieces together with thread passed through holes in the pieces. Mark each lot so that it can be identified, weigh to nearest 0.1 g. and record weights. Lay aside 10 of the lots while the other 10 are being sterilized as follows: Make a solution containing 1 per cent. of actual HCl (about 2.8 per cent. of the usual strong C. P. acid) and 3 per cent. salt (C. P. NaCl). The weight of solution should be from 3 to 4 times that of the 10 lots of hide. Place the 10 lots in this solution, covered, at room temperature for 6 days. Then transfer with sterile forceps to a saturated solution of sodium bicarbonate that has been boiled and cooled under cover to avoid infection. After 3 days in this solution, transfer to sterile water at a temperature not above 20° C. Soak for three days, using fresh sterile water each day. At the same time that the sterile pieces are placed in water, start soaking the 10 remaining lots in cold water, changing the water every day and soaking three days.

Prepare four salt solutions, each about 16 times the weight of a pack of wet-salted hide, containing respectively 2, 5, 10 and 20 per cent. of pure NaCl by weight. Sterilize these by boiling and divide each into four parts in sterile covered vessels. In four other sterile vessels place a corresponding amount of sterile water, making altogether 20 vessels ready to receive packs of hide, each vessel containing an amount of liquid about four times the weight of a pack of hide. Divide the sterile packs of hide among the vessels so that two packs are in vessels of water, two in 2 per cent. salt solution, two in 5 per cent. salt, two in 10 per cent. and two in 20 per cent. salt. Divide the unsterilized packs in the same manner. The sterilized packs should be handled with sterile forceps and transferred quickly and carefully to avoid infection as far as possible. Divide the 20 vessels into two similar lots, each containing a sterile and a non-sterile pack in each of the kinds of liquid. Keep one of these lots of 10 at a temperature of from 15° to 20° C. for a week, and the other at a temperature of from 30° to 35° C. for the same time. Now determine the nitrogen in each solution in the manner described below, reduce it to hide-substance and express it as a percentage of the weight of the pack which was in that solution, in its wet-salted condition. Also express the hide-substance in solution as a percentage of the total hide-substance in that pack in the first place.

As a second experiment, take a piece of wet-salted hide with hair, flesh and fat removed as before, about 4 by 6 inches in size and cut it up into pieces about 1 by 2 inches, placing alternate pieces in each of the two lots, so as to get six pieces in each representing as nearly as possible the same kind and condition of hide. Weigh the two lots. Soak one in cold water and one in

5 per cent. salt solution at the same temperature for one day. Let the quantity of liquid be about four times the weight of the hide. At the end of 24 hours, remove the packs and place each in a fresh quantity of water and salt solution respectively, determining the total nitrogen in the used liquid. At the end of a second 24-hour period, again transfer the lots to fresh liquid, and again determine the nitrogen. Repeat, soaking each lot at least five days, and determine the total nitrogen in each soak as hide-substance.

Examination of Sample of Original Hide.—Mince the pieces into dice not more than 3 millimeters in size. Mix thoroughly. Weigh out 10 g. and ash in a platinum dish, keeping the temperature as low as possible to avoid volatilization of salt. It is not necessary to burn out the last traces of carbon. Pulverize the ash with glass rod, take it up in hot water and wash into a 250 cc. flask through a filter and make up to the mark. Titrate an aliquot part of the cool and well-mixed solution with $AgNO_3$ solution and calculate the result to per cent. salt in hide (wet-salted condition as taken). It is convenient to use 25 cc. of the solution from the ash and titrate with a silver solution of which 1 cc. is equivalent to 0.01 g. of chlorine.

Dry another 10-g. portion of the minced hide to constant weight at about 100° C. This may be done by putting the hide in a glass dish on an extract oven over night. Calculate moisture in original sample.

Determine nitrogen in triplicate samples of 0.7 g. each in the same manner as for leather, and calculate to hide-substance in original sample.

Examination of Used Solutions.—If the volume of solution does not exceed 125 cc., wash the whole into a long-necked Kjeldahl flask, add 25 cc. strong H_2SO_4 and carry the digestion through directly. If the amount exceeds 125 cc., put in about 100 cc. with the 25 cc. of acid, and after the volume is reduced by evaporation to about 50 cc., let the flask cool and add the rest of the solution slowly and carefully, then finish digestion and determination of N in the usual way.

Results of the experiments are given in the accompanying tables.

EXPERIMENT I.

Figures show percentage of the original quantity of hide-substance in the packs which were found in the solutions.

	Warm		Cool	
	Small 30°-35°	Balderston 32°-33°	Small 15°-20°	Balderston 15°-16°
		(Unsterilized hide)		
Water	1.99	Liquefied	0.21	1.48
2% salt	1.10	Liquefied	0.59	2.23
5% salt	2.72	38.50	0.77	1.48
10% salt	0.82	2.00	0.51	0.75
20% salt	0.38	1.89	0.30	1.27
		(Sterilized hide)		
Water	0.51	2.66	0.30	0.57
2% salt	0.49	4.16	0.23	1.01
5% salt	0.43	1.84	0.22	0.42
10% salt	0.32	0.73	0.17	0.36
20% salt	0.05	0.46	0.06	0.30

HIDE ANALYSIS.

	Small	Balderston
Water	39.80	42.08
Salt	13.69	15.17
Hide-substance	46.25	39.33

EXPERIMENT II.

Room temperature.

Figures indicate percentage of the hide-substance originally present found in the solutions. B's results are average of duplicates.

	Small		Balderston	
	Water	5% Salt	Water	5% Salt
First day........	0.77	0.75	1.05	1.11
Second day.....	0.26	0.26	0.51	0.54
Third day.......	0.07	0.11	0.29	0.19
Fourth day......	0.02	0.06	0.16	0.22
Fifth day........	0.01	0.05	0.13	0.18
Total	1.13	1.23	2.14	2.24

In the work done in Small's laboratory, the solutions from which the hide had been taken were strained through cotton before determining nitrogen. The Chairman did not do this, and the wide differences between the two sets of results are probably chiefly due to this difference in procedure. It will be noticed that the water solution with unsterilized hide in the "cool" column of Small's results yielded only 0.21 per cent. of hide substance, against amounts several times as large for the 2 per cent. and 5 per cent. salt solutions. The condition of the water solution is reported as cloudy and of putrid odor, while the salt solutions are without odor. It seems to the Chairman unfair to filter out the cloudiness and report the putrid solution as containing one-third as much hide substance as the odorless ones.

In Experiment I the pieces of hide were soaked long enough to remove any loose material which could be filtered out with cotton, and it would seem that anything which was loosened afterward might fairly be regarded as loss due to soaking, and so in a sense "dissolved," even if it was not able to pass through a cotton plug. In the second experiment it is perhaps better to filter the solutions in the manner mentioned.

These results, taken as a whole, seem to indicate that wet-salted hide which has been soaked long enough to remove the salt and the loose nitrogenous material does not dissolve more rapidly in salt solution of any strength than in water, unless we consider the slight differences shown in the fourth and fifth days in the second experiment. The preservative effect of salt is clearly seen in the case of the more concentrated solutions.

The Chairman was inclined to think, from his own results, that there might be some special virtue in a 2 per cent. solution, since in each instance a solution of that strength gave the highest figures, but when the other set of results was received, it was evident that this difference was only accidental. If hide substance is more soluble in salt solution than in water, the difference must be looked for in fresh hide, and this has little practical interest to the tanner.

EXPERIMENTS RELATING TO THE ACTIVATED SLUDGE PROCESS OF SEWAGE PURIFICATION.*

By W. T. Lockett, M. Sc.

Previous communications to the Society of Chemical Industry relating to the activated sludge system of sewage purification have been a series of papers under the title, "The Oxidation of Sewage Without the Aid of Filters,"[1] by E. Ardern and the author, descriptive of experiments pertaining to the development of the activated sludge process which had been carried out with Manchester sewage, and a paper by S. E. Melling.[2]

A number of papers dealing with the subject have also appeared from time to time in various English and American journals, notably those by Fowler,[3] Duckworth,[4] Chalkley Hatton, of Milwaukee,[5] and Bartow and others, of the University of Illinois.[6]

In the present communication it is proposed to give the results of a series of investigations carried out with the sewage of a manufacturing town, attention having been given to—

1. The volume of air required for the efficient working of the process.
2. Possible means of effecting economy of air.
3. Experiments relating to the maintenance of the activity of the sludge.
4. Enquiries into the bacteriological nature of effluents.

The sewage dealt with in these investigations may be classed as one of "average" strength, and contained, in common with other sewages of manufacturing towns, a variety of trade wastes, including those, inimical in character, discharged from chemical works concerned largely at the present time with the production of material for war purposes. The apparatus employed, in gen-

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* *J. S. C. I.*, Mar. 15, 1917, pp. 264-9.

[1] *J. S. C. I.*, Part I, 1914, 33, 523–539; Part II, 1914, 33, 1122–1124; Part III., 1915, 34, 937. This J.,Part I, Abstr. 1914, p. 331; Part III, Abstr. 1915, p. 647, and 1916, p. 211.

[2] *J. S. C. I.*, 1914, 33, 1125.

[3] Inst. San. Eng., Feb. 1916. Surveyor, Feb. 4, 49, No. 1255.

[4] Sewage Wks. Managers' Assoc., Dec., 1915. Surveyor, 48, No. 1249. Inst. Mun. Eng., March, 1916. Surveyor 49, No. 1263.

[5] Eng. News, N. Y., 74, No. 3. July 15, 1915, etc.

[6] Eng. News, 73, March 25, 1915. Met. & Chem. Eng., 13, No. 15, Dec. 1, 1915, etc.

eral, was similar to that used in the previous experiments with Manchester sewage and consisted essentially of a series of aerating vessels (capacity 3-4 liters) fitted with porous tiles for aeration purposes; each vessel being connected to a separate and controlled air supply.[7]

I. VOLUME OF AIR REQUIRED FOR THE EFFICIENT WORKING OF THE PROCESS.

In a previous study of the economics of the activated sludge process as applied to Manchester sewage, it was demonstrated that, with the improved methods of aeration—diffused air—the minimum air supply necessary to maintain the maximum rate of oxidation of the sewage did not exceed the amount of air required for the adequate mixture and circulation of the sludge.

The early experiments with the sewage dealt with in the present investigations, indicated that purification of the sewage could be readily brought about by means of activated sludge and "diffused" air, and investigations were then made to determine the quantity of air required for the purification process. For this purpose it was necessary to determine, in the first instance, whether the above conclusion was applicable in this case also to the activated sludge process. Accordingly, a series of comparative experiments was carried out to ascertain the oxidation effected when using (*a*) quantities of air sufficient to obtain adequate mixture and circulation of the sludge and sewage, (*b*) air in excess. The following are the average results of these experiments:

RESULTS IN PARTS PER 100,000.

		Effluent obtained with 2 hours' aeration using quantities of air:—	
	Raw sewage	(a) sufficient for adequate mixture	(b) in excess
Four hours' oxygen absorption........	10.50	1.46	1.74
Free and saline ammonia.............	2.30	0.83	0.64
Albuminoid ammonia	0.99	0.115	0.15
Nitrite as NH_3	—	0.06	0.08
Nitrate as NH_3	—	0.71	0.94

Although the foregoing experiments showed that more highly

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[7] For detailed description and sketch see "Oxidation of Sewage without Filters." Part 3.

nitrified effluents could be obtained in a given time by the use of excessive quantities of air, demonstrating that the conclusion arrived at in the Manchester experiments was not strictly applicable in this particular case, the question remained whether, in general, when dealing with the sewage employed in these investigations, it would really be advantageous to use more air than that required for adequate mixture and circulation. As a guide to the solution of this problem, the conditions which would obtain in large-scale operations were first considered. The use of large volumes of air in practical operations would tend to reduce tank capacity, as the periods of aeration would be short, but this advantage would not compensate for the increased cost of air unless the extent of the oxidation were reasonably proportionate to the volume of air used.

To obtain a decision on this question and thus provide a satisfactory basis to work upon, a series of comparative experiments was carefully carried out with mixtures of sludge and sewage in the proportions of 1 : 4, using air at the rate of (1) 6 cu. ft. per hour per square foot, *i. e.*, with just sufficient air under experimental conditions to produce adequate mixture, (2) 12 cu. ft. per hour per square foot, and samples were taken after 1½ and 3 hours' aeration. In these experiments samples of strong sewage were used so that every opportunity was given for the beneficial effect of the larger volume of air to be shown. The following are the average results obtained:

RESULTS IN PARTS PER 100,000.

		Effluents obtained when usingai a the rate of:—			
	Raw sewage	6 cu. ft. etc., for		12 cu. ft., etc., for	
		1½ hrs.	3 hrs.	1½ hrs.	3 hrs.
Four hours' oxygen absorption...	10.34	—	1.26	—	1.30
Free and saline ammonia........	2.84	1.40	0.37	1.10	0.25
Albuminoid ammonia	1.30	—	0.13	—	0.13
Nitrite as NH_3	—	0.08	0.07	0.08	0.05
Nitrate as NH_3	—	0.59	1.39	0.78	1.52

From the foregoing results it will be seen that by the use of air at the rate of 12 cu. ft. per hour, etc., the oxidation effected with 1½ hours, aeration was by no means equal to that obtained by the use of 6 cu. ft. per hour, etc., for 3 hours—the extent of the oxidation not being reasonably proportionate to the volume of air used. Consequently, it was concluded that in the treatment of this sewage, no material advantage was to be obtained by the use of quantities of air in excess of that required for adequate mixture and circulation.

Purification Effected, Using Suitable Quantities of Air and Varying Proportions of Sludge.—Having arrived at a conclusion as to the quantity of air which could be most economically employed, a study was made of the purification effected when the sewage was aerated with that quantity of air, using 20 and 40 per cent. by volume of activated sludge. To obtain average samples of the sewage over the 24 hours was practically impossible, and so to avoid misleading results experiments were conducted with samples of strong sewage obtainable from the afternoon flow.

RESULTS IN PARTS PER 100,000.

	Sewage of a manufacturing town					Manchester sewage		
	Raw sewage	20 vols. of sludge to 80 vols. of sewage		40 vols. of sludge to 60 vols. of sewage		Raw sewage	20 vols. sludge to 80 vols. sewage	40 vols. sludge to 60 vols. sewage
		Effluents obtained after aerating for:—					Effluents obtained after aerating for:—	
		2 hrs.	3 hrs.	1 hr.	1½ hrs.		4 hrs.	2 hrs.
Four hours' oxygen absorption	12.25	1.63	1.44	1.30	1.13	12.41	1.76	1.39
Free and saline ammonia	2.82	1.03	0.53	0.84	0.41	3.71	1.83	1.14
Albuminoid ammonia	1.14	0.17	0.13	0.125	0.095	1.16	0.19	0.11
Nitrite in terms of NH_3	—	0.04	0.06	0.05	0.08	—	0.14	0.13
Nitrate in terms of NH_3	—	0.96	1.46	0.65	1.01	—	1.39	1.59
Percentage purification of raw sewage calculated on:—								
(1) 4 hours' oxygen absorption	—	87	88	89	91	—	86	89
(2) Albuminoid ammonia	—	85	89	89	92	—	84	91
Percentage loss of ammonia	—	63	81	70	85	—	51	72
Percentage ammonia oxidized (NO_2, NO_3)	—	36	53	25	39	—	41	46

In the above table, the average results are given of the series of experiments carried out under suitable temperature conditions, using mixtures of sludge and sewage strictly in the proportions of 1 : 4 and 2 : 3. The quantity of air employed, which was carefully determined both prior to and during each experiment, was as nearly as possible throughout the whole series equivalent to 6 cu. ft. per hour per square foot of the sectional area of the aeration vessel. Under these conditions well-oxidized effluents were obtained with the different proportions of sludge in 3 and 1½ hours respectively.

In the table, the average results of similar experiments carried out previously with average Manchester sewage under almost precisely the same experimental conditions are also given, for a purpose which will be seen later.

An Estimate of the Volume of Air Required for Large Scale Operations.—By a comparison of the results obtained in the preceding experiments with those obtained previously in similar experiments with Manchester sewage, it will be seen that strong samples of the sewage in question can be purified in approximately three-quarters of the time required to purify average Manchester sewage. Taking into consideration the superiority of the effluents produced by the treatment of the sewage dealt with, in 3 hours (20 per cent. sludge) and 1½ hours (40 per cent. sludge) over those obtained in 4 and 2 hours respectively with Manchester sewage, and the fact, known but not previously referred to, that frequently the weaker samples of the former sewage can be completely nitrified with 2 hours (20 per cent. sludge) and 1 hour (40 per cent. sludge) aeration, it may be concluded that the quantity of air required for the purification of the *average* sewage would be one-half to three-quarters of that required for the satisfactory purification of *average* Manchester sewage.

Accordingly, on the basis of an approximate estimate of the volume of air required for the purification of a definite volume of average Manchester sewage given in a previous paper,[8] it would appear that the volume of air necessary for the satisfactory purification of 1,000,000 gallons of the sewage dealt with in these investigations, in tanks 6 ft. deep, would be considerably less than 1,500,000 cu. ft. allowing for the application of air at the rate of 15 cu. ft. per hour per square foot of tank area (a quan-

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[8] "Oxidation of sewage without filters." Part 3.

tity of air more than sufficient under these conditions to produce adequate mixture and circulation), using sludge and sewage in the proportions of 1:4. With a higher proportion of sludge to sewage, *e. g.*, 2:3, the volume of air should not exceed 1,200,000 cu. ft.

These conclusions, in view of the character of the sewage, indicate strongly the eminent practicability of the activated sludge process.

II. POSSIBLE MEANS OF EFFECTING ECONOMY OF AIR.

The absolute minimum quantity of air requisite for the purification of any particular volume of sewage by means of activated sludge, apart from that required for agitation, depends upon the strength and nature of the sewage to be dealt with and the oxygen needed to maintain the vital processes of the sludge. In actual practice, the quantity of air required for the satisfactory working of the activated sludge process greatly exceeds the absolute minimum requirements, and thus it would appear that the introduction of more suitable means to bring about the circulation of the sludge and sewage would lead to appreciable economy of air.

In the opinion of many engineers, agitation can be more economically produced by the use of air than by the application of mechanical devices. Accordingly, to reduce the disparity between the large volumes of air required for the satisfactory working of the process and the absolute minimum requirements, improvements must be looked for in the methods of applying the air to the sewage, and the experiments described in the following relate to the possibility of effecting economy by applying air "intermittently" instead of "continuously" as hitherto.

That appreciable economy of air might be obtained by the adoption of intermittent aeration has been known for some time to those concerned with the development of the activated sludge process, although, I believe, the original suggestion is to be attributed to Mr. Makepiece, the Borough Engineer of Stoke-on-Trent. Without desiring to depreciate the merit of others who may be working on similar lines, I record the results of certain experiments which I have carried out in this particular line of inquiry, with a view to their possible usefulness in the mutual endeavor of sewage chemists and engineers to render the activated sludge process an economic success.

Intermittent Aeration Experiments.—In the first series of experiments, the oxidation of sewage obtained by two hours' "continuous" aeration was compared with that obtained by two hours' "intermittent" aeration, excessive quantities of air being used in both cases.

At the outset, to the mixture of sludge and sewage to which intermittent aeration was applied, air was admitted continuously for 10 to 15 minutes to ensure a complete mixture of sewage and sludge; afterwards, in this particular series of experiments, excessive quantities of air were admitted for two out of every four minutes. Thus, during the total aeration period of two hours air was admitted for 68 minutes only. The following average results show the purification effected by the two methods of aeration:

Results in Parts per 100,000.

		Effluents obtained after two hours' aeration	
		Air applied:—	
	Raw sewage	Continuously	Intermittently
Four hours' oxygen absorption........	14.21	2.34	2.36
Free and saline ammonia.............	2.57	1.16	1.22
Albuminoid ammonia	1.34	0.135	0.14
Nitrite in terms of NH_3.............	—	0.13	0.10
Nitrate in terms of NH_3.............	—	1.06	1.04

As the results of the foregoing experiments showed that with excessive quantities of air, the stoppage of aeration for short periods had little effect upon the purification process, the experiments were carried further to observe the effect when reasonable quantities of air were employed.

In these later experiments, in which air was applied at the rates of 12, 10, 8, and 6 cu. ft. per hour, etc., it was found that as the rates at which the air was applied were reduced from 12 to 10, etc., it was necessary to increase gradually the total aeration period for the mixtures aerated intermittently in order to produce effluents equal in quality to those obtained by two hours' continuous aeration, and thus with the extension of the total aeration period the percentage saving of air was gradually reduced, until eventually, it became questionable whether intermittent aeration possessed a direct economic advantage over continuous aeration when the latter was applied in the most economical manner.

To obtain some definite information with regard to this question, a series of carefully controlled experiments was carried out as follows: Two similar aerating vessels were taken, the air supply to each regulated to the requirements of the experiment, and the vessels filled with similar mixtures of sludge and sewage in the proportions of 1:4. In the one case, the mixture was aerated continuously for two hours in the most economical manner, *i. e.*, with a quantity of air equivalent to 6 cu. ft. per square foot per hour, known to be the minimum quantity of air which can be used satisfactorily for continuous aeration under the conditions of experiment. In the second case, the mixture was aerated intermittently throughout, the volume of air used being 3 to 4 cu. ft. per square foot per hour, and the aeration of the mixture was continued until a quantity of air had passed equal to that used in the control experiment in two hours, *viz.*, 12 cu. ft. per square foot. Thus, in these experiments the only altered factor was the means of applying the air, as ultimately each mixture received approximately the same volume.

During the short periods of time when air was admitted to the intermittently aerated mixture, the air was applied at the rate of 8 cu. ft. per square foot per hour, a quantity of air found by experience to be the minimum amount possible under conditions of working to produce adequate mixing and stirring of the sludge and sewage within a short period of time.

Particular care was exercised to determine as accurately as possible the quantities of air used and, if anything, the tendency has been slightly to over-estimate rather than under-estimate the quantity of air applied intermittently, so that any advantage shown by intermittent aeration over continuous aeration in the following results may be taken as the minimum to be obtained by the use of the former.

The following are the average results of a series of experiments carried out as described:

RESULTS IN PARTS PER 100,000.

	Raw sewage	Effluent obtained when air was applied:— Continuously	Intermittently
Four hours' oxygen absorption	10.03	1.26	1.12
Free and saline ammonia	2.36	0.79	0.65
Albuminoid ammonia	0.98	0.10	0.075
Nitrite in terms of NH_3	—	0.06	0.07
Nitrate in terms of NH_3	—	0.83	0.87
Length of aeration period	—	2 hr.	3-3½ hr.

From the above results it will be seen that with intermittent aeration, effluents can be obtained distinctly superior to those produced by continuous aeration (applied in the most economical manner) using approximately the same quantity of air in each case. The direct economic advantage to be obtained by applying air intermittently appeared, however, from these experiments to be small.

It was thought that the above results could be considerably improved upon if the best method of applying air intermittently could be found, and accordingly a large number of experiments were carried out applying air intermittently in many different ways, by varying the length of the short aeration periods, etc. These experiments were not productive of results which could be considered a striking improvement upon those previously obtained; it appeared, however, that in the application of air intermittently to a mixture of sludge and sewage the following were matters of importance: (1) That the periods of time for aeration should be sufficiently long or the amounts of air passed should be sufficiently great to produce adequate mixture. (2) That the periods of rest should be reasonably short, so that use may be made of any remaining momenta of the particles of sludge.

The following are the results of a series of experiments carried out under careful control, in which ample provision was made to fulfill these apparently requisite conditions for the satisfactory application of air intermittently. Short aeration periods of a few seconds' duration were employed and approximately equal volumes of air passed in each case.

RESULTS IN PARTS PER 100,000.

		Effluent obtained when air was applied:—	
	Raw sewage	Continuously	Intermittently
Four hours' oxygen absorption	11.09	1.15	1.0
Free and saline ammonia	2.36	0.61	0.39
Albuminoid ammonia	1.22	0.14	0.13
Nitrite in terms of NH_3	—	0.02	0.02
Nitrate in terms of NH_3	—	0.71	0.91
Length of aeration period	—	2 hr.	3-3½ hr.

The results obtained in these later experiments show some slight improvement upon the earlier ones and definitely establish the fact that sewage can be purified with reduced expenditure of air by intermittent aeration. On the other hand, the time required for the purification of any particular volume of sewage is materially increased.

On the basis of the foregoing results it would appear that the economy of air to be obtained by intermittent aeration, whilst appreciable, is not great, and in view of the increased tank capacity which would be required, it becomes a debatable point whether on a practical scale its adoption for general purposes would be productive of a substantial reduction in the cost of the purification of sewage. It is to be remembered that besides the increased capital cost a certain annual expenditure would be needed for the upkeep of the additional tiles, so that much would appear to depend upon the "life" of a porous tile and the cost of replacing it.

Consequently, whilst it is realized that the possibility of purifying sewage with a reduced expenditure of air by applying the air intermittently instead of continuously, may lead eventually to important practical developments, and further experiments are in progress with this object in view, it is felt that the evidence accumulated up to the present is not of sufficient strength to warrant a general recommendation of intermittent aeration.

The facts elicited by the foregoing investigations are of such a character, however, as to suggest that intermittent aeration may be of considerable practical value if its application to the activated sludge process is limited to certain occasions. For instance, the author considers that it would be particularly useful and would effect appreciable economy of air, if utilized for dealing with the night flow of sewage. Moreover, its use would be of considerable help in providing for the treatment of storm water.

With regard to the former it may be said that on the "fill and draw" system, it would be advantageous to treat the weak sewage and reduced flow which obtains during the night time by air applied intermittently, with a view to lengthening the period of aeration to obviate the loss of activity of sludge by standing and incidentally establish a check upon the consumption of air during the time of relaxed supervision. On the "continuous flow" system, intermittent aeration should be exceptionally useful. Under continuous aeration conditions presumably an equal amount of air would be passed during the night as through the day in order to maintain the circulation and mixing of the sludge and sewage, notwithstanding the fact that considerably less sewage, and that very much diluted, would be dealt with. Intermittent aeration might be applied in this case for 12 out of the 24 hours and would effect an appreciable saving of air.

In connection with the treatment of storm water it is suggested that certain tanks might under dry weather conditions be operated on an intermittent aeration basis. In the time of storm, by changing the method of applying the air, *i. e.*, to continuous aeration, an appreciable increase in tank capacity would result, as sewage could then be more rapidly purified.

III. Experiments Relating to the Maintenance of the Activity of the Sludge.

It has been known from the outset of the investigations with regard to the activated sludge process that when a quantity of activated sludge is quiescent for some length of time certain changes take place and the sludge loses much of its activity.

The present investigations were carried out to ascertain what effect known periods of standing without aeration have upon the activity of the sludge, with a view to a knowledge of the conditions requisite to maintain the activated sludge process at its highest efficiency.

The following experiment illustrates the method of investigation adopted, and the results obtained are typical of those yielded by a number of experiments carefully carried out on similar lines.

A large volume of a recently aerated mixture of activated sludge and completely oxidized sewages was taken and allowed to settle for 20-30 minutes. At the end of this period, the supernatant liquor of oxidized sewage was decanted and the whole of the sludge remaining was collected, thoroughly mixed, and divided into several equal portions. A large volume of sewage was similarly divided. A mixture of one portion of sludge and one portion of the sewage was then made and immediately put on for aeration for a definite period of time, excessive quantities of air being used for aeration purposes. Samples were taken as required. Later, according to the time allowed for standing, a second portion of sludge was mixed with a second portion of sewage and aerated under similar conditions. Similarly with the third, fourth, etc., portions of sludge and sewage.

The following results show the nitrification effected with one and two hours' aeration, using fresh sludge and quantities of the same sludge after standing without aeration for periods of 4, 6, 8 and 10 hours respectively.

RESULTS IN PARTS PER 100,000.

	Composition of effluents after aeration for:—			
	One hour		Two hours	
Sludge employed	Free and saline ammonia	Nitrite and nitrate as NH_3	Free and saline ammonia	Nitrite and nitrate as NH_3
1. Fresh sludge	1.13	0.71	0.33	1.33
2. Sludge after 4 hours' standing	1.23	0.39	0.41	1.12
3. Sludge after 6 hours' standing	1.33	0.34	0.67	0.87
4. Sludge after 8 hours' standing	1.50	0.25	0.86	0.80
5. Sludge after 10 hours' standing	1.73	0.22	1.04	0.63

Free and saline ammonia content of original raw sewage = 2.86.
Temperature of experiments 17° C.

The quantities of free ammonia remaining unoxidized and the quantities of nitrate produced in the several cases, after one and two hours' aeration, demonstrate the desirability of reducing to a minimum the period of non-aeration for sludge both in the "fill and draw" and "continuous flow" systems.

Experiments which have been carried out in connection with the changes taking place in the sludge during the periods of standing, indicate a rapid removal of the dissolved oxygen and nitrate present in the containing water of the sludge itself, accompanied by the formation of increasing quantities of free ammonia. From the following results it will be seen that appreciable quantities of ammonia are produced within short periods of time by the fermentation of the sludge whilst standing.

One liter of activated sludge yields 0.97 mg. NH_3 in 2 hours, 2.06 mg. in 4 hours, 3.13 mg. in 6 hours, 4.10 mg. in 8 hours, and 10.40 mg. in 24 hours.

From a consideration of the whole of the facts ascertained with regard to the harmful effect of non-aeration upon sludge, it would appear that the activity of the oxidizing bacteria contained in the sludge is not so seriously impaired as one would at first be inclined to think. The fact that sewage is not so perfectly purified by sludge which has been standing as by fresh sludge, is due to a large extent to the additional bacterial energy required to oxidize the accumulated products of the secondary fermentations. In this connection it may be interesting to state that the activity of activated sludge can be recovered by prolonged aeration even after standing several days. In one particular case a sludge which, when fresh, completely oxidized a sewage in 2 hours, after 48 hours' standing, completely oxidized a sample of sewage of similar character in 6 hours and subsequently rapidly improved, so that by the following day complete activity was regained and the sludge produced clear and well nitrified effluents with reasonable periods of aeration.

IV. ENQUIRIES INTO THE BACTERIOLOGICAL NATURE OF EFFLUENTS.

A number of determinations of the bacterial content of effluents have been made during the course of the foregoing investigations, and from the results obtained it is evident that the purification of sewage by air and activated sludge is accompanied by an effective removal of bacteria.

From estimations of the number of organisms per cubic centimeter contained in raw sewage, and in effluents obtained after 3 hours' aeration (20 per cent. sludge) and 1½ hours' aeration (40 per cent. sludge), it has been found that rather more than 99 per cent. of the organisms contained in the raw sewage are removed during the periods of aeration mentioned.

The following are the average results of a large number of estimations:

NUMBER OF BACTERIA PER CC.

	Gelatin at 20° C.	Agar at 37° C.
Raw sewage	8,500,000	4,200,000
Effluent	66,000	30,000
Percentage removal	99.2	99.3

Experiments have also been made to determine the nature of the bacteria contained in the effluents, principally to ascertain whether the purification of sewage by aeration and activated sludge is accompanied by an effective removal of intestinal organisms. From a large number of determinations made it would appear that in general there is a high percentage removal of such organisms, although effluents of exceptional clarity and eminently satisfactory from a chemical point of view have been found to contain more than 1,000 *B. coli* and more than 10 spores of *B. enteritidis sporogenes* per cc. It is to be remarked, however, that usually these high results for effluents were obtained when the original raw sewage gave a correspondingly high return for these particular organisms.

In these investigations extensive use was made of Klein's *B. enteritidis sporogenes* and the MacConkey bile salts tests although a number of effluents have been examined in greater detail. Below, the results are given of a detailed bacteriological examination—carried out on the lines suggested by Dr. Houston in the 2nd Royal Commission Report on Sewage Disposal—of a raw sewage and two corresponding effluents, obtained by the aeration of the sewage with (1) 20 per cent., (2) 40 per cent. sludge for 3 and 1½ hours respectively. The results of a chemical examination of the sewage and effluents are also given.

	Raw sewage	Effluents obtained after aerating for:—	
		3 hours (20% sludge)	1½ hours (40% sludge)
Bacteriological results:			
Number of organisms per cc.:—			
Gelatin at 20° C.	4,400,000	36,000	48,000
Agar at 37° C.	1,700,000	23,000	24,700
	cc.	cc.	cc.
B. coli	+0.0001	+0.01	+0.001[10]
***B. enteritidis sporogenes* (spores)**	+0.01	+1	+1
Gas test	+0.001	—1	+1
Indole test	+0.00001	+0.01	+0.001
Neutral Red broth test	+0.001	+0.01	+0.01
Bile salt broth test	+0.00001	+0.001	+0.001
Litmus-milk (modified test)	+0.00001	+0.001	+0.001
	GAC	GA (C?)	GAC
Chemical results.			
Parts per 100,000.			
Four hours' oxygen absorption	12.23	1.12	1.00
Free and saline ammonia	3.36	1.16	0.83
Albuminoid ammonia	1.11	0.115	0.10
Nitrite in terms of NH_3	--	1.02	0.02
Nitrate in terms of NH_3	—	1.05	0.92

In conclusion, the author begs to acknowledge his great indebtedness to the Worshipful Company of Grocers for their continued material help, and to the members of the staff of the Municipal and Sanitary Engineering Department, School of Technology, Manchester—Prof. Radcliffe and Mr. Herring-Shaw, M. Sc.—for their generous assistance and helpful interest in the research.

ABSTRACTS.

Chemical Investigation of the Substances in Birch. GEORGE GRASSER. *Collegium*, 1916, No. 560, pp. 445-52 (continuation of research abstr. this JOURNAL, [7] 42). Young birch leaves (*Betula alba*) were collected in April and without drying extracted with cold toluol. The evaporated extract was a brown waxy mass which was freed from ethereal ingredients over the water-bath, then re-dissolved in ether, evaporated and heated, yielding a brittle brown resin, insoluble in H_2O, but completely soluble in

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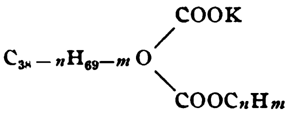
[9] **Sludge of usual density, similar to that produced by 2 hours settlement of mixtures of sludge and sewage equivalent to 25 to 50 grms. of dry matter.**

[10] **+0.001 cc.= positive result with 0.001 cc.; negative result with 0.0001 cc., or at least 1000 organisms in the cubic centimeter but less than 10,000.**

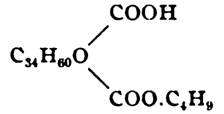
alcoholic soda, glacial acetic acid, alcohol, ethyl acetate, CS_2, petroleum ether, $CHCl_3$, acetone and concentrated H_2SO_4. The melting point was 62° and the elementary analysis computed for $C_{40}H_{70}O_5$. These results showed that the resin which was obtained from the dried leaves is chemically identical with that from the fresh leaves and is an individual substance. Further, by repeated conversion into salt, and re-precipitation with acids, a substance of constant melting point 62°, and constant solubility and acidity is obtained. Titration of an ethereal solution with alcoholic KOH agreed well for one free carboxyl group. Titration after saponification with hot alkali for ½ hour computed well for an additional carboxyl group. To the salts from these two analyses were assigned the formulae



$$C_{38-n}H_{69-m}O\begin{matrix}\diagup COOK \\ \diagdown COOC_nH_m\end{matrix}$$

and $C_{38-n}H_{69-m}O(COOK)_2$. In order to de**termine the group C_nH_{2m}, the ester was boiled with nitric acid and the resulting di-carboxylic acid separated and purified, the final product being a brittle, transparent resin. This analyzed 75.25% C, 10.95 H, approximating $C_{37}H_{64}O_5$ or $C_{36}H_{62}O_5$.**

A molecular weight determination by elevation of the boiling point of solvent ethyl ether gave 556, 558, nearest for $C_{36}H_{62}O_5$ (574), giving to the original ester the formula



$$C_{34}H_{60}O\begin{matrix}\diagup COOH \\ \diagdown COO.C_4H_9\end{matrix}$$

. The two free carboxyl groups in the resin acid were proven by treatment with alcoholic potash, and titrating back with HCl; K used = 0.0735 gram, theory 0.0744; 0.0821, theory 0.0833. The author proceeded to further determine the carboxyl groups by acetylization (!). The free acid was acetylized with anhydride, the compound purified, and 5 grams saponified with alcoholic KOH. The product was distilled with H_3PO_4 for acetic acid and the final titration was 15.2 cc. N/1 NaOH; theory = 16.69 cc. for 2 acetyl groups substituted for the 2 hydroxyls in the carboxyl groups (*sic.*).

The residual O atom in the $C_{34}H_{60}O$ rest is not aldehydic, failing to reduce ammoniacal Ag solution, neither did treatment with PCl_5 chlorinate sufficiently for a ketone, the final product containing 11.0 per cent. Cl (theory for $C_{34}H_{60}O(COCl)_2$, 11.6).

In the summary, it is stated that the oxidation of the ester with HNO_3 leaves the di-carboxylic acid intact and that only the side group C_4H_9 is oxidized away to butyric acid which may be recognized. Kosmann (*J. ph.*, 26, 107) earlier found in the young leaves of the birch betuloretinic acid, $C_{36}H_{66}O_5$. The author thinks it probable that the resin here examined is the primary butyl ester of this acid, with a slightly different empirical formula.

W. J. K.

Sewage Disposal. W. P. MASON (Press and Publicity Com., A. C. S.). Being familiar with the fact that stable manure is a marketable article and commands no inconsiderable price, the average man is not a little mystified over the apparent difficulty met with in disposing city sewage. Most people are impressed, and rightly so, by the enormous tonnage of fertilizing material that is daily dumped to waste by our great cities; not alone in the shape of garbage, but also in the more or less liquid form flowing in the sewers. The aggregate volume of this sewage flow is great indeed; thus New York City turns into the local tide-waters no less than 600,000,000 gallons every twenty-four hours and proportionate amounts are disposed of in various ways by all cities and towns throughout the land. One hundred gallons of sewage per capita per day is not an unreasonable amount whereon to base an estimate, so that, with this figure in mind, the great flood of municipal waste to be cared for throughout the whole country certainly becomes impressive.

What many, if not most, of the people do not see is why this great bulk of fertilizer should be considered as waste material at all. Why is it not an asset? Why can it not be used to improve large tracts of land that now remain idle and well nigh valueless because of the poverty of the soil?

Persons who have seen the operation of the slow-sand filters that purify many of our municipal water supplies are aware of the millions of gallons of water that pass through these beds per day; and, knowing that the filtration process is a continuous one for weeks at a time, they anticipate a similar, or nearly similar, manner of procedure when sewage is the liquid to be filtered.

Although the form of oxidation termed "nitrification" is what is sought when slow-sand filtration is employed to improve either water or sewage there is a striking difference between the methods in which the sand beds are used in the two instances. Even the poorest water contains but little oxidizable matter compared with that in sewage, and so the amount of dissolved air present can easily furnish sufficient oxygen to accomplish all the work required to be done without need of actual re-aeration of the sand layer.

With sewage the matter is quite different. Much oxidation work is required and the quantity of oxygen in solution is practically nil, so that frequent admission of the atmosphere to the very depths of the bed is imperative as otherwise improvement of the effluent would quickly cease.

Given a favorably located stretch of sandy soil, a proper intermittent use of such an area would allow of between 5,000 and 10,000 gallons of sewage being turned upon it per acre per day, which would be equivalent to the setting apart of say 1,000 to 2,000 acres of land for the disposal of the sewage from a city of 100,000 people. Should the character of the soil be less favorable its area would naturally have to be greater in order to do the same amount and character of work. We can thus see how easy it would be to quickly water-log an unfit type of soil by turning upon it the sewage of comparatively few people and how easily a nuisance could be developed. A number of successful sewage farms now do exist, but their example cannot be universally applied as a means of sewage disposal, and the very best of these farms can take care of only a limited volume of sewage.

The problem of handling sewage is one which has recently received considerable attention from the American Chemical Society, and it is hoped that the time is not far distant when the enormous waste now going on may, by the efforts of the chemist, be turned to a source of profit.

Recent Advances in Leather Manufacture. ALLEN ROGERS. Address before N. Y. Section, S. C. I., April 13. The damage caused by the warble is discussed. It is stated that the fly lays her eggs on the fetlock and they are taken into the gullet. (This view has been clearly disproved. See this J., 1915, p. 199.—ED.) The use of sodium bisulphite in preventing salt stains is noted. Artificial bates and "arazym" which unhairs and bates are briefly discussed. White washable leather is being made by a combination chrome process. Extract tannage is discussed briefly, also improvements in the methods of patent leather manufacture.

Biochemical Treatment of Sewage with Special Reference to the Actitivated Sludge Method. GEO. T. HAMMOND. *J. Ind. and Eng. Chem.,* April, 1917. Address, Am. Chem. Soc., New York, Sept., 1916. The principal object of sanitary engineers in designing disposal plants is to bring together in the most suitable and efficient manner the decomposable materials, the oxidizing bacteria and a supply of air. All forms of sewage disposal on land, in the method known as broad irrigation or sewage farming; all filtration methods, such as the sand filter, the percolating or sprinkling filter (called in England a bacteria bed), the contact filter, etc.; and the various methods of aeration by compressed air, depend on the same fundamental principle, which is also nature's method as illustrated in the purification of streams, the principle of biochemical oxidation. The name "activated sludge" is due to Dr. Gilbert Fowler, of Manchester, England. The process antedates the name, Dr. Fowler having seen the work of Clark at Lawrence, Mass., in 1912, and given him his share of credit for the development of the process. The activated sludge method produces a clear effluent without smell or nuisance. The ground required for installing a plant is probably the least for any method of sewage treatment, and the tanks are less costly than filters capable of producing an equally stable effluent. First among the difficulties is the amount of sludge that must be disposed of, 0.2 to 0.4 per cent. on the volume of sewage, and having a water content of about 97 per cent. The sludge is highly putrescible unless dewatered, and methods of dewatering are relatively expensive. Filter pressing, centrifuging and the Dickson yeast process (see abstr., this J., 1915, p. 383) are discussed.

Chemical Control in the Leather Industry. D. Q. HAMMOND. *Chemical Engineer,* Feb.-Mar., 1917, p. 12. General sketch of the tanning process, followed by suggested problems for research. What kind of water is best for soaks? How does lime act on hide? How can hair be bleached? How should sulphonated oils be analyzed? The paper concludes with a plea for more confidence on the part of manufacturers in American chemists.

Consumption of Russian Stock of Hides. *Commerce Reports,* April 12. The Bureau of Foreign and Domestic Commerce is in receipt of advices that the stocks of hides and skins in Moscow are being rapidly reduced because Russian tanners have made great progress and are working all the calf, sheep, goat, and colt skins they can procure. The quality of the output is not irreproachable, but the demand causes defects to be overlooked.

Russian Leather Situation. COMMERCIAL ATTACHE WILLIAM C. HUNTINGTON, Petrograd, Jan. 23; translation from Explanatory Memorandum of the Russian Minister of Finance to the Budget of 1917. *Commerce Reports,* April 12. The leather industry was confronted with many problems, the most important being that of discovering the sources of skins and hides suitable for manufacture of sole leather and speeding up the production of the latter. The attention of private parties interested as well as Government institutions was focused on these questions from the very beginning of the war. Russian skins have always been considered too light for sole leather and were used mostly for uppers. The leather industry therefore was in no small way dependent upon the imports of heavy skins from Australia and South America. Russia imported about 1,200,000 such skins annually. This quantity, together with imports of sole leather and footwear, was ample to satisfy the normal demand for footwear, aggregating 40,000,000 to 50,000,000 pairs yearly. About 2,000,000 pairs represented boots for the army, the remainder the demand of the internal markets of the country. During the period of safe navigation in 1914, Russia imported approximately one-third of the normally required quantity of raw skins from America. During 1915 and 1916 only insignificant quantities were received. Comparing this with the normal demand for this three-year period it will be readily seen that the shortage of raw hides exceeded 3,000,000 skins, from which it would be possible to prepare soles and heels for 60,000,000 pairs of boots. The demand for boots and shoes meanwhile had practically doubled, while the needs of the army reached enormous proportions. The inevitable result was sharp advance in prices in raw materials, finished sole leather, and footwear. The disorganized condition of the leather market, coupled with speculative operations in hides and leather, eventually brought about Government supervision. On November 4, 1915, a special leather committee was appointed to consider the solution of various problems; among them, regulation of sales of raw skins and finished leather to insure tanneries with hides and shoe factories with the finished product. The question of equipping the factories and tanneries with tanning acids was solved by the All-Russian Association of Leather Manufacturers, which undertook to supply these requisites at reasonable prices. Some time later other organizations were called upon to assist. Pursuant to instructions of the Minister of War and the Minister of Trade and Industry, practically all raw hides were taken over by Government control. The duties of collecting the hides and carrying out all technical operations were assigned to the All-Russian Zemstvo Union and the Association of Leather Manufacturers.

As opposed to the condition of the heavy hide market, there is an abundance of light skins, such as pony skins, horsehides, and calfskins. According to estimates of the information bureau of the Nizhni Novgorod fair, the total number of calfskins in the country is 10,000,000. Since these skins have not been needed by the army and existing conditions make it almost impossible to finish them into chrome leather, it is not surprising that business in these hides was not active. The remaining skins (sheepskins, etc.) were much in demand by both the population and the army, and the quantities used doubled during the last year when compared with 1914 and 1915. Another factor worthy of note is the constantly increasing production of factories and tanneries. In 1914 the Siberian factories produced 400,000 semi-finished skins, whereas in 1916 these same factories produced over 600,000 semi-finished light skins. Of the many peculiarities connected with the leather situation it is interesting to note that, in the opinion of the provincial merchants, both Petrograd and Moscow lost their importance as leather centers. The buyers were convinced that it was much more difficult to make suitable purchases in either of these cities than it was in the country. Even the merchants and footwear manufacturers of Petrograd and Moscow are sending their representatives to provincial towns to make purchases of hides and skins, which, after their transport to Petrograd or Moscow, are either used for manufacturing purposes or sold at much higher prices.

Nizhni Novgorod Fair, 1916. *Commerce Reports.* The hide market was less important than usual. In the past Nizhni Novgorod has served as intermediary between the hide-producing region of Siberia and Central Asia and the central and riparian industrial regions of European Russia. Shipments were so light that the hide market assumed a wholly local character, buyers arriving only from neighboring tanning centers. Fresh cowhides brought $0.30 to $0.31 per pound before the end of the fair, as against $0.25 to $0.27 at the beginning. Horsehides were $0.30 to $0.65 higher per hide than in the spring. Siberian hides weighing about 18 pounds sold for $3 to $3.35 each, as against $1.66 to $2.33 in 1915. Russian horsehide of the same weight sold for as much as $3.66, against $2.16 to $3 in 1915, and 20-pound hides sold up to $4 and even $4.16. The shortage of hides at the fair caused considerable business for future delivery, a feature previously almost unobserved at this fair. This was the distinguishing feature of the trade in unclipped Siberian sheepskins, which were not brought to the fair at all. But transactions for shipment from the places of production were also small, as this article had been bought up to a great extent by factory agents working on military orders. Ural and a number of sorts of Caucasian and Persian sheepskins, which were more abundant than those from Siberia, were snapped up quickly at rising prices. The closing prices were as follows: Ural sheepskins, $1 for 7-pound skins, $0.80 for 5½-pound skins, $0.60 for 4⅓-pound skins, $0.43 for $2^4/_5$-pound skins; Caucasian sheepskins, $0.46 to $0.62 for the larger sorts and $0.33 to $0.46 for medium grades; Persian sheepskins, $0.70 to $0.73 for the heavier sorts and $0.53 to $0.66 for medium and light weight skins. In addition to cowhides, horsehides, and unclipped sheepskins, important articles of commerce at the fair under the heading of raw materials for the leather industry were calfskins, colt skins, goatskins, clipped sheepskins, etc. In calfskins remaining in the storehouses at Nizhni Novgorod from former years, there were a number of purely speculative deals, at prices ranging from $7.50 to $8 per pood ($0.208 to $0.222 per pound) for fallen goods and from $10.83 to $11.33 per pood ($0.30 to $0.314 per pound) for slaughter-house products. This registered a rise of prices amounting to about 50 per cent. as compared with 1915. Colt skins were taken at the beginning of the fair, Siberian at $0.53 to $0.66 per skin and Russian at $0.73 to $0.83. The scarcity of cowhides heightened the demand for camel skins, prices rising from $8 to $10 per pood ($0.222 to $0.277 per pound) of fresh goods. The necessity of furnishing leather footwear to the army explained the absence of finished leather from the market, with the exception of cuttings. The situation with raw leather was not much better. There was every reason to believe that no leather fair would take place at all, but, nevertheless, this fair not only took place but was considered comparatively successful.

The adaptability of the Russian market to new conditions of business was to be noticed in the fur market. Hitherto it had been thought that the Russian fur trade was strong only through its connection with foreign markets, and that the bulk of the fur business at the fair was done by foreigners. Many disasters were prophesied owing to the closing of the frontiers and to the discontinuation of foreign business. It was expected that the enormous stocks of karakul, which usually were exported to the United States through German brokers, would remain unsold and that the prices for karakul would drop. It was also expected that the market would suffer, owing to the shortage of imported furs. However, the results showed that all these fears were exaggerated.

Requisition of Skins in Hungary. CONSUL GENERAL WILLIAM COFFIN, Budapest. *Commerce Reports,* April 13. A decree of the Hungarian Government published February 16 states that persons in possession of lamb, sheep, or goatskins must declare them and offer them for sale within seven days from the issue of the order to the Military Institution for Taking Over Leather, at Budapest. The price to be paid for such skins will be fixed by a committee attached to the above-named institution. On and after the issuance of order, shearing the skins of the above-mentioned slaughtered animals is prohibited and the skins must be delivered unsheared.

Shark Skins Offered from South Sea Islands. *Commerce Reports.* Sources of shark skins for the manufacture of leather in the United States have been found as far away as the South Sea Islands during the campaign that has been conducted in behalf of this industry by the United States Bureau of Fisheries. One company recently advised the bureau that it has clients in the islands who are able to supply large quantities. Many others have given assistance in the development of this source of leather. Skins of various other species of fish are also being tested as possible raw material for leather production. The bureau has placed skins of 227 sharks and about 50 skins of other fishes, including cod, hake, grouper, garfish, and stingray, in the hands of tanners for experimentation. The tanned skin of one of the large sharks and small samples of others have been received. Several of these look very promising and indicate that satisfactory tanning processes are being developed. The skin of the large shark has been submitted to the Bureau of Standards for testing as to tensile strength, wearing qualities, etc. Two firms have advised the bureau that they are in the market for large quantities of fish skins and that they are utilizing these products. Two others recently perfected processes and are preparing to tan fish skins. Companies and fishermen in a position to obtain supplies of the raw materials are being advised as to where they may market them and have been furnished with information as to methods of skinning, salting, and boxing the raw hides for shipment. Manufacturers of leather goods are asking for samples of the finished product and later will be furnished with such samples, or advised where samples may be obtained. The bureau will also give attention to determining to what special uses these new leather products are best suited.

Production of Hides in British East Africa. CONSUL HENRY P. STARRETT, Mombasa. *Commerce Reports.* During the past ten years cattle hides from British East Africa and Uganda have become an important factor in the importation of that product into England, France, and Italy. The total exportation for the fiscal year ended March 31, 1915 (the last available detailed statistics), amounted to 48,054 hundredweight, of 112 pounds, valued at $1,034,982, of which Great Britain took 55 per cent., France 15 per cent., Italy 12 per cent., and Germany about 5 per cent. It is believed that some of these hides reach the United States by re-exportation from Liverpool and Genoa, and especially during the past year, when several large shipments were made indirectly. Owing to military operations in this territory, abnormal quantities of cattle have been used for transport purposes and for food, resulting in a present scarcity of stocks. Since the war began large quantities of hides have accumulated at the trading centers throughout German East Africa, and the movement of these stocks is now being facilitated. Heretofore East African hides have not borne a good reputation among European tanners owing to the careless way they are prepared for the market. As the product is sold by weight, the native is inclined to leave flesh on the hide in order to increase the weight. This, of course, provides an opening for injurious insects which abound in this climate, and results in destroying, to some extent, the texture of the hide. The native is also given to unnecessary branding of cattle, regardless of the effect on the hide, which is brought out in the tanning process. Although there has been considerable improvement in the methods of preparing hides for the market, it is but gradual, and the product consequently suffers a corresponding reduction in prices when offered for sale. The method of packing hides for export at Mombasa, the great entrepôt of the east coast, is as follows: All native hides are divided into four classes—"calfskins" (weighing up to 6 pounds each), packed 50 to 60 to the bale; "lights" (weighing from 6 to 12 pounds), packed 30 to 40 to the bale; "mediums" (weighing from 12 to 18 pounds), packed 25 to the bale; and "heavies" (weighing 18 pounds and up), and averaging 18 pieces to the bale. All bales weigh 300 to 380 pounds each, with an average of about 350 pounds, and the measurement ranges from 30 to 40 cubic feet per bale. Formerly hides were shipped loose or roughly tied together in bundles, but, due to present high freight rates and the practice of shipping companies to charge on the basis of cubic measurement, crude pressing machines have been introduced, which has resulted in more than doubling the weight per cubic ton. The present quotations for mixed lots of hides average about 28 cents per pound f. o. b. ship Mombasa or Kilindini. In normal times—during the early part of 1914, for instance—the price averaged about 16 cents per pound. The present through freight rate on this product from Mombasa to New York, with transshipment at Genoa, Liverpool, or Durban (Natal), is about $39 per ton of 40 cubic feet. The customs export duty on hides is 10 per cent. ad valorem, the value for customs being fixed quarterly by the Government, the present valuation being 18 cents per pound. In order to ship these goods to the United States, or approved countries other than British, special permission may be granted by the chief of customs at Mombasa by means of an application through the National Bank of India (Ltd.).

Tests for Neradol: Determining Extent of Tannage (under the title "Contributions to the Knowledge of Military Accoutrements, IV"). E. SEEL and A. SANDER. *Zeitschr. angew. Chem.*, 29, 325-6, 333-5 (1916), through *Chemical Abstracts.* Detection of artificial tannins in leather: Neradol D shows a pronounced phenol character; Neradol ND does not (being a condensation product of naphthalene-B-sulpho acid and formaldehyde and containing no phenolic OH groups). On treating solutions of Neradol ND with oxidizing agents, a phenol character similar to that of Neradol D was produced, probably due to the introduction of OH groups. The blue color obtained with Neradol D and 10 per cent. ferric ammonium alum is not very sensitive and is not applicable in the presence of other tannins. Cinchonin sulphate as pointed out by Appelius and Schmidt (abstr. this JOURNAL, 1914, p. 567) forms with Neradol D in the presence of HCl an insoluble precipitate in contrast to its action with most vegetable tannins. A precipitate is also formed with sulphite-cellulose extract. The same is true of the Procter-Hirst test (aniline and HCl). Furthermore, these reactions are carried out in such small concentrations, in which other tannins beside Neradol may be present (in leather extracts), that the tests are not sufficiently sensitive. The biological test of Kobert (abstr. this JOURNAL, 1915, p. 580) is not adapted to practical work. On adding potassium ferricyanide to a not too dilute solution of Neradol D, a green color is produced (may be noted in a 0.2 per cent. solution). Alkali turns the solution cherry red. With traces only of Neradol D as well as Neradol ND the reaction is not generally indicated. With tannin mixtures the characteristic color never appears. The *p*-nitroaniline reaction proposed by Laufmann for the detection of Neradol D acts similarly. Diazotized benzidine is more sensitive, giving a scarlet color (with Neradol D in alkaline solution), which becomes blue violet on treating with concentrated sulphuric or hydrochloric acid. Plant tannins, however, give a similar color; mangrove red, becoming carmine red with concentrated acids, and mimosa (wattle) a red-brown, becoming brown-red with acids. Owing to the similar colors, these azo dyes are not suited for the detection of Neradol in tannin mixtures. The authors found the oxyazo reaction a characteristic color test for identifying Neradol D in the presence of other tannins, and proceed as follows: Prepare the diazo solution by dissolving *p*-aminophenol or its hydrochloric acid salt in dilute hydrochloric acid, mix with ice and carefully diazotize in the cold till a slight excess of nitrous acid is detected; the solution must be kept ice cold to avoid decomposition. Test about 5 cc. of the leather extract with excess of alkali, cool by adding ice, add half of the volume of alcohol, and 3 or 4 drops of the reagent. Generally a distinct blue color results; otherwise acidify with HCl, shake with ether, draw off ether layer, wash with water, add caustic soda solution, obtaining with Neradol D a blue to blue-green color in the water. At the zone of contact a dark bluish-green ring forms. Other tannins (including Neradol ND) give under these conditions a yellow to yellow-green solution. The diazo solution should be tested against an alkaline phenol solution, yielding a dark blue color. Neradol ND gives the above test (blue color), only after treating with sodium hypochlorite; the leather extract or the tannin solution is heated a short time with a few drops of the hypochlorite solution, quickly cooled, an excess of ammonia added, and the test made as above. The best test for the detection of even traces of Neradol D (and combined with sodium hyposulphite for Neradol ND) in leather extracts is the indophenol reaction. All the tests recommended in the literature, without exception, failed in such cases. To make the test, add a drop of the dimethyl salt solution to 5 cc. of the extract, render alkaline with caustic soda, add 1 or 2 drops of a 5 per cent. potassium ferricyanide solution. In the presence of Neradol D a blue color forms at once or after some time. The reaction becomes sharper by adding alcohol to the alkaline solution and then the ferricyanide; on standing a blue zone forms, which on longer standing passes into the alcohol. This reaction will show distinctly the presence of traces of Neradol. Neradol ND gives the test after treating with hypochlorite as above. In preparing extracts from leather, the Neradol should be concentrated and interfering admixtures removed. The simplest procedure is the Stiasny formaldehyde reaction: Heat 20 grams of the leather in small cubes for ¼ to ½ hour with 250 cc. of water; to 100 cc. of the hot filtered solution add 20 cc. of a mixture of equal parts of 40 per cent. formaldehyde, concentrated HCl and water and boil ½ hour under a reflux condenser, cool and filter. Evaporate the filtrate on the water bath, filtering if necessary; or dialyze, changing the water frequently. Evaporate the solution obtained by dialysis to a small volume. On adding lime water or a calcium salt to an extract after neutralizing with ammonia the tannins other than Neradol can be precipitated. Filter off the dark precipitate and evaporate the dark brown solution to a small volume on the water bath. All of the solutions obtained by the above methods give strong positive tests if the materials contained Neradol.

Microscopic Examination to Determine the Completeness of Tannage.—The usual method is simple inspection of a strip cut from the skin, the part not tanned being observable as a brighter colored stripe in the middle of the section. The acetic acid test, the Fahrion hot water test, and the Grasser indigotine test are valuable for works control. With Neradol D leather, ferric ammonium alum is a good indicator, the tanned part only being colored a deep blue. A series of experiments on the adaptability of various dyes for coloring leather sections fully confirmed the assumptions of Hundeshagen (*Chem. Zentr.*, 1902, 751-4), relative to the use of combination colors in differentiating albumens. Owing to the acid character of the tannins, basic dyes have a greater affinity for the tanned hide. On treating leather with a basic dye, only the tanned portion is really dyed, the color may be washed out of the untanned part with water and alcohol. Acid dyes also make differentiation possible, as they dye the untanned parts against the action of alcohol, in tones corresponding to the dye used, while the tanned parts give other tones. Especially good results were obtained with double dyeing: using first a basic dye, washing with water and alcohol, and then using an acid dye, followed by washing with water and alcohol. In making permanent preparations, the colored sections must be very carefully and thoroughly washed. The authors give a table showing the best results of a number of experiments with the following dyes: malachite green, brilliant green, methyl green, Bismark brown, rhodamine, eosine, patent blue, alkali blue, brilliant green and eosine, rhodamine and patent blue. Less characteristic colorings were obtained with naphthol yellow S and azo-acid blue. Many basic dyes, as safranine and methyl violet, gave less valuable results, being easily removed with alcohol. Other dyes, as methylene blue, color the tanned and untanned parts in similar tones and are unsuited for selective coloring. The extent of tannage of the colored sections is quickly determined microscopically, and this method is preferred to the acetic acid test. The sections are best obtained from the moistened leather by means of a strong microtome instead of a razor. Numerous references to the literature are given.

Skins for Fancy Leather Purposes. ANONYMOUS in *Leather Manufacturer,* April, 1917. Review of methods of tanning and dyeing. Boric acid is recommended for deliming and formic acid for pickling. Tannage with quebracho, to which alum and salt may be added, is followed by sumac.

Tests of a New Process of Sewage Purification. ROBERT S. WESTON, Asst. Professor of Public Health Engineering, Mass. Inst. of Technology. *Boston City Record,* March 3, 1917. The process in question has been patented by George W. Miles, 88 Broad St., Boston. Experiments were conducted by E. S. Dorr, Engineer of the Boston Public Works Dept., between 1911 and 1914, and by the Sanitary Research Laboratory of the Mass. Inst. of Technology, under the auspices of the Boston authorities, in July and November, 1915. The method is to add an acid to the sewage, which promotes the settling of a sludge with less than the ordinary water content, and it may therefore be dried and the grease extracted from it, so that the grease is made available, and the residue is much more satisfactory for fertilizer use than a grease-containing sludge. In the experiments tried, the acid used was sulphurous, sulphur dioxide being bubbled through the sewage before it passes to the settling tank. One effect of the sulphur dioxide is to reduce the bacterial content of the sewage from millions to hundreds per cubic centimeter. The deodorizing effect of the SO_2 prevents the sewage treatment from creating a nuisance in the neighborhood. The acid treatment decomposes soaps present in the sewage, so that the quantity of fats recoverable is more than that indicated by ether treatment of the dried sewage. A summary of results of the July, 1915, experiments is as follows: Moisture in sludge, average, 81.6 per cent.; pounds of dry sludge per 1,000,000 pounds of sewage, 249; fats (by ether) on dry sludge, 22 per cent.; parts per 1,000,000 of grease in a sewage, 56; ammonia in dry sludge, 3.6 per cent. November experiments: Average moisture in sludge, 93.5 per cent.; pounds dry sludge per 1,000,000 pounds sewage, 177; fats (by ether) on dry sludge, 24 per cent.

Utilization of Horsehide. *La Halle aux Cuirs,* March 4, 1917. A Government circular has been issued in relation to the utilization of horsehides. Such hides are to be assigned to tanners who are equipped to tan them in the manner prescribed. The hides are to be cut into bellies, heads, shoulders and butts. The butts are to be tanned with bark and used for taps for repairing soles. The bellies and heads are to be chrome tanned after splitting, so as to furnish leather about 0.032 inch thick, for tops of shoes. The shoulders are to be bark-tanned into leather about 0.1 inch thick for cavalry leggings. The method of cutting is prescribed, and prices for the several kinds of leather are fixed. L. B.

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CORRECTION.

In the May issue, page 190, Sumac table, non-tannin column, the sixth number should be 18.23 instead of 10.23.

FOURTEENTH ANNUAL MEETING.

The Fourteenth Annual Meeting of the American Leather Chemists Association will be held at the Marlborough-Blenheim, Atlantic City, N. J., June 7, 8 and 9, 1917. Terms for rooms at the hotel were given in the April Journal. Members will please make their own reservations.

Meetings will be in the West Solarium, beginning at 10 A. M. and 2 P. M.

PROGRAM.

THURSDAY MORNING.

Opening Remarks by the President........................C. R. Oberfell

Report of the Secretary and Treasurer......................H. C. Reed

Committee Reports:

- Comparative Analysis...............................R. H. Wisdom
- The Testing of Dyes for Leather.......................G. T. Creese
- Solubility of Hide in Salt Solution and Effect of Alkali on Soaking Dry Hides ....Lloyd Balderston

THURSDAY AFTERNOON.

Address:

Nigrosines ....Dr. J. Merritt Matthews

Committee Reports:

Analysis of Sulphonated Oils..........................W. K. Alsop

Effect of Hard Water on Tannins......................T. A. Faust

Sulphuric Acid in Leather..........................C. R. Oberfell

Specifications for Kaolin..............................R. W. Frey

Analysis of Tannery Effluent............................W. A. Fox

Address:

Studies Conducted by the Public Health Service in Regard to the Sanitary Disposal of Tannery Wastes............H. B. Hommon

FRIDAY MORNING.

Anthrax Symposium:

Addresses:

Anthrax............................Dr. A. S. Ross, Camden, N. J.

Practice and Theory on Treatment and Diagnosis of Anthrax
Dr. H. Z. Frisbie, Elkland, Pa.

The Nature of Anthrax and Anti-Anthrax Serum
Dr. John Reichel of H. K. Mulford Co.

Studies on the Disinfection of Tannery Wastes.......A. M. Buswell

Anthrax and Disinfection of Hides...................V. A. Wallin

The Future of Hide Supply.................Alfred Seymour-Jones

Discussion..........Dr. Hickman of the Bureau of Animal Industry

FRIDAY AFTERNOON.

Tanners and Chemists "Round Table" discussion.

Address:

Drum Tannage ....Oskar Reithof

SATURDAY MORNING.

Address:

Borax and Boric Acid in the Tannery and Currying Shop
H. L. Harris

Discussion of recently advanced ideas on "Theory of Leather Formation"

John Arthur Wilson
Dr. L. Balderston
Robert W. Griffith
Dr. William Klaber
H. C. Reed
F. H. Small
Dr. Allen Rogers
J. H. Yocum

SATURDAY AFTERNOON.

Executive Session.

Election of Members of the Council.

Council Meeting.

DISINFECTION OF TANNERY WASTES.

By D. D. Jackson and A. M. Buswell.

A. Discussion.

- Historical.
  - Nature and prevalence of anthrax.
    - *a.* Among cattle.
    - *b.* Among hide and leather workers.
  - Prophylaxis.
    - *a.* Vaccination.
    - *b.* Disinfection.
  - Previous work.
    - *a.* Treatment of tannery effluent without disinfection.
    - *b.* Disinfection of tannery effluent.
- Instigation of Present Work.
- Results of Present Work.
  - I. Laboratory Tests.
    - The different disinfectants used: SO_2, $CaCl_2O$, with $CaCl_2O$, H_2SO_4.Cl_2.
    - The amounts of these disinfectants required to kill highly resistant anthrax spores:
      - *a.* In pure water.
      - *b.* In "Anderson's Mixture."
        - Notes: 1. Objection to using artificial organic mixtures in testing disinfectants.
        - 2. The reaction $Cl_2 + H_2O \rightleftharpoons HClO + HCl$.
      - *c.* In effluent from contact beds (town plant).
      - *d.* In tannery effluent.
        - 1. Settled.
        - 2. Screened.
    - The attenuation of spores not actually killed by the disinfectant.
  - II. Tests on Entire Tannery Effluent.
    - Description of the screening and chlorinating plant.
      - *a.* Flow.
      - *b.* Size of screens.
      - *c.* Disposal of screenings.
      - *d.* Chlorine regulator.
    - Efficiency of screens (amount and character of suspended matter removed).
    - Effect of disinfection.
      - *a.* With hypochlorite.
      - *b.* With liquid chlorine.
      - *c.* With liquid chlorine after screening.
    - Conclusions.

B. Experimental.

- I. Laboratory.
  - Source of cultures, biochemical reactions, virulence.
  - Relative resistance of different strains.
    - *a.* To boiling.
    - *b.* To chlorine.
  - Preparation and assay of disinfectants.
    - Neglect of previous workers in this respect, especially where so-called solutions of chlorine were used.
  - Tables showing resistance of strains 27c to SO_2, $CaCl_2O$, $CaCl_2O$ with H_2SO_4, Cl_2.
    - *a.* In pure water.
    - *b.* In "Anderson's Mixture."
    - *c.* In effluent from trickling filters.
    - *d.* In tannery effluent.
      - 1. The composition of the tannery effluent.
      - 2. Settled.
      - 3. Screened.
  - The attenuation of surviving spores.
- II. Examination of the Tannery Effluent, Treated and Untreated.
  - Efficiency of chlorination.
    - *a.* Method of sampling.
    - *b.* Preparation of portions for inoculation.
      - 1. Pasteurization.
      - 2. Settling.
    - *c.* Autopsy.
    - *d.* Results of tests on plant (dates and results of autopsy).
      - 1. Using hypo.
      - 2. Using Cl_2.
      - 3. Using Cl_2 after screening.

Historical.

Nature of Anthrax.—Anthrax,[1] or charbon, may be defined as an infectious disease which is caused by specific bacteria known as anthrax bacilli, and which is more or less restricted by conditions of soil and moisture to definite geographical localities. While it is chiefly limited to cattle and sheep, it may be transmitted to goats, horses, cats, certain kinds of game, and even to man. Smaller animals, such as mice, rabbits and guinea pigs speedily succumb to inoculation. Dogs and hogs are slightly susceptible, while fowls are practically immune. The variety of domesticated animals which it may attack makes it a question of great economic importance.

It[2] is a disease that is widely spread throughout the world, and in the United States is coming to be recognized as a matter worthy of extensive scientific investigation. In certain sections it is more frequent than in others. It appears to be particularly prevalent in the Southern States, and since no determined effort has been made towards its suppression it seems to be on the increase, its presence now being recorded in localities where it has never before been known.

Anthrax[3] is primarily a disease of the herbivora, attacking especially cattle and sheep. Infection not infrequently occurs in horses, hogs and goats. In other domestic animals it is exceptional. Man is somewhat susceptible to the disease and contracts it either directly from the living animals or from the hides, wool, or other parts of the cadaver used in the industries.

The history of the disease dates back to the most ancient periods and anthrax has, at all times, been a severe scourge upon cattle- and sheep-raising communities. The plague invoked upon the Egyptians referred to in Exodus ix, 3-10, and the "Army's plague" referred to in the first book of Homer's Illiad appear to have both been anthrax. Seneka, Ovid, Plinius, Plutarch and Livy give descriptions which can be recognized as anthrax. Of all infections attacking the domestic animals no other has claimed so many victims. In Russia, where the disease is most common, 72,000 horses are said to have succumbed in one year (1864).[4]

Especial historical interest is attached to the anthrax bacillus in that it was the first micro-organism proved definitely to bear a specific etiological relationship to an infectious disease. The discovery of the anthrax bacillus, therefore, laid as it were, the cornerstone of modern bacteriology. The bacillus was first observed in the blood of infected animals by Pollender in 1849, and, independently, by Brauell in 1857. Davaine,[5] however, in 1863, was the first one to produce experimental infection in animals with blood containing the bacilli and to suggest a direct etiological relationship between the two. Final and absolute proof of the justice of Davaine's contentions, however, was not brought until the further development of bacteriological technique, by Koch,[6] had made it possible for this last observer to isolate the bacillus upon artificial media and to reproduce the disease experimentally by inoculation with pure cultures.

(1) The cause of anthrax is a microscopic organism known as the anthrax bacillus. In form it is cylindrical, or rod-like, measuring 5 to 10 microns in length and 1 micron in diameter. Like all bacteria, these rod-like bodies have the power of indefinite multiplication, and in the body of infected animals they produce death in about 3 or 4 days. In the blood they multiply in large numbers by becoming elongated and then dividing into two, each new organism continuing the same process indefinitely. Outside of the body, however, they multiply in a different way when under aerobic conditions. Oval bodies, which are called spores, appear within the rods, and remain alive and capable of germination after years of drying. They also resist heat and chemical reagents to a remarkable degree. The bacilli themselves, on the other hand, show but little resistance to heat and drying. It has long been known that the anthrax virus thrives best under certain conditions of the soil and on territories subject to floods and inundations. The particular kinds of soil upon which the disease is observed are black, loose, warm, humous soils, also those containing lime, marl and clay, finally peaty, swampy soils resting upon strata which hold the water, or, in other words, are impervious. Hence, fields containing stagnant pools may be the source of infection. The infection may be limited to certain farms, or even to restricted areas on such farms. Even in the Alps, over 3,000 feet above sea level, where such conditions prevail in secluded valleys, anthrax persists among herds.

Meteorological conditions have an important share in determining the severity of the disease. On those tracts subject to inundations in spring, a hot dry summer is likely to cause a severe outbreak. The relation which the bacillus bears to these conditions is not positively known. It may be that during and immediately after inundations or in stagnant water the bacilli find enough nourishment to multiply and produce an abundant supply of spores, which are subsequently carried in a dry condition by the winds during the period of drought, and disseminated over the vegetation.

Another source of the virus, and one regarded by most authorities as perhaps the most important, is the body of an animal which has died of anthrax. It will be remembered that in such bodies the anthrax bacilli are present in enormous numbers, and wherever blood or other body fluids are exposed to the air on the surface of the carcass, there the formation of spores will go on in the warm season of the year with great rapidity. It will thus be readily understood how this disease may become stationary in a given locality and appear year after year and even grow in severity if the carcasses of animals which have succumbed to the disease are not properly disposed of.

We have thus two agents at work maintaining the disease in any locality—the soil and meteorological conditions, and the carcasses of animals which have died of the disease. Besides these dangers which are of immediate consequence to cattle on pastures, the virus may be carried from place to place in hides, hair, wool, hoofs and horns and it may be stored in the hay from infected fields and cause an outbreak among stabled animals.

Prevalence of Anthrax.—The importance of the problem of the control of anthrax may be readily seen from the following statistics: In Germany[7] there were in the period 1900-1908, 1,042 cases of anthrax in man and 49,458 in animals. In England there were 162 human cases and 26 deaths from 1910 to 1912. In France during the same period there were 134 cases. In Russia from 1904 to 1909 there was an average of 16,000 cases per year. In the United States from 20 to 25 human deaths from anthrax have been reported yearly.

Anthrax among cattle has not been unusual in New York State[8] and for many years certain foci of the disease have been recognized. In 1912-13 there were 27 cattle outbreaks in 15 counties with 116 deaths; in 1913-14 there were 35 outbreaks in 16 counties with 83 deaths, a total of 62 outbreaks in 2 years in 21 counties, with 189 deaths. Only 10 counties in the 1913 list responsible for 22 outbreaks and 80 deaths appear in the 1914 list with 29 outbreaks and 60 deaths.

Prophylaxis.—There are three methods for preventing the spread of anthrax. First: The vaccine treatment originated by Pasteur and improved by later workers. We can not include here a detailed account of the technique of this treatment. Suffice it to say, however, that while the method is effective it can not be carried out except by an experienced person and since there is a small mortality from the treatment its use is not recommended except in localities known to be infected. Second: General sanitary precautions. Wet infected ground should be fenced off or drained. Carcasses of animals dead of anthrax, should be burned or buried deep without being opened, and the place where they have lain should be burned over or disinfected. Third: Since it is impossible to enforce such sanitary regulations in countries other than our own, infected hides cannot be excluded from importation. In this case imported hides should be disinfected and the effluent from tanneries should be treated so that they will not infect streams into which they are emptied nor pasture lands through which such streams may flow.

Previous Work.—The treatment of tannery wastes has up to the present time been limited to the removal of putrescent matter and suspended solids. The aim has been principally to prevent nuisance. The work of Eddy and Vrooman[9] and that of Clark[10] may be cited as typical of the methods of handling tannery wastes. Eddy and Vrooman, working at Gloversville, N. Y., found that 70 per cent. of the solids from tannery effluents could be removed by sedimentation. The effluent from the sedimentation tanks was easily treated by biological processes. The presence of chemicals such as lime, arsenic, dyes and so forth did not inhibit the bacterial action in septic tanks and sprinkling filters. For the combined tannery and domestic sewage, about two of the former to three of the latter, after sedimentation of the tannery waste at the tanneries, sprinkling filters at a rate of 1,000,000 gallons per acre per day with sedimentation and sand filtration of the sprinkling filter effluent were recommended. Clark, experimenting for a period of 14 years at different tanneries in Massachusetts, found that sedimentation followed by sand filters operating at a rate of 50,000 to 75,000 gallons per acre per day gave a satisfactory effluent. Trickling filters operating at 500,000 to 1,000,000 gallons per acre per day gave good results. Coke and iron filings removed most of the arsenic.

Hein[11] attempted the bacterial purification of soak liquors, adding various reagents until the odor and turbidity were removed. The results of his experiments may be seen from the following table:

	Reagents in parts per 1,000,000		Bacterial count (Original 2,000,000/cc.)
$Fe_2(SO_4)_3$ Bleach	250 200	added together	640
$Ca(MnO_4)_2$	100		0
NaClO	3,000		8,500

The author states that the cost of such treatment would be excessive.

Winterberger[12] found that in average tannery effluent, bleach to the extent of 700 parts per 1,000,000 of available chlorine killed anthrax spores in most cases in 2 to 4 days, 1,700 parts per 1,000,000 available chlorine was effective in most cases in 3 days, 7,000 parts per 1,000,000 available chlorine was always effective and that 1,700 parts per 1,000,000 available chlorine + 700 parts per 1,000,000 of HCl was always effective. The cost of a treatment such as these experiments would indicate would be quite prohibitive.

Aside from the article last cited little seems to have been done to disinfect tannery wastes or the effluent from the various clarification operations mentioned above. As far as we are aware the installation to be described below is the only one where disinfection of a tannery effluent for the prevention of spread of anthrax has been attempted on a large scale and over a long period.

The anthrax bacillus belongs to the group of spore bearing bacteria, *i. e.*, it may produce small oval bodies known as spores, which are highly resistant to heat and to the action of chemical disinfectants. In the disinfection of water supplies and domestic sewage, it has usually been considered necessary to destroy only the non-spore bearing group of intestinal bacteria. The problem of tannery waste disinfection is essentially a new one in that it is necessary to kill or attenuate these resistant bacterial spores.

Instigation of the Present Work.—About two years ago an epidemic of anthrax was said to have been caused by the infection of meadows by the waste from a tannery. The authors were requested to investigate the subject and devise means for treating the effluent from the tannery which would prevent the possibility of any further spread of infectious matter.

Results of Present Work.—The investigation showed that anthrax was at times present in the factory effluent. Accordingly laboratory experiments were carried out with various disinfectants to determine what was the most effective and least expensive method of treating the sewage. The results of these experiments in which highly resistant anthrax spores were used, may be summarized as follows:

Sulphur dioxide, when added to the extent of 20 parts per 1,000,000, reduced the count of a water suspension of spores from 800 to 500 in one hour. Potassium permanganate in a concentration of 20 parts per 1,000,000 reduced the count of the same emulsion to 550 in one hour. Calcium hypochlorite, "bleach," when added to the extent of 20 parts per 1,000,000 of available chlorine reduced the count of a water suspension of spores from 45 to 1 in one hour while 3 parts per 1,000,000 of chlorine gas reduced the count from 700 to 0 in 45 minutes.

Three hundred parts per 1,000,000 of chlorine gas had no apparent effect upon a suspension of 2,000 spores per cubic centimeter in Anderson's gelatin peptone solution.[13] These data emphasize the danger of drawing conclusions from the results obtained with artificial organic mixtures when testing disinfectants. From the data given by Rideal[14] one calculates that gelatin and peptone will combine with about a third of their weight of chlorine to form insoluble compounds. Since Anderson's solution contains 5 per cent. gelatin and 10 per cent. peptone no disinfecting action could be expected until more than 5,000 parts per 1,000,000 of chlorine had been added. Such a mixture bears no relation to tannery effluent as will be seen by the data presented in the experimental part.

Some authors[15] have assumed or led one to infer that chlorine and hypochlorites (or hypochlorous acid) have practically the same disinfecting action, and have reported experiments with chlorine when in reality they were using hypochlorous acid. It is well known, of course, that when chlorine dissolves in water a certain amount of hypochlorous and hydrochloric acids are formed according to the reaction:

$$Cl_2 + H_2O \rightleftharpoons HClO + HCl.$$

That this reaction is reversible is equally well known, for if one adds a considerable amount of strong acid to a concentrated solution of hypochlorous acid or a hypochlorite, chlorine gas is given off. But the speed of this reaction is low in either direction. Jakowkin[19] for instance found that at 0° it required apparently 20 to 24 hours for a chlorine solution to come to equilibrium and that at 10° it required about 6 hours for equilibrium to be established. He also states that a freshly prepared solution of hypochlorous acid when shaken with carbon tetrachloride lost scarcely a trace of chlorine to the carbon tetrachloride. After standing some time in contact with the HClO solution, a small amount of Cl_2 was dissolved by the CCl_4. Our experience has been that the disinfecting action of these reagents is complete in ½ to 2 hours. Unless Abt[15] and Winterberger[12] prepared their acidified solutions of hypochlorite some time before they were used they could not have contained an appreciable amount of free chlorine. Jakowkin's data show that a solution of Cl_2 in the presence of $^1/_{40}$ *N* HCl is 20 per cent. hydrolized to form HCl and HClO at equilibrium. Since this is roughly the concentration of acid used by Winterberger, his solutions would not have contained more than 80 per cent. of their "available chlorine" as Cl_2 if they had been allowed to come to equilibrium.

Since the ionization constant of HClO is about one-tenth as great as that for the first H ion of H_2CO_3 we may assume that in natural waters and sewages $CaCl_2$ reacts as follows:

$$2CaCl_2O + 2H_2CO_3 \rightleftharpoons CaCl_2 + Ca(HCO_3)_2 + 2HClO$$

This reaction is sometimes written

$$CaCl_2O + H_2CO_3 = CaCO_3 + HClO + HCl,$$

which is obviously incorrect, since HCl is almost completely ionized in these dilutions and could not exist in the presence of $CaCO_3$.

We know that chlorine may act in three ways on organic compounds, namely, substitution, addition and oxidation. That halogens have a rather special action on gelatin and peptone is shown by the work if Rideal cited above.

From these theoretical considerations we would expect chlorine to have a greater disinfecting action than hypochlorites or hypochlorous acid. That this is indeed the case has been shown by Jackson[16] and others when the B. coli group were used as the test organisms. When anthrax spores are used to test the disinfecting action, chlorine has a decided advantage as shown by the data cited above.

Bleach, when added to the extent of 20 parts per 1,000,000, to a suspension of anthrax spores in tannery effluent which had settled for 20 minutes to remove the heavier solids, reduced the count from 500 to 350 in 2½ hours. The addition of 20 parts per 1,000,000 of sulphuric acid to the 20 parts per 1,000,000 of bleach did not materially increase the bactericidal effect. Chlorine gas, however, was found to be a very effective agent in the presence of organic matter. Fifteen to 20 parts of chlorine per 1,000,000 will kill anthrax spores when suspended in the effluent from trickling filters and 50 parts per 1,000,000 will kill anthrax spores when suspended in tannery effluent which had settled for 20 minutes. In the above cases a time of 2 hours was allowed for the disinfecting action to take place. Tannery effluent from which the coarser particles of hair and fleshings had been removed by a Reinsch Wurl screen with 2- by $^{2}/_{64}$-inch slots was next tried as a medium for the suspension of spores. When as large a number as 1,200 to 3,000 per cc. of anthrax spores were suspended in this medium, and treated with 50 parts per 1,000,000 of chlorine the spores were not all killed. The surviving spores appear, however, to be strongly attenuated. One cc. portions of five disinfected test flasks which showed 20-60 colonies per cc. when plated on agar, were injected into guinea pigs. In all cases the pigs inoculated with this disinfected effluent survived.

This question of attenuation is of great importance. As in the case of the treatment of drinking water supplies, disinfection does not necessarily imply absolute sterilization, but a treatment which renders the effluent non-infectious.

Tests on Entire Effluent from Tannery.—As soon as it was found that anthrax was at times present in the tannery effluent, treatment with hypochlorite to the extent of 20 parts per 1,000,000 was started. This treated effluent was tested for anthrax with the result that anthrax was found in both the sludge and the supernatant liquid after 20 minutes settling. In the meantime the laboratory experiments referred to above, had shown that chlorine gas was very much more efficient than hypochlorite. Accordingly Wallace and Tiernan's chlorine regulating device was installed and the effluent was treated with 50 parts per 1,000,000 of chlorine. Tests on the effluent treated with chlorine showed that anthrax survived in the sludge but that it was not present in the supernatant liquid after 20 minutes settling.

There were two reasons why it did not seem practicable to settle the tannery effluent at the factory if it could be disinfected without sedimentation. First, on account of the location of the tannery and the contour of the surrounding land, the construction of sedimentation tanks would have been difficult. Second, at the time this investigation was commenced, facilities had already been provided for such treatment by the village in which the tannery was located. The tannery effluent flowed into the village sewer and was carried with the village sewage to the village disposal plant. This disposal plant consisted of sedimentation and septic tanks, and contact beds, and was designed to handle the entire flow of the village and tannery, about 1,000,000 gallons per day.

In order to remove the coarse suspended matter, Reinsch Wurl screens 8 feet in diameter with slots $^2/_{64}$ inch by 2 inches were installed to screen the effluent from the tannery which average 500,000 gallons per day. These screens remove from four to six barrels per day of matted hair, fleshings, and small pieces of hide. In other words, the most likely carriers of anthrax spores, the matted hair and fleshings, are removed by the screens. The screenings are shipped to a fertilizer plant where they are disinfected by steam. The screened sewage is treated with 50 parts per 1,000,000 of liquid chlorine by means of Wallace and Tiernan's chlorine regulating apparatus.

This complete installation has been in operation for 14 months and during that period raw and treated sewage has been frequently tested for anthrax. At no time since the installation was complete, have we found anthrax in the treated sewage. On six occasions during this period anthrax was found in the raw sewage but not in the treated. Further proof of the efficiency of this method of treatment is the fact that there have been no further outbreaks of anthrax among cattle in the district which was liable to infection from the tannery.

Naturally the strength of the factory effluent or its absorption of chlorine should be tested in each individual case to insure efficient results. However, we feel justified in concluding as a result of this extensive series of experiments carried out in the laboratory, and corroborated by actual practical tests on a large scale, that for average conditions fine screening followed by chlorine treatment to the extent of 50 parts per 1,000,000 is effective for preventing the spread of anthrax from tannery wastes.

B. EXPERIMENTAL.

Source and Characters of Anthrax Strains.—The strains of anthrax used in the laboratory investigations of the efficiency of various disinfectants were isolated from samples of tannery effluent. No variation was observed in the growth of the different strains on agar, gelatin, milk, broth and peptone; there was some variation in the reduction of nitrates, and in the size of the cells in the different strains. There was no great variation in the virulence, all strains killed guinea pigs in two to four days. It is our purpose to investigate in detail the characteristics of the strains which have been isolated. The importance of such an investigation and its bearing upon the question of the necessity for a polyvalent vaccine is obvious, and we regret that we have not been able to carry it out in connection with the present work.

Relative Resistance.—Of four strains investigated three resisted boiling for two minutes and one, number *27c*, resisted boiling for three minutes. The boiling tests were made as follows: Water emulsions of the growth on potato were prepared, and sealed into thin-walled capillary tubes, the melting-point tubes of the organic chemist. The sealed tubes of emulsion were immersed in boiling water for the desired length of time, cooled in cold water and transferred to broth media by breaking one end of the tube and holding this open end in the mouth of the culture tube while the other end was heated in the flame. These boiling tests were carried out on a day when the barometric pressure was such that the water boiled at 100° C.

Eight strains were selected more or less at random to determine whether there was any considerable variation in their resistance to disinfectants.

The results of tests made with Cl_2 as the disinfectant are shown in Table I, and the results of tests made with calcium hypochlorite as the disinfectant are shown in Table II. An examination of these tables shows that strain *27c* is decidedly the most resistant. This was the strain selected for the laboratory experiments on the disinfection of sewage described below.

Preparation and Assay of Disinfectants.—As mentioned above some authors have not been explicit in describing the way in which their disinfectants were prepared, and how the strength of their preparations was determined. For example, some have failed to distinguish between chlorine and hypochlorites or hypochlorous acid. We therefore have inserted here an account of the preparation and assay of each of the disinfectants used by us.

Sulphur dioxide was purchased in cylinders in the liquid state, from which a strong aqueous solution was prepared. The strength of this solution was determined by titrating against sodium hydroxide, using methyl orange as an indicator. This solution was then diluted to a convenient strength for use and the strength of the diluted solution was checked by titration as above.

Potassium permanganate was weighed out in the calculated amount and dissolved in water.

"Bleach," or calcium hypochlorite, of good quality was dissolved in water to make about a 2 per cent. solution. The available chlorine in this solution was determined by acidifying with acetic acid, adding the necessary amount of potassium iodide and titrating against $N/_{10}$ sodium thiosulphate. This solution was then diluted to a convenient strength for use and the dilution checked by titration as above.

Chlorine was obtained as a liquid in cylinders or was prepared by allowing concentrated hydrochloric acid to drop on potassium permanganate. A saturated aqueous solution of chlorine was prepared and its strength determined by titrating against thiosulphate after the addition of the necessary amount of potassium iodide. A dilute solution of convenient strength for use was prepared and its strength checked by titration as above. The dilute solutions of bleach and chlorine were never prepared more than an hour before they were used.

Discussion of Tables I to XII.—In the viability tests reported in the following tables, a water emulsion of the growth on agar of our strain *27c* was used. The emulsion was heated to 80° C. for 30 minutes to kill all vegetative forms. Measured amounts

TABLE I.—VIABILITY TEST.

Test Organism—B Anthracis 8 strains.
Suspended in water.
Germicide—Cl_2.

Strain Number	32		7		131c		1231/265		12/5/40s		29/2		818/42		27c	
	Colonies developing after exposure															
Time	15′	60′	15′	60′	15′	60′	15′	60′	15′	60′	15′		15′	60′	15′	60′
P. P. Mil. of Cl_2																
0	150		200		1000		185		400		23		550		685	
0.3	75	5	150	200	1000	1000										
0.7	150	100	150	185	1100	1150										
1.0	100	0	125	0	150	0										
1.5	95	0	200	1	1150	0	17	0	100	0	12	0	600	0	520	300
2.0	1	0	20	0	400	0										
2.5							31	0	0	0	1	0	520	0	88	1
3.0	0	0	8	0	0	0									35	0

of this suspension were added to sterilized 100 cc. portions of water or the various natural and artificial organic mixtures as indicated in the tables. After the addition of the desired amount of disinfectant 1 cc. portions were withdrawn from the disinfected mixture at stated intervals and plated on agar. The number of colonies developing on the plates after incubation is indicated in the tables.

TABLE II.—VIABILITY TEST.

Test Organism—B Anthracis 5 strains.
Germicide—Bleach.

Strain Number	1231/268		1215/408		29/2		818/42		27c	
			Colonies developing after exposure							
Time	15"	60"	15"	60"			15"	60"	35"	15"o
P. P. Mil of Cl_2										
0	185		400		38		550		45	—
10	0	0	6	0	1	0	70	7	20	—
20	0	0	0	0	2	0	3	1	1	1
25	—	—	—	—	—	—	—	—	7	—
50	—	—	—	—	—	—	—	—	7	—
75	—	—	—	—	—	—	—	—	1	—
100	—	—	—	—	—	—	—	—	0	0

As mentioned above, Tables I and II show the relative resistance of different strains to the action of chlorine and bleach. A comparison of these tables shows that chlorine is very much more efficient as a sterilizing agent than bleach.

TABLE III.—VIABILITY TEST.

Test Organism—B Anthracis 27c.
Suspended in water.
Germicide—Cl_2.

Colonies developing after exposure for minutes.

Time	15	30	45	60	75	90	105	120	
P. P. Mil. of Cl_2									
0	600		840		660		630		Av. 685
1.0	—	—	—	520	—	500	450	430	
	700	660	600	540	560	600	380	550	
1.5	520	350	390	230	—	—	—	—	
	500	330	380	370	—	—	—	—	
2.0	130	66	17	1	1	0	0	0	
	120	60	22	4	1	0	0	—	
2.5	91	24	0	0	—	—	—	0	
	85	26	1	1	—	—	—	0	
3.0	26	2	0	0	0	—	—	0	
	45	4	0	0	0	—	—	0	
3.5	2	0	0	0	—	—	—	—	
	7	14	0	0	—	—	—	—	

Table III shows the rate of action of various concentrations of chlorine on anthrax spores when suspended in distilled water at room temperature.

TABLE IV.—SHOWING LOGARITHMIC RELATION.

	2 P. P. Mil.			2.5 P. P. Mil.		
Time	N	Log N	K	N	Log N	K
0	685	2.83569	——	685	2.83569	——
15	125	2.09691	0.0495	88	1.94448	0.059
30	62	1.79588	0.0347	25	1.39794	0.048
45	20	1.30103	0.036	1	1.000	0.063
60	2.5	0.39794	0.040	—	——	——
75	1.0	0.00000	0.038	—	——	——

Table IV shows that disinfection proceeds as an orderly time process and that the mortality is a logarithmic function of time. Chick[17] previously made the same observation and suggested that the phenomenon was analogous to a monomolecular reaction and governed by the mass law.

The mass law, however, was developed to explain reactions in homogeneous systems and does not necessarily apply to heterogeneous systems. Furthermore, it has been pointed out[18] that the expression for the rate of diffusion has the same mathematical form as that for a reaction of the first order, and that any reaction depending on rate of diffusion will appear to be a monomolecular one. It is not our purpose to enter into the discussion of the mechanism of disinfection reactions but merely to call attention to the danger of arguing from analogy where an analogy cannot be proved to exist.

TABLES V AND VI.—VIABILITY TEST.

Test Organism—B Anthracis 27c.
Suspended in water.
Colonies developing after exposure.

	Germicide SO_2				Germicide $KMnO_4$			
Time P. P. Mil. disinfectant	30"		60"		30"		60"	
0	850		800		850		800	
1	610	650	750	700	700	750	780	740
5	700	650	540	600	620	650	600	660
10	640	580	580	520	300	560	580	520
20	500	—	—	—	—	—	—	—
	550	—	500	400	460	600	560	548

Tables V and VI show the effect of sulphur dioxide and potassium permanganate on anthrax spores. It will be observed that these reagents have little germicidal effect in concentrations of 20 parts per 1,000,000 after an exposure of one hour and in the absence of organic matter.

TABLE VII.

Test Organism—B Anthracis 27c.
Suspended in Anderson's Mixture.
Germicide—Cl_2.

Colonies developing after exposure.

Time P. P. Mil. of Cl_2	1¾ hrs.	3 hrs.
0	2,200	
100	1,600	1,600
300	2,050	1,600

Table VII shows the effect of chlorine on anthrax spores when suspended in Anderson's solution.[18] These results have already been referred to in the discussion.

TABLE VIII.

Test Organism—B Anthracis 27c.
Suspended in effluent from trickling filters.
Germicide—Cl_2.

May 30th. June 12th.

Colonies developing after exposure.

Time P. P. Mil. of Cl_2	2 hrs.	P. P. Mil. of Cl_2	2 hrs.
0	900	0	500
20	0	5	Spreaders
35	0	10	Spreaders
50	0	15	Spreaders
—	—	20	0

The data in Table VIII shows the amount of chlorine required to kill anthrax spores when suspended in the effluent from contact beds.

The tannery effluent used in the experiments reported in Tables IX, X, X*a*, X*b*, contained 2 per cent. of solids as determined by 20-minute sedimentation in an Imhoff cone and the supernatant liquid was deep reddish brown. This is about the average character of the effluent from this tannery. The sample of effluent used in the experiments reported in Tables X*c*, XI and XII contained 4 per cent. of settleable solids and the supernatant liquid was so dark as to be opaque in comparatively thin layers. This was much heavier than the average run.

TABLE IX.

Test Organism—B Anthracis 27c.
Suspended in settled tannery effluent.
Germicide—Bleach with and without H_2SO_4.

Colonies developing after exposure.

Time P. P. Mil. Bleach	½ hr.	2½ hrs.
0	500	500
20	500	350
100	200	100
20 + 20 p. p. mil. H_2SO_4	300	300

Table IX shows the effect of hypochlorite with and without sulphuric acid, on anthrax spores when suspended in tannery effluent, the heavier portions of which had been removed by 20-minute sedimentation. The figures in the right-hand column indicate parts per 1,000,000 of available chlorine.

TABLE X.

Test Organism—B Anthracis 27c.
Suspended in settled tannery effluent.
Germicide—Liquid Chlorine.

Colonies developing after exposure.

Time P. P. Mil. of Cl_2	15"	30"	60"
0	30	—	21
5	13	18	18
10	19	14	10
20	13	12	6

TABLE X*a*.

Test Organism—B Anthracis 27c.
Suspended in settled tannery effluent.
Germicide—Liquid Chlorine.

Colonies developing after exposure.

Time P. P. Mil. of Cl_2	30"	60"	120"
0	26	—	16
20	9	3	6
35	6	3	2
50	2	2	0

TABLE X*b*.

Test Organism—B Anthracis 27c.
Suspended in settled tannery effluent.
Germicide—Liquid Chlorine.

Colonies developing after exposure.

Time P. P. Mii. of Cl_2	30"	60"	120"
0	22	—	20
20	14	9	8
30	12	7	3
40	12	5	—
50	6	3	0

Tables X, X*a*, and X*b* show the effect of chlorine on anthrax spores when comparatively small numbers are suspended in settled tannery effluent of average strength. It will be noted that 50 parts per 1,000,000 were sufficient to sterilize the test flasks after 2 hours exposure. Table X*c* gives the results of experiments with screened and settled tannery effluent to which much larger numbers of spores were added. As shown in the table 50 parts per 1,000,000 produced a 99.2 to 99.75 per cent. reduction in the number of anthrax spores and 75 parts per 1,000,000 of chlorine completely sterilized the test flasks.

TABLE X*c*.

Test Organism—B Anthracis 27c.
Suspended in settled tannery effluent.
Germicide—Chlorine.

April 12th.

Colonies developing after exposure.

Time P. P. Mil. of Cl_2	105"	180"	48 hrs.
0	2,200	2,100	—
50	6	5	0
75	0	0	—

April 20th.

Colonies developing after exposure.

Time P. P. Mil of Cl_2	15"	30"	45"	60"	75"	90"	105"	120"
0	1,100	—	—	—	—	—	—	—
50	700	135	79	12	16	11	36	8

TABLE XI.

Test Organism—B Anthracis 27c.
Suspended in screened tannery effluent.
Germicide—Chlorine.

April 12, 1916.
Colonies developing after exposure.

Time P. P. Mil. of Cl_2	15'	60'	90'	20 hrs.	24 hrs.	48 hrs.
0		2,400 to 3,300		—	—	—
40	——	270	—	175	—	175
50	1,950	225	200	27	95	55 & 60*
60	——	230	—	8	—	45
75	1,900	—	200	—	30	—
100	2,100	—	300	—	10	—

April 20, 1916.
Colonies developing after exposure.

Time P. P. Mil. of Cl_2	15'	30'	45'	60'	75'	90'	105'	120'
0	800	—	—	—	—	—	—	—
50	900	400	360	88	103	143	60	26*

* 1 cc. portions of the 5 samples thus marked were injected into guinea pigs. All 5 pigs survived.

June 13, 1916 June 14, 1916
Colonies developing after exposure

Time P. P. Mil. of Cl_2	2 hours		P. P. Mil. of Cl_2	2 hours
0	2,000		0	1,600
50	0	0	50	Spreaders*
50	1	2	50	9*
	—	—	55	8*

* 1 cc. portions of the 5 samples thus marked were injected into guinea pigs. All 5 pigs survived.

Table XI shows the effect of chlorine on anthrax spores when suspended in tannery effluent which has passed through a Reinsch Wurl screen with a $^2/_{64}$-inch slot. In these experiments from 1,000 to 3,000 spores were used per cc. of tannery effluent. It will be noted that 50 parts per 1,000,000 of chlorine produces a substantial reduction in the number of spores after one to two hours exposure. The asterisk indicates the test flasks from which 1 cc. portions were withdrawn and injected into guinea pigs at the same time that the petri dishes were inoculated. As stated in the table these pigs survived, indicating that the spores which were not killed were attenuated.

TABLE XII.

Test Organism—B Anthracis 27c.
Suspended in screened tannery effluent (*very heavy*).
Germicide—Chlorine.

May 16, 1916.
Colonies developing after exposure.

Time P. P. Mil. of Cl_2	0	40	80	120	160	200	240	280
	1000	1000	40	Lost	0	0	0	0
	900	800	75	4	1	0	0	0

From Table XII it is seen that it would require from 160 to 200 parts per 1,000,000 of chlorine to sterilize the tannery effluent. At 10 cents a pound for chlorine this would cost $200 per 1,000,000 gallons for the chlorine alone, as compared to $50 for disinfection. That the effluent is disinfected is shown clearly from the tests on the treated effluent given below.

Following the tables is a list of all samples of tannery effluent, vat liquors and so forth which we have tested. The samples were heated for 30 minutes to 80° C. and then allowed to settle for at least 20 minutes. One cc. of the sludge was withdrawn from the bottom of the sample with a pipette and transferred to a hypodermic syringe with which a guinea pig was inoculated subcutaneously on the flank. "L" following the sample number indicates that 1 cc. of the supernatant liquid was used instead of the sludge. The asterisk indicates that the samples so designated were not heated before inoculation.

In performing the autopsies smears were made from the heart and spleen and agar slants were inoculated from the same points. If typical bacteria were seen in the smears and the growth on agar was typical, the diagnosis was anthrax, indicated by "A" in the table under "Autopsy." In case of doubt the result was confirmed by a second inoculation. When the bacteria in the smears were similar to *B. edematis* and no growth occurred on agar slants, the diagnosis was malignant edema, indicated by "M E" in the table under "Autopsy." In several cases as is seen from the table there was a mixed infection of anthrax and malignant edema.

The installation of the screens was not completed until March 1, 1916. Up to that time the tannery effluent was treated first by the addition of bleach and later with liquid chlorine to the extent of 50 parts per 1,000,000, indicated by "Cl_2" in the table under "Treatment." During this period 21 samples of the untreated tannery liquors were tested, in 8 of which anthrax was found, and of 15 samples of treated effluent 8 showed the presence of anthrax in the sludge. Since the installation of the screens 16 samples of the untreated, and 4 samples of the screened but not chlorinated effluent have been tested, of which 7 contained anthrax. Anthrax was not found in any of the screened and chlorinated samples tested, of which there were 13 during this period.

INOCULATIONS 1915.

Sample number	Sample of	Treatment	Date of Inoc.	Date of death	Autopsy
A	G. T. E.	None	2/7	—	o
B	S. A. hide soaks	o	2/7	—	o
C	Domestic hide soaks	o	2/7	2/10	A
D	General effluent	o	2/7	—	o
—	Culture from C above	—	2/22	2/24	A
2	Domestic hide soak	o	3/7	—	o
3	Chinese hide soak	o	3/7	—	o
—	Growth on plate after treatment w. 20 p. p. mil. av. Cl_2 in sewage suspension	—	—	—	A
42	G. T. E.	20 p. p. mil. av. Cl_2 (bleach)	8/18	8/20	A*
42	"	"	8/18	8/21	A
42	"	"	12/24	12/26	A
42L	"	"	12/24	12/26	A
111	"	o	8/18	8/23	A*
111	"	o	8/18	8/21	A
1	"	o	10/16	—	o
1	"	o	10/16	—	o*
7	"	50 p. p. mil. Cl_2	10/16	—	o
7	"	"	10/16	—	o*
1	"	"	11/12	11/16	A
1	"	"	11/16	11/19	A
1	"	"	12/24	12/26	A
1L	"	"	12/24	—	o
2	"	o	11/12	11/16	A
3	"	50 p. p. mil. Cl_2	11/18	11/20	M E

Sample number	Sample of	Treatment	Date of Inoc.	Date of death	Autopsy
6	"	0	11/18	—	0
5	"	0	11/23	—	0
7	"	Cl_2	11/23	11/26	A
7	"	"	12/31	1/2/16	M E + A
7L	"	"	12/31	—	0
4	"	"	11/24	—	0
8	"	0	11/24	11/29	A
24	"	Cl_2	12/1	—	0
42	"	0	12/1	12/6	Not A
14	"	Cl_2	12/4	12/7	A
14	"	"	12/24	12/26	A
14L	"	"	12/24	—	0
21	"	0	12/4	12/7	A
11	"	Cl_2	12/9	12/11	M E + A
32	"	0	12/9	12/11	M E + A
40	"	Cl_2	12/15	12/17	M + A
40L	"	"	12/15	—	0
52	"	0	12/15	12/17	M E
52L	"	0	12/15	—	0
25	"	Cl_2	12/24	12/26	A
25L	"	"	12/24	—	0
28	"	0	12/24	—	0
28L	"	0	12/24	—	0
51	"	Cl_2	12/31	—	A
51L	"	"	12/31	—	0
44	"	0	12/31	—	0
44L	"	0	12/31	—	0
26	"	Cl_2	12/31	1/2/16	M E + A
26L	"	"	12/31	1/2/16	A
39	"	0	12/31	1/2/16	A
39L	"	0	12/31	—	0

INOCULATIONS 1916.

22	G. T. E.	Cl_2	1/7	—	0
22L	"	"	1/7	1/10	No. bact.
53	"	0	1/7	—	0
53L	"	0	1/7	—	0
36	"	Cl_2	1/7	1/10	M E
36L	"	"	1/7	—	0
15	"	0	1/7	1/10	M E + A
15L	"	0	1/7	1/10	A
1	Effluent from village plant	Cl_2 at tannery	3/4	—	0
1L	"	"	3/4	—	0

Sample number	Sample of	Treatment	Date of Inoc.	Date of death	Autopsy
2	G. T. E.	o	3/4	3/7	A
2L	"	o	3/4	—	o
3	Green hide soak	—	3/4	—	o
4	Dry hide soak	—	3/4	—	o
V	G. T. E.	Screened & Cl_2	3/21	3/24	Tetanus
VL	"	"	3/21	—	o
VII	"	—	3/21	—	o
VIIL	"	—	3/21	—	o
1	Tannery effluent taken in duplicate of samples taken by Dr. Litch	—	4/14	4/16	M E
1L	"	—	4/14	—	o
1a	"	—	4/14	—	o
1aL	"	—	4/14	—	o
2	"	—	4/14	4/16	M E
2L	"	—	4/14	—	o
3	"	—	4/14	4/16	M E
3L	"	—	4/14	4/16	M E
7	G. T. E.	Screened & Cl_2	7/8	7/11	M E
7L	"	"	7/8	—	o
R	"	o	7/8	—	o
1	"	o	8/4	8/7	A
3a	"	Screened & Cl_2	8/4	—	o
3b	"	"	8/4	—	o
3b	"	"	8/4	—	o
78	"	o	8/4	8/7	A
72	"	Screened & Cl_2	8/4	—	o
20	"	o	8/4	8/7	A
80	"	Screened & Cl_2	8/4	—	o
12	"	o	8/4	—	o
104	"	Screened & Cl_2	8/4	8/7	M E
88	"	"	8/10	—	o
88L	"	"	8/10	—	o
107	"	o	8/10	—	o
128	"	o	8/23	8/27	Not A
135	"	Screened & Cl_2	8/23	—	o
135L	"	"	8/23	—	o
41	"	o	8/23	8/27	A
17	"	Screened & Cl_2	8/23	—	o
17L	"	"	8/23	—	o
X	Creek w. dead fish	—	10/6	—	o

Sample number	Sample of		Date of Inoc.	Date of death	Autopsy
1	Lime vat sludge dump	—	12/8	—	0
2	"	—	12/8	—	0
3	"	—	12/8	—	0
4	"	—	12/8	—	0
5	"	—	12/8	—	0
6	"	—	12/8	—	0
	INOCULATIONS 1917.				
A	Lime sludge dump pile	—	1/30	—	0
B	Lime vat sludge	—	1/30	—	0
C	Chrome paddle vat	—	1/30	—	0
1	G. T. E. 11.15 a.m.	Screened & Cl_2	1/30	2/2	M E
3	" 11.00 "	0	1/30	2/1	M E
4	" 11.00 "	Screened	1/30	2/1	M E + A
6	" 11.00 "	"	1/30	2/2	M E
2	" 4.30 p.m.	Screened & Cl_2	1/30	2/3	M E
5	" 4.20 "	Screened	1/30	2/2	A
7	" 4.00 "	0	1/30	2/3	M E
8	" 4.15 "	Screened	1/30	—	0
6	"	0	2/21	—	0
12	"	Screened	2/21	—	0
17	"	Screened & Cl_2	2/21	2/23	M E
1	Screenings	0	2/21	—	0

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A MODIFIED DICHROMATE METHOD FOR THE ANALYSIS OF GLYCERINE.

By Ernest Little (Instructor in Chemistry at Pratt Institute), and Benj. C. Fenner (Head Chemist at Kirkman's Soap Factory, Brooklyn).

Due to the increasing number of tanneries which are being operated under chemical control, it is necessary that the leather chemist should have a quick and accurate method for the analysis of all material used in the tannery. Among these materials glycerine is of no small importance. It is well known that the ordinary methods of glycerine analysis are long and bewildering to one not expert in this line of work.

The Official Methods recommended by the International Committee (*J. Ind. Eng. Chem.* 3, 679) are the acetin and the dichromate methods. The acetin method is accurate, and is the one used when buying or selling crude glycerine. There are several objections to this method. The length of time required to make the test, the need of special apparatus, the inaccuracy when working with material containing less than 50 per cent. glycerol, and the need of expertness in manipulation acquired only by experience are some of the limitations of this method.

The dichromate method is more rapid, easier of manipulation, and better adapted to general glycerine work. This method however requires a two-hour oxidation, the use of an outside indicator, and rather complicated calculations are necessary.

There are many modifications of the dichromate method which eliminate one or more of the above objections. The Richardson and Jaffe method which is a modified Hehner method (*J. Soc. Chem. Ind.*, 1898, page 330), shortens the time of oxidation to 20 minutes by the use of strong sulphuric acid, but the outside indicator is still required. Dr. W. Steinfels (*Seifensieder-Ztg.*, 42, 721-3, 1915) does away with the use of an outside indicator by a thiosulphate titration similar to the one outlined below. However, his method for the standardization of the thiosulphate is unnecessarily long, and the two-hour oxidation is employed. In a previous article (*Seifenfabricant,* 1910) he also mentions the possibility of shortening the time of oxidation by heating over a free flame.

The writers make no claim of originality for the method outlined below; so far as known, however, it has never been used in the form here given, which is an adaptation of the good points found in the various methods which have come to our attention. The method is as follows:

Solutions Needed.—1. Basic Lead Acetate: Dissolve 236 grams of lead acetate in 1,000 cc. of water. Heat to boiling. Add while stirring 165 grams of litharge. Boil and stir 15 minutes. Filter and make up to 1 liter.

2. Silver Acetate: A cold saturated solution.

3. Dilute Sulphuric Acid: About 15 per cent. (150 cc. concentrated sulphuric acid and 850 cc. of water).

4. Thiosulphate Solution: A fifth normal or tenth normal solution standardized against C. P. potassium dichromate which has been dried at a temperature of 110°-120° C. The standardization is carried out under the same conditions as those used in the titration of the excess dichromate in the analysis given below.

5. A 10 per cent. solution of potassium iodide.

Sample.—The size of the sample depends upon the approximate glycerine content of the material, and ranges from a 15-gram sample for a 0.5 per cent. glycerine to 1 gram for a 90 per cent. glycerine. The sample should be weighed by difference in order to prevent changes due to loss or gain of moisture.

Purification.—Wash sample into a small beaker, using about 100 cc. distilled water. Add slowly and in small amounts the basic lead acetate solution. Stir and let settle after each addition. Add the acetate until no further precipitation occurs. Care should be taken to avoid a large excess of the precipitate. Filter into a 250 cc. graduated flask. Add 12 cc. of the saturated silver acetate solution to precipitate the soluble chlorides and prevent undesirable reactions due to aldehydes. Enough 15 per cent. sulphuric acid is now added to precipitate the excess of lead and silver. Make up to about $^1/_{16}$ inch above the mark, mix thoroughly, and filter into a glass-stoppered flask.

Oxidation.—From the approximate glycerol content calculate the amount of $K_2Cr_2O_7$ necessary to oxidize the glycerine in a 25 cc. portion of the purified solution. Add 0.2 to 0.3 gram in excess of the required amount, *e. g.*, suppose 1.5 grams of an 80 per cent. crude were taken for analysis. This would contain 1.2 grams of glycerine. One gram of $K_2Cr_2O_7$ is equivalent to 0.1341 gram of glycerol. One-tenth of 1.2 or 0.12 gram is the amount of glycerol in the 25 cc. portion. Therefore, 0.12 divided by 0.1341 gives about 0.90 gram of $K_2Cr_2O_7$; adding 0.2 of a gram excess would give 1.1000 grams of $K_2Cr_2O_7$ to be weighed into a liter Erlenmeyer flask. From an accurately graduated pipette run in 25 cc. of the glycerine solution, 25 cc. of distilled water, and finally 25 cc. of concentrated sulphuric acid. Add the acid slowly, and rotate the flask. This will prevent having an excess of acid in any one part of the solution, and thus avoid local oxidation. Variable results will be obtained if this precaution is not observed. If the solution should turn blue, it is an indication that too little dichromate has been added. More dichromate can be added, or better, take a fresh portion and use a larger amount of dichromate. Place the flask, covered with a watch glass, on the steam bath for ½ hour. Care should be taken not to oxidize more than ½ hour, as prolonged oxidation with concentrated sulphuric acid may oxidize some of the acetic acid which is always present in the glycerine solution. Remove from steam bath and cool.

Determination of Excess Dichromate.—Dilute the oxidized solution to about 500 cc., add 25 cc. of 1 : 1 HCl, 15 cc. of 10 per cent. potassium iodide solution, and titrate immediately with thiosulphate solution in the usual way, using starch as an indicator. The end-point is recognized by the sudden change from a deep blue to the green color of the chromic salt. This end-point is very distinct, provided not over 0.2 to 0.3 gram excess of dichromate have been added.

Calculation of Results.—The number of cubic centimeters of thiosulphate multiplied by the glycerol value of 1 cc. gives the glycerol equivalent of the excess dichromate. The 1.1000 grams of dichromate added to the oxidation mixture is equivalent to 1.1000 × 0.1341 or 0.1475 gram of glycerol. This quantity minus the glycerol equivalent of the excess dichromate gives the glycerol oxidized. This figure divided by $^1/_{10}$ of the original sample and multiplied by 100 gives the per cent. of glycerol.

The above method is being used for control work in a large Brooklyn soap factory and glycerine refinery. It was first used for lyes containing less than 1 per cent. of glycerol, and gradually adopted for lyes of higher per cent. ranging from the ordinary spent lye of 3 to 4 per cent. glycerol to crude and finally distilled glycerine. It has also been tried out in the Chemical Laboratories at Pratt Institute, and found to give entire satisfaction.

The following table shows results which have been obtained by using this method for the analysis of solutions containing a wide range of percentages of glycerine, and how it checks the standard dichromate method in each case.

Sample No.	Thiosulphate method per cent.	Standard dichromate method per cent.
1	0.48	0.48
2	2.18	2.17
3	2.89	2.93
4	3.32	3.25
5	19.03	18.70
6	49.25	49.28
7	78.54	78.68
8	80.69	80.61
9	80.54	80.61
10	93.24	93.19

THE ADSORPTION OF CHROMIUM OXIDE BY HIDE POWDER.*

By A. W. Davison.

The question as to the constitution of leather is still a widely debated one. The adherents of the chemical compound theory on the one hand are pitted against the supporters of the physical adsorption theory on the other. Neither faction is ready to accept, in their entirety, the claims of the other. As a representative of those supporting the chemical compound viewpoint, Fahrion[1] points out that leather is a salt, in which the oxidized hide, being amphoteric in character, may play the rôle of either acid radical or basic radical; and the tanning agent, that of basic or acid radical. Whether the hide functions as acid or base will depend solely upon the character of the tanning agent.

The adherents of the physical adsorption theory believe that the changes wrought in hides by tanning are of a physical rather than a chemical nature; and that they are analogous to those brought about in cotton by mercerization; rubber by vulcanization; or in cellulose by nitration; all of which are now regarded as adsorption phenomena.

Some authors go a step farther, and claim that although the process of tanning is one of adsorption, pure and simple, further slow changes may take place with time. Stiasny[2] holds that since in the majority of cases tan stuffs are taken up from their colloidal solutions, the adsorption becomes immediately irreversible. He does not deny that slow chemical reactions may later take place between the hide fiber and the tanning agent.

As a preliminary to some extended work on the theory of tanning which is to be carried on in this laboratory, it was deemed desirable to substantiate, if possible, the claims of the physical theorists that the first process in tanning is one of straight adsorption. Further, and later changes, of whatever nature, are without the province of this paper.

The author has chosen the phase rule method of attack, because it so readily lends itself to the solution of problems of this character. Chromium has been selected as the tanning agent,

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* *J. of Phys. Chem.*, March, 1917, pp. 190-7.

[1] *Zcit. angew. Chem.*, 22 (2), 2083, 2135, 2187 (1909).

[2] *Zeit. Kolloid Chem.*, 2, 257 (1908).

since it, as a typical metallic tan, affords ease and certainty of analysis.

Although chromium salts are known to harden gelatine,[3] it was believed to be more advisable to use hide powder as the adsorbing agent, for the reason that one would thereby be working nearer be actual tanning conditions; and he could be more certain of dealing with a uniform, readily replaceable material. The hide powder used was the variety known as American Standard, obtained from Daigger & Company, Chicago. Although this product is somewhat coarse, it was found to be sufficiently porous to be thoroughly permeated by the tanning solutions. The powder was kept in a tightly closed metal can, and was weighed directly, without previous treatment, into the shaking flasks.

The tanning solution was made after a "single bath" formula by Flemming.[4] Transposed into the metric system, this formula calls for: solution A, chrome alum, 120 grams in 1,000 cc. water; solution B, sodium carbonate, 30 grams in 100 cc. water. Solutions A and B are to be slowly mixed, and any resulting precipitate removed by filtration. Throughout the remainder of this article, the resulting solution is called "strong tan solution."

The final solution in which hides are to be tanned consists, for, say, 10 kilograms of wet skin:

Strong tan solution	2.5 liters
Water	66.3 liters
Salt	70.0 grams

After the tanning process has been going on an hour, 2½ additional liters of strong tan solution should be added; this addition of strong tan solution should be continued until the hides are fully tanned. In all, about 8 liters of strong tan solution are said to be required for 10 kilograms of skin.

In order that conditions in all of the tanning flasks might be perfectly uniform, it seemed desirable to complete the impregnation of the hide fibers at one operation. The usual method of "strengthening up" the solution after each hour leaves entirely too much uncertainty of equilibrium. Then, too, when one is dealing with powdered hide, which has previously been soaked in salt water, there is no tendency toward "case hardening," or

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[3] Neuner: *Zeit. Kolloid Chem.*, 8, 144 (1911).

[4] "Practical Tanning," p. 225.

uneven tanning, because the solution so easily permeates the entire fibrous mass. At least, in these experiments, microscopic examination of the tanned powder failed to reveal uneven tanning.

The soaking and tanning operations were carried out in 500 cc., rubber-stoppered, Erlenmeyer flasks. These were clamped to a rotating device in such a manner that the flasks were turned about a horizontal shaft perpendicular to their axis of symmetry. The radius of rotation was 12 inches; the flasks revolved 50 times per minute. This insured perfect agitation, since the total volume of solution in each 500 cc. flask was only 275 cc. The whole device was immersed in a thermostat at 28° C.

Two grams of hide powder were weighed directly into each flask, and 250 cc. of salt solution, containing 10 grams of sodium chloride per liter, added. The flasks were then rotated for 1 hour, in order to insure perfect and uniform soaking of the material. Then the strong tan solution was introduced. The actual amount of tan liquor added is of little import, since interest centers only around concentrations at equilibrium, and the solutions were all to be analyzed at a later stage. The volumes varied roughly from 1 to 25 cc. Since it was highly necessary to hold the salt concentrations in the various flasks constant, the tan liquor added was in every instance diluted to 25 cc. Thus, in the case of the flask to which 10 cc. of strong tan solution were to be added, 15 cc. of distilled water were mixed with the chrome liquor before the latter was added to the tan flask. The conditions in all flasks were, therefore, the same, except for varying amounts of tan liquor.

The tanning process proper was run for 4 hours. Preliminary experiments showed that equilibrium was fully established in that time. Two gram portions of hide powder were soaked 1 hour, then tanned for varying times, using in each instance 20 cc. of strong tan solution. At the end of each hour, a flask was removed, and the solid phase analyzed. The results are shown in Table I.

It will be noticed that after 4 hours there was a loss in the weight of Cr_2O_3 found. This may be attributed to experimental error, or it may be caused by disintegration and solution of the finer particles of tanned powder after so long a time in the rotating device.

TABLE I.

Hours in contact with tan liquor	Weight Cr_2O_3 in solid phase
1	0.1795
2	0.2038
3	0.2093
4	0.2120
5	0.2115
6	0.2117

The separation and analysis of the different phases under consideration presented by far the most difficult and perplexing problem. In order to obtain concordant results, there must be no solution adhering to the tanned powder, and the latter required quantitative treatment. Once tanned, however, hide powder is not difficult to operate upon; it does not tend to stick to chemical glassware, neither does it present serious difficulties in filtration. However, the removal of adhering solution requires the utmost care. Washing with any solvent whatever is entirely impossible; hence some simple method of mechanical separation was desired. The author believes that the problem was solved, within reasonable limits of error, by first filtering off the solid phase, then removing the adhering liquid with a centrifuge. Had it been possible to use the centrifuge alone, more accurate results might have been secured, because the uncertain amount of chromium adsorbed from the solution by the filter paper would have been eliminated. Unfortunately, when one attempted to run the solution containing the tanned powder directly into the centrifuge while it was rotating, small particles of leather clogged the orifice.

A number of methods for obtaining a rough separation, giving a solid-liquid mixture of sufficiently small volume to be introduced into the stationary centrifuge, were tried; but the only successful one consisted in filtering off the solid phase on small 4-cc. Büchner funnels, using hardened filter paper, and removing the last particles of tanned powder from the Erlenmeyers by washing with some of the solution which had already been through the filter. This rough separation could be easily effected in 20 minutes. The liquid at this point was saved for analysis.

The solid phase still contained considerable solution, but the maximum amount of this could now be removed with the centrifuge. The latter was the usual Dulin Rotarex laboratory type. Each sample, after being carefully separated from the small disc of filter paper, was. centrifuged 30 minutes, at the maximum speed; and at the end of that time the assumption had to be made that they were uniformly dry. It has been pointed out by Leighton[5] that where one is dealing with dilute solutions, the nature of an adsorption curve is changed but little, when there is a marked difference in the amount of water adsorbed by the solid phase at different concentrations of the liquid phase.

Since extreme care was exercised in the centrifugal process in order to secure uniformity of drying, it was not deemed advisable or necessary to determine the actual amount of water taken up in every instance.

The concentration of chromium in the solutions at equilibrium was determined volumetrically. The chromium in aliquot portions of each solution was oxidized by boiling with sodium peroxide, and converted into sodium dichromate, with acid. A measured excess of tenth normal ferrous ammonium sulphate was run in, and the unoxidized iron determined with tenth normal dichromate, using diphenylcarbazide for indicator.[6]

These concentrations represent true values at equilibrium, except for the small amounts of chromium solution adsorbed by the filter papers in the Büchner funnels. Analyses of these papers showed the amount of water and chromium, taken up by so small a disc to be entirely negligible when compared to the large volume of solution (275 cc.) dealt with.

In Table II, concentrations of the solutions are expressed in terms of the number of cubic centimeters of tenth normal ferrous ammonium sulphate equivalent to the dichromate from 100 cc. portions of the liquid phase.

At first the chromium in the solid phase was determined as follows: The tanned hide powder was dried at 80°, pulverized, and fused with sodium peroxide, in nickel crucibles. The resulting mass was next dissolved in boiling water, acidified, and filtered. The chromium, now present as sodium dichromate, was

[5] *Jour. Phys. Chem.*, 20, 47 (1916).

[6] *Jour. Am. Chem. Soc.*, 35, 156 (1913).

determined by titration, as in the case of the liquid phase samples. But the quantitative fusion of so large a mass of tanned hide powder was found to be entirely too uncertain and troublesome, so a more simple method of analysis was devised. The dried product from the centrifuge was treated with a few cubic centimeters of nitric acid, placed in porcelain crucibles, and ignited at dull red heat in an electric furnace. This treatment burned out the gelatine of the hide, leaving behind the chromium oxide, sodium chloride, potassium sulphate, and the ash of the hide powder. The sodium chloride and potassium sulphate were washed out, and the residue weighed. This, minus the weight of the insoluble ash from 2 grams of hide powder, was called Cr_2O_3. In Table II, the concentration of chromium in the solid phase is given in grams of Cr_2O_3 taken up by 2 grams of hide powder.

TABLE II.

Concentration in liquid phase: cc. n/10 $FeSO_4$ equivalent to dichromate produced by chromium in 100 cc. solution	Concentration in solid phase: gram Cr_2O_3 adsorbed by 2 grams hide powder
0.08	0.0743
0.17	0.0873
0.43	0.1093
0.78	0.1238
1.49	0.1421
2.09	0.1591
3.12	0.1740
4.78	0.1940
6.29	0.2041
8.05	0.2120
11.37	0.2244
14.90	0.2352

Concentration values for both the liquid and the solid phase are given in Table II.

When plotted for the results appear in Fig. 1.

An inspection of the curve will reveal the fact that no breaks, horizontal, or vertical portions, exist. The phase rule, therefore, tells us that we are dealing with an adsorption isotherm; and that no compounds between the hide powder and the tanning agent have been formed. In the case of chrome tanning, therefore, the contention of the physical theorists, that the first step is one of pure adsorption, had been verified.

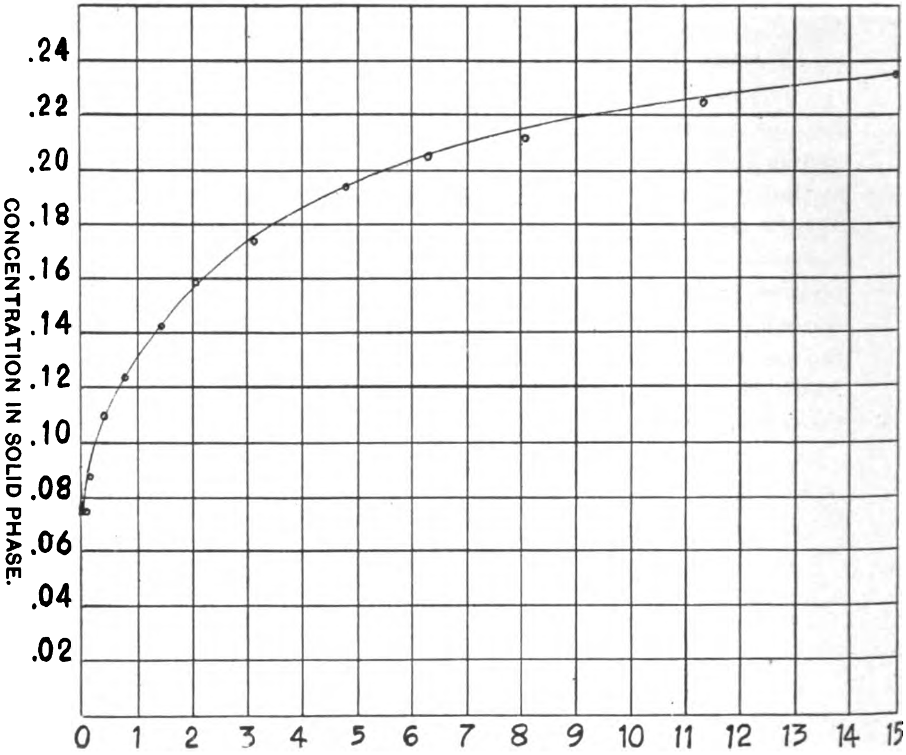

FIG. 1.—Adsorption of Chromic Oxide by Hide Powder.

The author desires to express his appreciation to Professor W. D. Bancroft for certain suggestions; and to Mr. E. K. Files, of this laboratory, for carrying out the analyses of the solid phases.

Laboratory of Physical Chemistry,
University of Cincinnati.

[EDITOR'S NOTE.—It would seem from Mr. Davison's references to Fahrion's theory of tannage that he has not seen F.'s more recent publications on the subject. In *Collegium*, 1914, pages 708-10, in an article entitled "Theory of Leather Formation" (abstract this JOURNAL, 1915, pages 76-7), in answer to Povarnin, he says explicitly that he abandoned his early theory of salt formation as long ago as 1909, and that Povarnin's criticism of his views is due to Povarnin not having read his more recent publications.]

SOLUBILITY OF HIDE IN SALT SOLUTION.

Note in Addition to the Report of This Topic in the May Journal.

The work done at the Graton and Knight Laboratory should have been credited to Mr. F. W. Oehme. The Chairman wishes to apologize for this oversight. Messrs. Oehme and Small remark that the Chairman's criticism in regard to straining of the solution after removal of pieces of hide is hardly justified, since the experiments were intended to determine hide substance *in solution,* and the very loose cotton plug used only took out pieces of material of appreciable size. They also remark that the action of bacteria seems to be the main factor in the irregularity of the results in the case of the unsterilized pieces, and that therefore further experiments with unsterilized hide would not be likely to be of value.

Mr. Oskar Riethof submits the following extract from a lecture by Haenlein, which was received too late to be included in the report as published last month.

Haenlein states that salt acts in two ways in the preservation of hides. First, it dehydrates the hide, the salt dissolving in water taken from the hide, a large part of the resulting solution escaping so as to leave the weight less than before salting. Second, salt acts as a preventive of putrefaction. Hide placed in solutions of salt containing from 10 to 25 per cent. according to temperature, does not decay. Weak solutions cannot prevent decay, but delay it. Solutions containing 2 per cent. or less of salt, however, have little or no preservative effect. It is sometimes stated that salt acts as a solvent of hide substance. The quantity thus dissolved is very small, so long as decay is not going on at the same time. Where a loss of hide substance occurs, the loss is due not to the salt but to the insufficient quantity used, which could not prevent fermentation.

ANALYSIS OF SULPHONATED OILS.

Report of 1917 Committee.

By W. K. Alsop.

The work of the Committee this year consisted of the analyses of two samples of oil. Sample A was a highly sulphonated cod oil treated with ammonia, and sample B consisted of 70 per cent. A, 15 per cent. cod oil and 15 per cent. mineral oil. It seemed to the Chairman that these samples were reasonably well suited to test the accuracy (or at least the concordance in results to be expected) of the various determinations. The directions sent with samples were as follows:

1. MOISTURE.

(a) Weigh between 30 and 40 g. (depending on amount of water present) into a flask of 250 to 300 cc. and add 75 cc. water saturated xylol, prepared by heating a mixture of water and xylol with frequent shaking and subsequently removing the water in a separatory funnel. Connect to a Liebig condenser and place flask in a bath of paraffine or a heavy lubricating oil. Distill moderately until the distillate comes clear. Collect distillate in a tube graduated to $^1/_{10}$ cc. and wash condenser with a stream of xylol from a wash bottle. Place graduated tube in hot water and when the distillate is clear, cool. The percentage of moisture is obtained by dividing the volume of water in the distillate by the weight of oil taken.

(b) Weigh accurately about 1 g. of oil into a platinum crucible. Heat gently over a small flame until the first puff of smoke appears. Cool and weigh. Determine in duplicate and results should agree within 0.2 per cent.

2. ASH.

Weigh any convenient quantity into a dish or crucible. Ignite gently, allowing the oil to burn and complete incineration until all carbon is consumed.

3. UNSAPONIFIABLE.

Weigh approximately 10 g. of oil into an 8-ounce Erlenmeyer flask and add 5 cc. aqueous KOH solution (50 g. KOH in water and dilute to 100 cc.), 45 cc. ethyl alcohol and a few glass beads. Boil 1 hour with reflux condenser. Add 100 cc. water and cool.

Transfer to separatory funnel and shake at least three times with petrolic ether (B. P. 40° to 75° C.) using 50 cc. each time. Wash ether layer at least three times with 50 cc. water containing 10 cc. ethyl alcohol. Use alcohol to break emulsion. Evaporate ether extract in tared vessel, cool and weigh.

NOTE.—If the contents of the flask bump violently during saponification, add 25 cc. petrolic ether, and proceed.

4. TOTAL AND COMBINED SO_3.

(a) Weigh approximately 4 g. into an Erlenmeyer flask and boil for 40 minutes with 30 cc. HCl (1 : 5). Shake frequently. Cool, transfer to separatory funnel and shake out with sulphuric ether. Draw off aqueous layer and wash ethereal layer three times with 75 cc. of water. Combine washings with main aqueous portion and the sulphuric acid determine as barium sulphate. From the amount thus found, the quantity as determined in *(b)* is subtracted and the difference calculated as SO_3.

(a-1) Weigh out about 4 g. into a platinum dish, add about ½ g. of anhydrous Na_2CO_3 and after mixing with a rod, heat gently until water is driven off, then raise heat until the oil is thoroughly charred. Extract with hot water, filter, return filter to dish and burn off charcoal. Treat ash remaining in dish with hot water, filter, and add this filtrate to the one first obtained. Determine SO_3 in the usual way.

(*b*) Dissolve 4 g. in ether and shake out several times with 25 cc. concentrated brine free from sulphates. Combine the washings, dilute, filter and determine the sulphuric acid as barium sulphate.

5. TOTAL FATTY MATTER.

Place the ether solution from 4*a* in tared dish or flask, evaporate or distill off ether and dry, cool and weigh residue.

6. AMMONIA.

Extract 10 g. of the oil dissolved in 150 cc. sulphuric ether in a separatory funnel four times with 10 cc. dilute H_2SO_4 (1-15). Determine ammonia by distillation as in the Kjeldahl method.

7. NEUTRAL OIL.

1. Weigh about 10.0 g. in Erlenmeyer flask, add 50 cc. alcohol,

boil reflux 5 minutes and titrate with normal NaOH till permanent pink, using phenolphthalein as indicator. Then wash into separatory funnel and extract unaltered oil with petrolic ether as in non-saponifiable.

2. Thirty g. dissolved in 50 cc. water, 20 cc. ammonia and 30 cc. glycerol added, and the mixture exhausted twice with petrolic ether, using 100 cc. each extraction. The ethereal solution is then washed with water as in non-saponifiable. Evaporate ether extract in tared vessel. Cool and weigh. (Lewkowitsch, Vol. III, page 159.)*

The results given in Table I were received from the following members of the Committee:

Dr. Gebhardt Bumcke, F. S. Walton Co., Phila.
Rudolph Boehringer, Newark, N. J.
J. H. Yocum, Newark, N. J.
L. J. Vaudreuil, Graton & Knight Mfg. Co. Laboratory, Worcester, Mass.
L. A. Cuthbert, Elk Tanning Co. Laboratory, Ridgway, Pa.
W. A. Fox, Elk Tanning Co. Laboratory, Ridgway, Pa.

Table No. 2 shows the average analysis of sample A as reported by the analysts, the figured results for sample B taking analysis of A for a basis and the average results actually obtained with sample B.

Some of the comments or recommendations made by the collaborators in reference to the various methods are as follows:

MOISTURE.

DR. BUMCKE: For the moisture test (*a*) with xylol, I recommend the use of a 500 cc. Erlenmeyer flask and 100 cc. xylol instead of 75 cc. Drops of water adhering to the side of bulb or tube may be pushed down by means of a feather attached to a wire.

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* In the Elk Tanning Co. we usually use half the quantities of oil, water, ammonia and glycerine and exhaust the mixture three times with 50 cc. of sulphuric ether. We also find it advantageous to add about 1 cc. of alcohol to the mixture and shake before adding ether.

TABLE I.—SAMPLE "A."

	Bumcke	Boehringer	Yocum	Vaudreuil	Cuthbert	Fox	Average	Greatest Difference
Moisture—(a) Xylol	24.6	22.2	23.7	25.6	24.2	23.8	24.0	3.4
(b) Crucible	23.9	23.95	24.2	25.8	23.8	24.0	24.25	2.0
Ash	0.03	0.00	0.03	0.01	0.04	0.04	0.025	0.04
Unsaponifiable	0.35	0.34	0.17	0.48	0.30	0.31	0.33	0.31
Ammonia	1.21	1.22	1.18	1.22	1.17	1.14	1.19	0.08
Total SO_3—(a) HCl	4.53	3.99	4.44	4.44	4.65	4.58	4.44	0.66
(a-1) Ash	——	4.44	4.58	4.21	4.65	4.59	4.50	0.44
Inorganic SO_3	0.79	0.57	0.86	0.47	0.90	1.12	0.79	0.65
Organic SO_3 (a)	3.74	3.42	3.56	3.97	3.75	3.46	3.65	0.55
Organic SO_3 (a-1)	——	3.87	3.72	3.74	3.75	3.47	3.71	0.40
Sulpho-fatty acids (Bumcke) (a)	17.8	16.25	16.9	18.85	17.8	16.45	17.3	2.60
Sulpho-fatty acids (Bumcke) (a-1)	——	18.4	17.7	17.8	17.8	16.5	17.6	1.90
Neutral oil 1	11.2	9.9	9.6	11.85	9.55	9.2	10.25	1.93
Neutral oil 2	14.25	*	8.7	——	11.8	11.75	11.65	5.55
Total fatty matter	66.9	73.0	67.5	67.9	68.3	68.5	68.7	5.5

* Unsatisfactory.

SAMPLE "B"

	Bumcke	Boehringer	Yocum	Vaudreuil	Cuthbert	Fox	Average	Greatest Difference
Moisture—(a) Xylol	16.9	15.95	16.85	16.9	16.95	16.90	16.75	1.0
(b) Crucible	16.95	16.9	17.20	17.7	16.8	17.0	17.10	0.9
Ash	0.04	0.07	0.05	0.01	0.06	0.06	0.05	0.06
Unsaponifiable	15.2	15.0	14.7	15.15	15.05	15.15	15.04	0.06
Ammonia	0.87	0.88	0.83	0.85	0.81	0.87	0.85	0.07
Total SO_3—(a) HCl	3.24	3.07	3.13	3.17	3.20	3.20	3.17	0.17
(a-1) Ash	——	3.27	3.32	3.21	3.30	3.28	3.28	0.11
Inorganic SO_3	0.51	0.43	0.56	0.39	0.78	0.67	0.56	0.39
Organic SO_3 (a)	2.73	2.64	2.57	2.78	2.42	2.53	2.61	0.36
Organic SO_3 (a-1)	——	2.84	2.76	2.82	2.52	2.61	2.71	0.32
Sulpho-fatty acids (a)	12.97	12.54	12.20	13.20	11.45	12.02	12.40	1.75
Sulpho-fatty acids (a-1)	——	13.50	13.11	13.4	11.97	12.40	12.88	1.53
Neutral oil 1	35.10	34.10	33.9	36.53	35.14	34.00	34.80	2.63
Neutral oil 2	37.95	——	32.3	——	36.4	36.05	35.68	5.65
Neutral fatty oil 1	19.9	19.1	19.2	21.4	20.09	18.87	19.76	2.53
Neutral fatty oil 2	22.75	——	17.6	——	21.35	20.89	20.65	5.15
Total fatty matter	78.6	80.6	77.31	79.6	76.95	77.67	78.46	3.65

TABLE II.

	Average analysis of sample A	Analysis of sample A Figured to sample B	Average analysis of sample B 70% A, 15% Cod, 15% Mineral
Moisture (a)	24.00	16.8	16.75
Moisture (b)	24.25	16.98	17.10
Ash	0.025	0.047*	0.05
Unsaponifiable	0.32	15.22	15.04
Ammonia	1.19	0.85	0.85
Total SO_3 (a)	4.44	3.11	3.17
Total SO_3 (a-1)	4.50	3.15	3.28
Inorganic SO_3	0.79	0.55	0.56
Organic SO_3 (a)	3.65	2.56	2.61
Organic SO_3 (a-1)	3.71	2.60	2.71
Neutral fatty oil 1	10.25	20.12**	19.76
Neutral fatty oil 2	11.65	21.10**	20.65
Total fatty matter	68.7	78.09	78.46

* Mineral oil = ash 0.2 per cent.

** Cod oil = 86.27 per cent. neutral oil.
13.73 per cent. fatty acids.

For the moisture test (*b*) I strongly recommend the use of more than 1 gr., about 6-10 gr. When made on an iron steam-box where the temperature does not exceed 120°-125° C., overheating is impossible while this may occur by the use of a small flame. The use of a flame makes the loss of ammonia more probable, while this loss seems immaterial when heated on the steam-box.

Accurate determination of the NH_3 should be made to determine any loss of ammonia when heating one way or the other.

The method (*b*) seems to me especially desirable if only a small sample is at hand, as the contents of the crucible may be further used for the determination of the ash or total SO_3 or total fatty matter, while the quantity used for method (*a*) is entirely lost for other tests.

Mr. Boehringer: Method (*a*) is not necessary, provided a satisfactory check analysis is made with method (*b*). Method (*b*) is always used in our laboratory with very good results.

We think, however, the description of method (*b*) is entirely inadequate and we suggest as follows:

"Weigh accurately 1 g. of oil into a platinum crucible, heat very gently over a very small flame, not over 1½ inches in height, keeping the flame constantly moving under the crucible. At the first sign of smoking, the flame is instantly removed and a cold glass plate applied to the top of the crucible. Moisture is indicated by the deposition of minute water globules on the cold glass, and if such appear the heating should cautiously continue until dew ceases to form when the cold glass is applied. Cool and weigh."

In view of the much greater rapidity and convenience of this method over method (*a*), and the fact that with care the results check very closely, I suggest that (*b*) be adopted as the regular method, making (*a*) the alternate.

I note that one member suggests the use of 5 g. I see no objection to the use of a quantity larger than 1 g., but 5 g. appears to be an inconveniently large amount to work with.

MR. YOCUM: I believe that the moisture should be determined by the xylol method when ammonia is present in the oil. Ammonia not being present, the crucible method is entirely satisfactory. In using the platinum dish method, it has been the custom of this laboratory to use 5 g. of oil, as I think that the end point is more distinct and the chances for error less. I am of the opinion, however, that the xylol method should be made official, and that the crucible method should be made optional.

MR. VAUDREUIL: Method (*b*) should be alternative, and would suggest using 5 g. insteam of 1 g. A more distinct end point is obtained, also after weighing, the residue may be used for the ash determination.

FOX AND CUTHBERT: The crucible method is easier to manipulate, and from the results obtained by this committee as well as considerable laboratory experience, we believe it as accurate as determination with xylol, and therefore, it should be included as an alternate method.

UNSAPONIFIABLE.

All members of the Committee are in favor of changing the present method where it reads, "Add 100 cc. water and cool." The addition of 50 cc. of water seems preferable. No other suggestions in reference to this determination were made except the following from Dr. Bumcke: "Only 40 cc. of water were added instead of 100 cc. so that the solution contained about 50 per cent. alcohol, the washing was also done with 50 per cent.

alcohol. The separation is quicker and dissociation of the soap is avoided."

TOTAL SO_3.

DR. BUMCKE: According to a recommendation by Benedict for the complete separation of SO_3 I dissolve the 4 g. of sulphonated oil in 25 cc. water and add a little ammonia to make the solution slightly alkaline before I add the hydrochloric acid. Boiling must be continued until both layers, oil and water, appear to be clear. Complete washing of the solution of oil in ether in the separator and of the filter through which I filter all acid water and wash water is necessary to avoid losses. If this procedure is strictly adhered to I do not think that any loss of SO_3 occurs or that any SO_3 remains in the oil. My figures obtained by method (*a*) are nearer the average figures of method (*a-1*) than the average of (*a*).

I either wash until the wash water is neutral or if the separation is too slow with water, I use dilute HCl (1-20) and wash about six times with 25-30 cc.

MR. BOEHRINGER: The ash method is to be preferred. We, however, use considerably larger amount of Na_2CO_3 and add a small amount of Na_2O_2 to the solution to prevent loss of sulphur as H_2S.

MR. YOCUM: I believe that the ash method (*a-1*) as described, is the best method known for the determination of the total SO_3. While this method does not, in my mind, determine all the combined sulphates, it is nearer to the truth than the HCl method. I am, therefore, not in favor of the HCl method.

MR. VAUDREUIL: Both methods should be allowed. Personally I prefer the ash method as quicker.

FOX AND CUTHBERT: We believe that the ash method is more accurate and should be adopted at least as an alternative method. Using the present HCl method we have invariably found small traces of SO_3 in the ether extract. In cases where the total fatty matter as well as the total SO_3 are to be determined, we believe that the present HCl method can safely be used on condition that the total fatty matter be ashed with Na_2CO_3 and the SO_3 which is found be added to that already determined.

INORGANICALLY COMBINED SO_3.

DR. BUMCKE: Not 4 but 10 g. of oil should be used, dissolved in 100 cc. of ether. Only concentrated brine should be used. For the first washing 20-25 cc. are usually sufficient, only if the oil contains too much water the brine gets too dilute and the separation is slow or incomplete. In this case 30-40 cc. of brine or even 50 cc. may be necessary to get a complete separation, for the following three washings only 10 cc. of brine are necessary. The first settling usually takes 2 to 3 hours, while the following require about 1 hour. The brine drawn from the separator should be clear. If it is not clear it should be filtered undiluted and the filter washed with brine.

If after the dilution of the brine and the addition of HCl and heating, oil should show in appreciable quantity, this should be determined and a correction made as described on page 561, November, 1915, of our JOURNAL.

If a salt that contains only 0.001 per cent. SO_3 or less, is used for the brine a correction is hardly necessary, as 50 cc. brine represent about 13 g. salt or 0.00013 g. SO_3, or about 0.0004 g. $BaSO_4$. If the salt contains more SO_3 a correction seems to be necessary.

MR. BOEHRINGER: The chief difficulty in determining inorganic sulphur in sulphonated oils arises from the presence of organic matter dissolved by the salt solution. This seriously hinders the precipitation and also causes the precipitate to come down in a flocculent form, which is difficult to filter. Moreover, it is extremely difficult to ignite such a precipitate to whiteness. We have, therefore, found it advisable to thoroughly oxidize the solution prior to precipitation. The method we use is as follows:

"Place about 5 g. of the oil in a separatory funnel with 100 cc. of petroleum ether; shake well. Wash twice with saturated salt solution, using 60 cc. for each washing. Separate the clear salt solution from the ether layer, filtering same into a 12-ounce beaker. Add 1 cc. hydrochloric acid and 20 cc. of bromine water to oxidize any organic matter present. Make volume up to 300 cc. and boil; precipitate with hot barium chloride added drop by drop. Heat gently until the solution is clear, which usually does not require more than one hour."

MR. YOCUM: I think that the concentration of the brine solution should be specified in the method. As the method reads, 25 cc. of concentrated brine, may mean a solution containing from 15 to 20 per cent. of NaCl. I suggest that a 20 per cent. solution should be used, as I do not think that saturated solutions will remove all the free or inorganically combined SO_3.

MR. VAUDREUIL: Recommends further work be done on this determination.

FOX AND CUTHBERT: We are not entirely satisfied with the present method but believe that by using a practically saturated brine solution, filtering after extraction and also washing the paper with a saturated brine solution that the results will be improved.

TOTAL FATTY MATTER.

DR. BUMCKE: The Provisional Method, taking the difference between 100 per cent. and the sum of moisture, ash and unsaponifiable, should be discarded and the method in the 1917 directions adopted instead. The wording of No. 5, "Total fatty matter" seems to include all fatty matter, saponifiable and unsaponifiable, and this seems the reason why all collaborators have reported this amount as "Total fatty matter." I see that the different text books which I consulted in this matter all describe and determine as "total fatty matter" or "total oily matter" the sum of saponifiable and unsaponifiable, probably for the simple reason that the admixture of mineral oils to sulphonated oils is only a recent achievement and was not reckoned with in the former turkey red oils made from castor, olive or elaine red oil.

I think it is very important that we come to an agreement whether the "total fatty matter" shall include the unsaponifiable or not. Unsaponifiable from the original oil (cholesterol, etc.) is permissible under the heading "total fatty matter," while mineral oils certainly do not belong to the "fatty" matter. In the analytical report it should be given as "total fatty matter, unsaponifiable not included," and the unsaponifiable should be reported extra, or if this is not done the total amount must be reported as "total fatty matter, including unsaponifiable."

MR. BOEHRINGER: In view of the ambiguity of this term, I think it should be advisable to change this heading to "total saponifiable fatty matter," which appears to me a more definite term than "total fatty oil."

Apart from this matter of nomenclature, I regard the method for this determination satisfactory.

MR. YOCUM: This determination should, to my mind, be made by deducting the sum of the moisture, ash and unsaponifiables from 100.

MR. VAUDREUIL: Method in the directions preferable to the present provisional method.

FOX AND CUTHBERT: We believe that the present provisional method is inaccurate unless the NH_3 and total SO_3 are also deducted. The method suggested gives a truer value of the fatty contents although the unsaponifiable matter should not be included as total fatty matter. The small amount of unsaponifiable generally present in all fatty oils may as a rule be disregarded.

AMMONIA.

All agree that ammonia should be determined and that the method is satisfactory. Mr. Cuthbert remarks that the H_2SO_4 extract should be as free as possible from oil to prevent excessive frothing during distillation.

NEUTRAL OIL.

DR. BUMCKE: I cannot say which method is preferable, as both do not give results that agree as well as it may be desired. In our laboratory we have used method 2 with the changes as given on page 564, November, 1915, of our JOURNAL. The determination of neutral oil may seem to many rather immaterial, but it will help to explain why some oils hold more mineral oil or other oils in admixture than others, though this amount is perhaps more governed by the amount of sulpho-fatty acids.

MR. BOEHRINGER: Method 1 is the only one which we have found satisfactory. Method 2 gives fairly close checks on oils that contain only small amounts of unsaponifiable. If, however, the amount of unsaponifiable is large we have never succeeded in getting a satisfactory separation.

MR. YOCUM: I think that this determination is unnecessary, as neither of the methods so far devised, have any bearing on the quality of a sulphonated oil.

MR. VAUDREUIL: Method 1 is preferable.

MR. CUTHBERT: I believe that the determination of neutral oil according to method 2 should be incorporated in the methods. While neither one of the methods gives the most satisfactory results yet the determination of neutral or unaltered oil is important and until a better method is devised I think it advisable to do the best we can with what we have. Method 1 is incorrect, as the petroleum ether extract in a number of cases has been found to contain soap. In method 2 as suggested, half quantities and the addition of a small amount of alcohol before extraction with sulphuric ether will enable the operator to obtain quick and uniform results.

MR. FOX: I do not believe that the determination of neutral oil is important in determining the value of an oil although it may show something about the constituents of the oil. Method 1 is easier of manipulation and seems to give more concordant results.

RECOMMENDATIONS.

In view of the analytical work done and the recommendations and comments of the collaborators, the chairman makes the following recommendations:

Moisture.—That the method determining moisture with the use of xylol be unchanged and that the following be added as an optional method.

Weigh accurately 5 g. of oil into a crucible, heat gently over a very small flame which should be kept constantly moving under the crucible. At the first sign of smoking, remove the flame at once and apply a cold glass plate to the top of the crucible. If moisture is still present, a mist will be formed on the glass and if such be the case, heat cautiously until there is no condensation.

Unsaponifiable.—That the sentence in the fifth line of the present method reading, "Add 100 cc. water and cool," be changed to read, "Add 50 cc. water and cool."

Total and Combined SO_3.—That the present method for total SO_3 be the subject of further experimental work along the lines mentioned by Dr. Bumcke. Also that an ash method be made optional, the exact wording to be prepared by next year's committee. The advisability of adding an oxidizing agent to be considered. The method for inorganic SO_3 should be improved and the exact procedure to be used specified. The results by the method given vary more in proportion to the amount present than any of the other determinations. Further experimental work seems advisable.

Total Fatty Matter.—It seems to be the consensus of opinion that the present method of ascertaining total fatty matter be changed. The Chairman believes it the least important of any of the determinations under consideration in judging the value of a sulphonated oil and will leave the selection of a satisfactory method to a future committee. The present method is not satisfactory, no provision being made for ammonia or SO_3 combined with it. The organically combined SO_3 is also fatty matter.

By the other method tried, the mineral salts and all the SO_3 are eliminated and in addition any neutral oil subject to the action of the boiling HCl solution. If the total fatty matter is an indication of the value it seems hardly fair to fix the method so that a highly sulphonated oil will show the least fatty matter. Added unsaponifiable oil should of course be deducted from fatty matter.

Ammonia.—That the method given in the directions be incorporated in the provisional methods.

Neutral Oil.—Neither method seems satisfactory and the value of the determination somewhat doubtful. It is not recommended that either be incorporated in the methods.

We have been more successful with method No. 2 than No. 1. The results of the committee work, however, are in favor of method No. 1.

Mr. Yocum writes: "While the determinations as outlined may, in some instances, be of value, I believe that the value of a sulphonated oil should be measured by its emulsifying properties and its ability to carry mineral oil in emulsion. The moisture, ash and unsaponifiables should be determined and subtracted from 100 per cent., and the value of the oil should be based on the amount of fatty oil present."

As I understand Mr. Yocum, the value of a sulphonated oil, in his opinion, does not depend so much upon the content of SO_3 as upon the degree of neutralization. Perhaps the next committee can throw some light upon this matter. In considering emulsification tests, account should be taken of what the oils will do when mixed with other fatty or mineral oils as well as when used "straight."

Dr. Bumcke has submitted the following suggestions for experiments, both in laboratory and plant:

A. Is a higher amount of combined SO_3 more desirable for the quality of leather, provided the oils taken for comparison are made of the same base, differing only in combined SO_3? What are the desirable limits of combined SO_3 for upper leather and what for heavy leather?

B. Provided the combined SO_3 is the same, is a higher amount of oxidized fatty acids more desirable for the quality of the leather?

C. Is an oil finished with NaOH better than one finished with NH_3?

D. Is a higher amount of Na_2SO_4 or $(NH_4)_2SO_4$ detrimental for the leather, or what limit would be permissible?

E. Would it be desirable for the buyer to know the amount of a certain mineral oil (for instance, 35° neutral oil) that the sulphonated oil would hold in emulsion?

REPORT OF COMMITTEE ON DYESTUFFS.

By Guy T. Creese, Chairman.

As Chairman of your Committee on Dyestuffs, I submit the following report:

The Committee started the work with a membership of five, consisting of Dr. Kressman, Mr. Wisdom, Mr. Orthmann, Dr. Klaber and myself. On account of taking a new position Dr. Kressman was obliged to resign from the Committee.

Owing to war conditions, this has been a particularly trying year for the chemists in various laboratories and for this reason we have not accomplished more. Under the circumstances we thought it advisable to concentrate the efforts of the Committee on the subject of money values of artificial dyestuffs. The methods of procedure were outlined and sent to the members of the Committee. The same grade of yarn was furnished each member and the dyestuff samples Nos. 2 and 3 were diluted 10 per cent. and 25 per cent., with the exception of the basic samples, and these were diluted 25 per cent. and 50 per cent. The prices fixed on these dyestuffs are proportional to the dilution.

The object of money value tests is to obtain the real value of a product submitted, in terms of the cost of the product being used, or as it is known in the laboratory, the standard.

For shades other than black a 1 per cent. dyeing should be of sufficient depth, unless a very weak dyestuff is used. A 2 per cent. dyeing should give a good shade for a black, but when it is necessary to obtain a comparison of the tone of black produced, it will, of course, be necessary to use more than 2 per cent. of dyestuff. As a preliminary trial, measure 1 cc. of the standard (1 g. to 1,000 cc.) in a 50 cc. Nessler tube and make up to the mark with water. Do the same with the dyestuff in question. A comparison of the depth of shade produced will give an idea of the relative strengths. By matching the dyestuffs in solution, a match on yarn can be much more readily obtained.

Tests may also be made by dipping filter paper into the different solutions and noticing the difference in the depth of shade obtained. By changing the strength of solutions until a match is obtained, a rough estimate may be obtained as to their relative values.

EXAMPLE.

$$\frac{\text{cc. of standard} \times \text{price of standard}}{\text{cc. of sample required}} = \text{value of sample}$$

Standard	100 cc.	Solution	price	50¢
Sample #1	80 cc.	"	"	60¢
Sample #2	120 cc.	"	"	80¢
Sample #3	90 cc.	"	"	40¢

$$\#1 \quad \frac{100 \times 0.50}{80} = \$0.625 \text{ — real value of sample \#1}$$

$$\#2 \quad \frac{100 \times 0.50}{120} = 0.416 \text{ — real value of sample \#2}$$

$$\#3 \quad \frac{100 \times 0.50}{90} = 0.555 \text{ — real value of sample \#3}$$

Sample No. 3 would be the cheapest to use. Its value is $0.555, while its price is $0.40.

ACID DYESTUFFS.

Solution: Dissolve 1 g. of dyestuff in hot distilled water and make up to volume of 1 liter.

Dyeing: Work at boil for one hour.

1 per cent. dyestuff on weight of wool skein.
15 per cent. sodium sulphate (Glauber's salt).
Boil ½ hour.
3 per cent. sulphuric acid (168° T. W.).
Boil ½ hour.

NOTE: Yarn must be worked in bath to prevent uneven dyeing.

BASIC DYESTUFFS.

Mordanting the Cotton Yarn: Enter the yarn after boiling out, into a concentrated tannic acid bath at 140°-180° F. and let it remain in over night. Lift, squeeze out or wring, and fix for 20 minutes in a fresh cold antimony salt bath.

5 per cent. tannic acid or
20 per cent. extract stainless sumac.
2 per cent. tartar emetic.

Solution: Dissolve 1 g. dyestuff in warm water, add 1 cc. acetic acid and make up to liter volume.

Dyeing: The solution of the coloring matter should not be added all at once, but in three portions. Commence dyeing cold and when the greater part of the color has been taken up by the yarn, warm slowly to 140° F. and dye at this temperature for one hour.

MORDANT DYESTUFFS.

Preparation of Yarn: Mordant the yarn with 3 per cent. potassium (or sodium) bichromate and 2½ per cent. tartar. Boil for 1½ hours and then rinse well.

Solution: Dissolve 1 g. of dyestuff in hot distilled water and make up to volume of 1 liter.

Dyeing: Prepare bath and make up to volume of 500 cc. with water; add 2 cc. 10 per cent. acetic acid. Add one-half required color solution at 30° C., turn well, heat to 50° C., then add the other half of the color, raise to boil and boil one hour.

DIRECT OR SUBSTANTIVE DYESTUFFS.

Solution: Dissolve 1 g. dyestuff in hot distilled water and make up to volume of 1 liter.

Dyeing: Enter the yarn into the bath, which should be as concentrated as possible, and work at a boil for one hour.

1 per cent. dyestuff.
20 per cent. Glauber's salt.
5 per cent. sodium chloride.

LEATHER DYEING.

Leather for dyeing is cut in pieces so that each piece contains $^1/_{10}$ sq. ft., and the average weight of the pieces will be 10 g.

Dyestuff solutions are made 1 g. of color to 1 liter of distilled water.

Acid solutions and fat-liquors are made one part acid or fat-liquor to ten parts of water.

Dyeings are made by shaking the leather continuously in 1 pint E-Z type seal glass jars.

ACID DYESTUFFS.

Take 100 cc. of 1 to 1,000 dyestuff solution at 130° F. and shake the leather for 20 minutes; add 2 cc. formic acid solution and shake 10 minutes longer. Drain off solution and add 2½ cc. fat-liquor solution in 50 cc. distilled water at 125° F. and shake for 10 minutes. The leather is then slickered on the flesh side, tacked out and dried.

Basic Dyestuffs.

Where it is necessary to give a tannin mordant before dyeing (chrome leather) the leather should be treated to a bath of 5 per cent. extract sumac on weight of leather for 20 minutes. Drain off the liquor and run in fresh bath containing ½ per cent. tartar emetic for 10 minutes. Wash off with distilled water.

Solution: One g. color to ½ cc. acetic acid made up to liter volume.

Dyeing: One hundred cc. solution at 120° F., run ½ hour.

Fat-liquoring: Same as for acid colors.

Note.—In dyeing of methyl violet type colors, ¼ per cent. (25 cc.) dyeings are recommended.

Direct Dyestuffs.

Solution: One g. of color to 1 liter.

Dyeing: One hundred cc. of solution at 130° F., run ½ hour.

Fat-liquoring: Same as for acid colors.

Chrome Mordant Dyestuffs.

Same method as for acid colors.

Note.—Dyeings on vegetable-tanned leather should be at a temperature of 110° F.

Method of Calculating Results.

1 g. dyestuff—1,000 cc.
1 cc. = 0.001 g. color.
100 cc. × 0.001 g. = 0.1 g. color.
Leather measured $^1/_{10}$ sq. ft.
1 g. dyestuff to 1 sq. ft.
100 sq. ft. × 1 g. = 100 g. to 100 sq. ft.
$\frac{100}{28.35} = 3.52$ oz. per 100 sq. ft. leather.

ARTIFICIAL DYESTUFFS.

Tests on Textiles.

Acid Dyestuffs—Acid Methods.

(Creese) Wool Yarn.

	Amount	Price	Value	Comparative Cost
Standard	1.00%	\$0.28	\$0.28	\$0.28
No. 2	1.10%	.25	.255	.275
No. 3	1.30%	.21	.215	.273

Sample No. 3 is best money value.

(Wisdom) Wool Yarn.

	Amount	Price	Value	Comparative Cost
Standard	1.00%	$0.28	$0.28	$0.28
No. 2	1.10%	.25	.255	.275
No. 3	1.30%	.21	.215	.273

Sample No. 3 is the best money value.

(Klaber) Wool Yarn.

	Amount	Price	Value	Comparative Cost
Standard	1.00%	$0.28	$0.28	$0.28
No. 2	1.10%	.25	.255	.273
No. 3	1.25%	.21	.224	.262

Sample No. 3 is the best money value.

ARTIFICIAL DYESTUFFS.

Tests on Textiles.

Basic Dyestuffs—Basic Method.

(Creese) Tanned Cotton Yarn.

	Amount	Price	Value	Comparative Cost
Standard	1.00%	$0.80	$0.80	$0.80
No. 2	1.27%	.60	.629	.762
No. 3	1.89%	.40	.423	.756

Sample No. 3 is best money value.

(Wisdom) Tanned Cotton Yarn.

	Amount	Price	Value	Comparative Cost
Standard	1.00%	$0.80	$0.80	$0.80
No. 2	1.275%	.60	.628	.765
No. 3	1.90%	.40	.421	.76

Sample No. 3 is best money value.
Orthmann and Klaber not reporting.

ARTIFICIAL DYESTUFFS.

Tests on Textiles.

Direct Dyestuffs—Direct Method.

(Creese) Cotton Yarn.

	Amount	Price	Value	Comparative Cost
Standard	1.00%	$0.36	$0.36	$0.36
No. 2	1.175%	.32	.313	.368
No. 3	1.30%	.27	.276	.351

Sample No. 3 is best money value.

(Wisdom) Cotton Yarn.

	Amount	Price	Value	Comparative Cost
Standard	1.00%	$0.36	$0.36	$0.36
No. 2	1.175%	.32	.307	.376
No. 3	1.35%	.27	.267	.3645

Standard is best money value.

(Klaber) Cotton Yarn.

	Amount	Price	Value	Comparative Cost
Standard	1.00%	$0.36	$0.36	$0.36
No. 2	1.15%	.32	.313	.368
No. 3	1.30%	.27	.277	.351

Sample No. 3 is best money value.

ARTIFICIAL DYESTUFFS.

Tests on Textiles.

Mordant Dyestuffs—Mordant Method.

(Creese) Chrome Mordanted Wool.

	Amount	Price	Value	Comparative Cost
Standard	2.00%	$0.28	$0.28	$0.28
No. 2	2.20%	.25	.254	.275
No. 3	2.60%	.21	.215	.273

Sample No. 3 is best money value.

(Wisdom) Chrome Mordanted Wool.

	Amount	Price	Value	Comparative Cost
Standard	2.00%	$0.28	$0.28	$0.28
No. 2	2.10%	.25	.267	.2625
No. 3	2.20%	.21	.255	.231

Sample No. 3 is best money value.

Orthmann and Klaber not reporting.

From the remarks made by the various members of the Committee I have obtained the following general conclusions:

First, that the leather test under these methods is unreliable in placing the valuation on dyestuffs, and under these circumstances the results obtained do not justify being reported upon.

Second, that some form of mechanical tumbler should be found which will insure the leather being kept in constant circulation and an even temperature maintained.

Third, that adjacent pieces of leather of the same surface and weight should be used for leather tests.

Fourth, that a yarn dyeing is capable of showing not less than a 5 per cent. difference.

Fifth, that when fine distinctions are necessary to determine the comparative money value, the only reliable test is on textiles.

Now, in conclusion, textile tests are all right for textiles, but they are not practical in the testing of dyestuffs for leather purposes and some method should be found whereby more accurate results of dyetesting on leather may be obtained, and there is no better way of getting these results than by a good, lively discussion of the subject here at this meeting. I sincerely hope that any of you who have opinions or ideas to offer will be prompt to present them for discussion.

FORM OF REPORT FOR THE ANALYSIS OF TANNING EXTRACTS.

By E. J. Haley, Chairman.

As chairman of the committee appointed to prepare a form for uniform analysis reports for tanning extracts, I beg leave to submit the following majority report of the Committee.

A mail vote was taken on several forms of report, for analysis of tanning extracts, resulting in a majority of the replies approving of the appended form. We therefore recommend that the Association adopt as an official form of report for analyses of tanning extracts the following:

Tannin
Non-tannins
Insolubles
Water
Total

Total Solids
Soluble Solids
Ash
Specific Gravity
Twaddell

Analyzed by the Official Method of the A. L. C. A. $\left.\begin{matrix}\text{Slowly}\\ \text{Rapidly}\end{matrix}\right\}$ cooled.

ABSTRACTS.

History of Pigskin Leather. S. M. Gusdorf. *Hide and Leather,* April 28, 1917. Pigskin leather has been gradually coming into use for insoles, counters, welting and even for outer soles. Its durability is very high in all these uses.

Is the Recovery of Nitrogen in Sewage Sludge Practicable? William R. Copeland. *J. Ind. and Eng. Chem.,* April, 1917, pp. 174-6. The answer to the question depends on three factors: (1) the amount of nitrogen contained, (2) cost of recovering and disposing of the nitrogen, (3) market value of nitrogen. Recovery of nitrogen in the suspended matter is the only subject discussed in the paper. The quantity of nitrogen in dry sewage sludge ranges from 1.2 per cent. for Imhoff sludge to 2.85 per cent. for plain sedimentation, according to Metcalf and Eddy, McClintock and others. The activated sludge process, however, by preventing the escape of nitrogen held in colloidal solution, and causing its precipitation in the sludge, yields sludge whose nitrogen content ranges from 6 to 10 per cent. on the dry material. Various methods of dewatering have been tried. By preliminary settling and decantation, followed by filter pressing, the percentage of water can be reduced to 75 per cent., and the press cake may then be dried to 10 per cent. moisture in a suitable drier. Two types of filter press are able to handle the sludge without addition of lime. Several samples of press cake were dried at a fertilizer factory, and yielded a satisfactory product, losing little of their nitrogen in the process of drying. The cost per ton of preparation and marketing, including all overhead charges, is estimated at from $8 to $12 per ton, and the market value of the product is from $9 to $15 per ton.

Tarwad Bark as a Tanning Agent. D. B. LIMAYE. Bulletin No. 1, Ranade Industrial and Economic Institute, Poona, India. Western India produces three commercially important tanning materials, "babul" bark, "tarwad" bark and myrobalans. The last is the only one which enters international trade to an important extent, being produced in the forests of the Western Ghats, etc., and exported to the value of from $2,000,000 to $2,500,000 annually. The other two materials are also products of waste land, which would under other conditions be clothed with forest. Tanners in West India use all three of these materials.

Tarwad bark is the product of a shrub, *Cassia auriculata,* which grows on waste land throughout India and is never cultivated. It is often the only plant, beyond a sparse growth of grass and weeds, occurring on large areas of uncultivated lands in the Deccan. It is regularly harvested in many districts, but though the trade is widely distributed, there is no way of determining its volume, as the only records available class all tanning barks together. Practically all of the barks so reported are either babul or tarwad. The total value of shipments from the Bombay Presidency to Madras is about $30,000 a year. Large amounts are used by the tanneries near Bombay also.

Much of the bark is obtained from stems of one year's growth. The stems are cut after the growth for the year is done. Stems more than one year old have a somewhat higher percentage of tannin. One-year stems average about 16 per cent. tannin, two-year stems about 17 per cent., and three-year stems about 18 per cent. The lands from which the bark is obtained are for the most part under Government control, and the privilege of collecting is sold out by auction. The plants are cut a few inches from the ground, leaving one or two small branches, so that the stump may sprout again. The leaves are removed, and the stems beaten with a wooden mallet until the bark is loosened, when the bark and stems are separated and the bark dried. The daily earnings of a worker who collects and barks the stems range from 6 to 8 cents. The yield of dry bark on the weight of the stems is about 10 per cent.

The tanning value of this bark has been recognized in India for a long time, but in spite of the fact that it has been often recommended to tanners in Europe, it has received little attention or even investigation. History of several investigations, from 1896 to the present is given, and the opinions of investigators are discussed. The latest investigator was P. V. Mehd, 1912. He obtained about 22 per cent. tannin and 11 per cent. non-tannins. He considered that a blend of tarwad with myrobalans gives a very good tannage, mellow and light colored.

The writer obtained bark from twelve districts for his investigation. The average rainfall of these regions is about 25 inches a year, the amount for November, December, January, February, March and April being about 3 inches. The analyses of these samples showed small differences, and the proportion of tannin to non-tannin was very constant, the ratio being about 10 to 6. A number of commercial samples were also examined. The percentage of tannin in these averaged nearly the same as in those collected by the author, but the non-tannins were somewhat lower.

The two great difficulties which stand in the way of extending the use of this material, whose quality is unquestionably high, are the fact that it is a jungle product, and cannot be furnished in large quantities unless it is cultivated, and second, that the percentage of tannin is so low that if it is to be exported it must first be converted into extract. No experiments in the raising of tarwad as crop have been undertaken.

Quality of Combination Soles. *S. and L. Rep.*, May 3, p. 23. A letter from one of the firms making substitute soles is given in full. It is to the following effect: the manufacture of soles of materials other than leather is rapidly increasing. It has to fight various difficulties, but the greatest danger to the business is the manufacture and sale of inferior soles. The case is the same as with the rubber sole. If nothing but good rubber soles had ever been offered for sale, this type of sole would not have got into such bad repute. Several companies are now making and selling soles of other materials than leather which are good and are sold at a fair price. Other manufacturers are making a very inferior quality of sole and are selling it at a low price, and are thus bringing the whole business into disrepute. A plea is made that the trade papers use their influence to discourage the use of the inferior materials. The editorial note in reply is as follows:

> We do not see what can be done to prevent the manufacture and sale of low grades of substitute soles. The demand for cheap articles which are really dear, quality for price, is based on a well known defect in human nature. Pinchbeck jewelry, shoddy clothing, weighted silks and adulterated foods like the poor are always with us. The manufacturers do not make inferior goods from choice, but for the reason that many millions of consumers insist upon low price and have little concern about quality. It is true that the producers of merchandise of intrinsic value frequently suffer from the competition of fabrics made to sell at popular prices, but their remedy does not consist in attempting to stop the manufacture of the low grades. The makers of the comparatively new combination soles are confronted by the same condition that exists in sole leather. There are more grades of sole leather than of combination soles. As long as cheap shoes are made and sold there will be cheap materials offered of which to construct them.

It seems to the editors of the JOURNAL that the *Shoe and Leather Reporter* has made one inaccurate statement in this reply: "The manufacturers do not make inferior goods from choice." The same statement is often made in regard to trashy periodicals: "We do not prefer to make this kind of paper, but the people demand it." By pandering to vicious tastes these papers do a great deal to lower the standard of taste. The makers of cheap sole material are simply using the popularity of the good kinds to make a market for their bad products. They do prefer to make that kind of goods, because they yield a better relative profit than good materials. The business of trading on somebody else's reputation by producing cheap imitations of his goods is a very old one, and it is not followed chiefly from necessity.

Notes on the Synthetic Tannins. J. E. EDWARDS. *Leather World,* April 12, pp. 197-8. Before the war the use of synthetic tannins in England had scarcely passed the experimental stage. Prices of these materials have risen from 10 to 20 per cent. since the war began, while such materials as gambier have increased much more. The price of formaldehyde is abnormally high, so that it may be hoped that after the war synthetic tannins may become cheaper relatively than vegetable materials capable of being used for the same class of work. Synthetic materials are being used in the early stages of tanning to increase the speed of penetration of vegetable tannins, which results also in the more complete sappage of the tail liquors. They are also being used to brighten the color of tanned leather, and for clearing turbid liquors. Light leathers are being made with synthetic tannin alone, but not to a very great extent. Leathers so made are thinner and lighter than those tanned with a mixture of vegetable and synthetic materials.

Platinum Deposits of the World. JAMES M. HILL, United States Geological Survey, Department of the Interior, in *Commerce Reports,* April 23, 1917. Platinum is a necessary metal in many industries closely connected with the war. In this article "platinum" includes not only the single metal but all of the metals of the platinum group—palladium, iridium, rhodium, ruthenium, and osmium. The known supply of this metal is quite limited; possibly 5,000,000 ounces have been produced in the world to date. Estimates based on the official figures of production from Russia since 1843, which are taken as 25 per cent. low, and on the assumption that Russia has supplied 95 per cent. of the world's output, indicate that the total quantity of crude placer platinum produced in the world since 1843 has been less than 4,632,000 Troy ounces, or about 109 short tons.

The United States alone apparently uses in the neighborhood of 65,000 ounces of fine platinum a year, of which approximately 50 per cent. is used in jewelry. In this connection it is interesting to note that in 1915 about 44,000 ounces of platinum were in use in the contact process for the manufacture of sulphuric acid in the United States, and it seems reasonable to assume that contact plants in the world have at least 500,000 ounces. The quantity of platinum in chemical and physical equipment in the world cannot be readily ascertained, but an estimate may be hazarded as 1,000,000 ounces. Electrical devices may have used half that quantity of platinum, but it seems probable that platinum now in use in that industry is not so large, say 250,000 ounces. The jewelry industry has probably consumed at least 1,000,000 ounces, and the dental industry about 1,000,000 ounces. Minor uses and hoarded platinum will account for the remainder of the probable supply derived from the known placer deposits.

With the exception of a little platinum and allied metals obtained by refiners of copper and nickel mattes and gold bullion, whose origin is not further discussed in this paper, all of the platinum in the world has been won from placer deposits. Attempts to trace platinum to its source have proved successful, particularly in Russia, Spain, and Canada, but none of the deposits of platinum in the mother rocks has been found of commercial grade under normal conditions. It should be mentioned that a primary deposit in Russia is reported under development at the present time, owing to the remarkably high prices of platinum. The mother rocks of platinum are basic igneous rocks, peridotite, pyroxenites, and dunites. The peridotites and pyroxenites are dark gray to black, heavy rocks composed principally of black or dark green iron-magnesium silicates, pyroxene, augite and hornblende, and olivine, plagioclase feldspar, chromite, ilmenite, and magnetite. Dunites are composed principally of olivine with some chromite. There is every gradation between these types or rocks and the less basic rocks. A characteristic of the basic rocks is their tendency to alter to serpentine, a soft greasy fibrous mineral of olive-green to black color that once seen is readily remembered.

The placer deposits containing platinum are all, so far as known, in the vicinity of areas of rocks of the type described above, and it would seem that in any search for new deposits of platiniferous gravels the first step is the search for outcrops of peridotite, pyroxenite, and dunite. When areas of these rocks have been found the gravels of the streams rising in them should be washed to ascertain if platinum is present. The heavy concentrates found in gravels carrying platinum are usually rich in chromite and olivine. The character of the rock particles often gives a clue to the source from which the gravels were derived. Platinum is not known in all countries in the world, but that all the deposits of this valuable metal are known is hardly possible. In fact, platiniferous deposits in southern Spain have been discovered quite recently by a geologist working on the assumption that the place to look for platinum was in areas of basic igneous rocks similar to the typical Russian rocks. Systematic search, based on similar assumption, in all countries may lead to the discovery of new deposits of platiniferous gravels of economic importance, but a note of warning should be sounded. In Russia such systematic work has been in progress for a number of years, and while new deposits have been found, they are not so numerous nor so rich as the hope of the explorers anticipated. The Russian platiniferous gravels are situated along a belt of discontinuous elliptical outcrops of basic igneous rocks, which are exposed near the summit of the Urals, particularly on the west side of the mountains, that are larger and more continuous in the north and central Urals than farther south. The concentration of platinum in the gravels is the result of a very long period of weathering and erosion, and the richer gravels have probably been reconcentrated. That is, the originally deposited gravels have been worked over and over by streams and their platinum content concentrated in a small bulk of gravel. The deposits most extensively worked are in the South Verkhotursh, Perm, North Verkhotursh, and Cherdinak districts, though several outlying deposits are known.

Colombia, South America, is the second largest producer of platinum in the world. The principal deposits are reconcentrated stream placers, located at the headwaters of the San Juan River, which enters the Pacific Ocean north of Buenaventura. Platinum is known to exist in the upper Atrato River, which flows north, entering the Caribbean Sea through the Gulf of Darien. Gold is associated with platinum in all the streams, but it is reported to be more abundant in the Atrato drainage than in the San Juan. Little is known concerning the geology of this part of the west slope of the Andes and Pacific coast region of Colombia, and scientifically conducted exploration in this region would appear to be well worth the careful consideration of capital. It is reported very recently that the Colombian Government, recognizing the need of detailed work, has planned for a scientific study of the mineral resources of the country. An American-controlled company is operating one dredge on the Condoto River and will shortly install a second boat. Two other small dredges are reported to be in operation in the district, but there are large areas of practically virgin ground which appear to be worthy of careful prospecting.

In Minas Geraes, Brazil, platinum has been known for some time in the gold washings of the Rio de Velhas, but apparently the supply is not large. Platinum is also reported to be present in the veins at Gorgo Seco and also in some of the itabirite of Minas. A study of these occurrences might be profitable, though it is believed that the studies of these occurrences already made would have led to development if any considerable bodies of platiniferous material had been found. Platinum is known to exist in streams in southeast Borneo, which rise in the Bobaris Mountains, which are composed of schists and gneisses that have been intruded by basic igneous rocks. A little scientific prospecting has been done in this region, but there appears to be a chance for more detailed work to be profitable. Platinum has been recognized in several of the Australian Provinces, notably New South Wales, Queensland, and Tasmania. On the east-coast beaches, near the boundary between New South Wales and Queensland, platinum occurs with gold, tinstone, and monazite, but in a very fine state of subdivision. The problem of saving the valuable materials is technologic and appears not to have been satisfactorily solved up to the present time. In the Fifield and Platina districts in east-central New South Wales platinum has been won from a buried gravel channel, the richer parts of which, according to the reports of the Government geologists, appear to be nearly worked out. Great difficulties were encountered in securing an adequate supply of water for washing, and the low-grade gravels have not been worked. In northwestern Tasmania, 20 miles west of Waratah, platinum has been obtained from the gravels of Nineteen Mile Creek and other tributaries of Savage River, and it was reported that the source of the platinum has been located in serpentinized basic rocks.

Within the last year scientific geologic exploration in the Sierra de Ronda Mountains in southern Spain resulted in the discovery of platiniferous gravel deposits, which may prove of economic importance. The results of this exploration show conclusively what can be done by a systematic geologic search for this essential mineral.

In North America platinum is known to exist in the gravels of a number of streams in the western mountains, both in Canada and the United States. The known Canadian occurrences are principally in the Tulameen district, not far north of Oroville, Wash. In the United States the production of placer platinum has been limited to streams rising in the belt of serpentine rocks in central California and from the serpentine areas in Siskiyou and Trinity Counties, in the northwestern part of the State, which continues northeast into Curry, Josephine, and Jackson Counties, in southwestern Oregon. Platinum has also been recognized in the gravels of streams rising in the Blue Mountains of eastern Oregon and at various places in the Cascade Mountains of central Washington. The United States Geological Survey has already made plans for an immediate survey of all possible areas in the Western States, with a view of developing both the well-known and new localities.

Quite recently platinum has been found in certain widely scattered stream placers in Alaska, and plans have been made for a study of the subject in that Territory by geologists of the survey.

Platinum Deposits in Spain. *Commerce Reports,* May 5. This account is taken from a volume issued by the Geological Institute of Spain in 1917. Mining engineers in studying the rocks of the Serrania de Ronda, between Malaga and Gibraltar, were struck with the similarity of the formations to the platinum-bearing rocks of the Urals. Examination of the gravels from the river beds showed the presence of platinum. A preliminary report was made in December, 1914, recommending further investigation. In January, 1915, such an examination was begun, and completed in October of the same year. It was found that the platinum-bearing sands are widely distributed, on 12 or more rivers, and that the yield in some zones is as high as 2 or 3 grams per cubic meter. The sands are free from clay and are easily worked. The Spanish Government arranged for a more extensive investigation, which was begun in February, 1916. This has not yet proceeded far enough to form the basis for a dependable estimate of the value of the deposits.

Jewelers to Save Platinum. *Commerce Reports.* The Jewelers' Vigilance Committee has adopted resolutions urging jewelers to discourage customers from buying platinum articles. The Press and Publicity Committee of the A. C. S. has issued an appeal to the wives and daughters of chemists to refrain from buying platinum jewelry, as the present extremely high price of this metal so necessary to chemists is due in large part to the increasing quantities being used for jewelry. In most lines, rise of price tends to limit consumption, but in this case the exact reverse has occurred, since the desirability of an article for ornamental purposes increases with the *n*th power of the cost.

Notes on Semi-Chrome Leather. ANONYMOUS in the *S. and L. Rep.*, March 15, 1917. Semi-chrome leather has the advantage over straight chrome are the leather known as East India kip, and Persian sheep and wet back after drying. It has greater elasticity and tensile strength than vegetable tannage. The materials commonly used for making semi-chrome are the leather known as East India kip, and Persian sheep and goatskins. These have been tanned in small native tanneries, and vary considerably, so that if they receive identical treatment the product will not be uniform. The skins are stripped to remove a part of the tannin, but especially to remove grease, which seriously interferes with the penetration of chrome. Borax or soda may be used for the stripping. From 2 to 2.5 per cent. of borax on the drained weight of the goods made into a warm solution in a paddle or drum works well. Thorough washing with warm water follows the stripping.

PATENTS.

Process of Treating Leather. U. S. Patent 1,225,389. PERCY ALEXANDER, Marblehead, Mass. A heated mixture of a dextrinous gum and Turkey red oil is applied to the leather.

Combined Fleshing and Unhairing Machine. U. S. Patent 1,223,424. CARLETON RUHE, Olean, N. Y.

Pneumatic Bed for Hide and Leather Working Machines. U. S. Patent 1,211,846. HENRY A. HOLDER, Lynn, Mass., assignor to Holder-Perkins Co.

Dissolving Apparatus for Extracts. British Patent 104,145. G. VAN DEWYER, London.

Synthetic Tanning Agents. British Patent 18,174. (Grant of Patent suspended.) M. WADE, 11 Hatton Gardens, London. Synthetic tanning-agents are prepared by condensing formaldehyde, or substances yielding formaldehyde, with aminonaphthol sulphonic acids, dioxynaphthalene sulphonic acids, or mixtures thereof, in aqueous or slightly acid solution, at ordinary or raised temperature. The reaction may be effected using two molecules of aromatic body to one molecule of formaldehyde, or using equimolecular proportions. The alkali salts of the above-mentioned aromatic bodies may be used in the process, acid being slowly added throughout the operation. According to examples, 2:8:6-aminonaphthol sulphonic acid, 2:3:6 dioxynaphthalene sulphonic acid, or its potassium salt are employed. The products can be used alone or together with vegetable, etc., tanning-substances for tanning hides.

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LLOYD BALDERSTON . . . . Associate Editor

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ELECTIONS.

ACTIVE.

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Samuel S. Sadtler, 210 S. 13th St., Philadelphia, Pa.
Irving W. Bogle, Helburn Thompson Co., Salem, Mass.
Robert Wright, 90 Bradford St., Brooklyn, N. Y.
Dr. Arthur W. Thomas, Havemeyer Hall, Columbia University, New York, N. Y.

ASSOCIATE.

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Fred W. Moseley, St. Hyacinthe, Quebec, Canada.
Walter Henry Barrho, % American Extract Co., Port Allegany, Pa.
C. Lee Peck, Elkland, Pa.
Edwin W. Eisendrath, 1101 W. Division St., Chicago, Ill.
Ernest D. Wilson, Mellon Institute, Pittsburgh, Pa.
William R. Rushworth, 130 N. 5th Ave., Chicago, Ill.

CHANGES OF ADDRESS.

Francis P. Howden, to 139 Walpole St., Norwood, Mass.
Francis W. Reilly, to % Northwestern Leather Co., Portville, N. Y.
R. L. Moore, to 584 Parkside Ave., Buffalo, N. Y.
Samuel J. Hefti, to 308 W. Randolph St., Chicago, Ill.
Thomas Harrington, to Juniper Point, Salem, Mass.

AMENDMENT TO THE BY-LAWS.

Section 20 of the By-Laws has been changed to read as follows:

> These By-Laws may be altered or added to at any annual meeting by a two-thirds vote of those present and voting. Written notice of proposed changes must be given the Secretary at least three months prior to the annual meeting, and he shall cause the proposed change to be printed in the JOURNAL at least one month prior to the annual meeting. Any member unable to be present may send his vote to the Secretary, who shall cast it at the annual meeting.

PROPOSED PROVISIONAL METHOD.

DETERMINATION OF TOTAL MAGNESIUM AS $MgSO_4$, $7H_2O$ (Epsom Salts) IN LEATHER ASH.

Moisten the ash with a few drops of water and dissolve in concentrated HCl. (If very high ash use 15 cc. HCl.) Add distilled water to 50 cc. and precipitate iron and aluminum with ammonia. Filter and wash with hot water. Dissolve precipitate with hot dilute (1 : 3) HCl, substituting beaker in which precipitation was made under the filter. Wash filter with hot water. Volume of filtrate should be about 50 cc. Reprecipitate with ammonia and proceed with filtering and washing as in first case.

Add second filtrate to first, volume of which will be about 150 cc. Note.—Very little aluminum is likely to be present and unless the ferric hydrate has a very characteristic appearance it is necessary to redissolve and precipitate a third time.

Bring filtrate from the iron precipitation to a boil and add 10 cc. saturated ammonium oxalate solution. If the filtrate from the iron precipitation contains a precipitate acidify the solution with HCl and then make slightly alkaline with ammonia and proceed with oxalate precipitation. Boil for 5 minutes or set on steam or water bath for 30 minutes. Filter and wash with hot water. Substitute beaker in which precipitate was made under the filter and dissolve by pouring through hot dilute (1 : 3) nitric acid. Wash filter with hot water. Volume of solution about 50 cc. Add a few drops of ammonium oxalate, bring to a boil and make alkaline with ammonia. Boil 5 minutes or set on steam or water bath for 30 minutes and filter through same filter as in first precipitation. Wash well with hot water and add second filtrate to first, the volume of which will be 250 to 300 cc.

The magnesium may be precipitated by one of two methods: (1) Evaporate the filtrate from calcium oxalate precipitation to 200 cc. Acidify with HCl. Cool in ice water to at least 15° C. Transfer to 500 cc. Erlenmeyer flask and add 15 cc. saturated solution of ammonium phosphate. Add 5 cc. concentrated ammonia, shake vigorously until precipitate begins to form, then add 15 cc. more of ammonia and shake for 15 minutes. Filter through alundum or Gooch crucible, washing with dilute ammonia water. Dry crucible and precipitate and ignite with blast lamp for 10 minutes. (2) Add to the filtrate from the calcium oxalate precipitation HCl until slightly acid, then add 15 cc. saturated ammonium phosphate solution and finally 20 cc. concentrated ammonia. Allow to stand for at least 6 hours and proceed with final filtration and ignition.

Factor for converting magnesium pyrophosphate to Epsom salts is 2.214.

FOURTEENTH ANNUAL MEETING.

The first session of the Convention was called to order by the President, C. R. Oberfell, in the west solarium of the Marlborough-Blenheim, Atlantic City, on Thursday morning, June 7, 1917. An incomplete list of those present at the various sessions follows: A. H. Lockwood, *S. and L. Reporter,* Boston; F. S. Klebart, J. B. Ford Co., Wyandotte, Mich.; W. F. Wilson, Cherry River Extract Co., Richwood, W. Va.; Louis E. Levi, Pfister and Vogel Co., Milwaukee; H. R. Davies, I. Levinstein & Co., Boston; Xavier M. Lehmann, I. Levinstein & Co., Boston; Dr. C. Gebhard Bumcke, F. S. Walton Co., Philadelphia; William Klaber, Castle Kid Co., Camden, N. J.; Oskar Riethof, W. F. Mosser Co., Richwood, W. Va.; John M. Seltzer, Kistler, Lesh & Co., Lock Haven, Pa.; H. H. Hurt, Robeson Process Co., New York; R. H. Wisdom, Stamford Mfg. Co., Stamford, Conn.; V. H. Kadish, Milwaukee Patent Leather Co., Milwaukee; L. A. Mantner, B. D. Eisendrath Tanning Co., Racine, Wis.; T. G. Greaves, J. H. Heald & Co., Lynchburg, Va.; George F. Rumpf and Edward J. White, Surpass Leather Co., Philadelphia; Walter H. Byron, W. D. Byron and Sons, Inc., Mercersburg, Pa.; F. P. Veitch, Bureau of Chemistry, Washington; W. H. Dickerson, Muskegon Extract Co., Muskegon, Mich.; Caspar Drueding, Philadelphia; Charles C. Smoot, III, and L. E. Stacey, Jr., C. C. Smoot and Sons, N. Wilkesboro, N. C.; George E. Cox, Barber Leather Co., N. Adams, Mass.; Harrison L. Clough, W. H. McElwain & Co., Merrimack, N. H.; Dr. R. Breves, Waukegan, Ill.; Sydney Davis, D. Strauss & Co., Philadelphia; P. J. Schwale, E. F. Houghton & Co., Philadelphia; Joseph Daoust, Daoust, Lalonde & Co., Ltd., Montreal, Can.; J. V. R. Evans, Badger State Tanning Co., Sheboygan, Wis; Walter H. Stifel, Pittsburgh; Thomas Harrington, R. W. S. Leather Co., Salem, Mass.; Alfred J. E. Schmidt, Genéral Leather Co., Newark, N. J.; H. L. Harris, Pacific Coast Borax Co., 100 William St., New York; Norman C. Hertz, Max Hertz Leather Co., Newark, N. J.; Irving Cohen, J. Paskus and Son, Inc., Middleburg, Pa.; F. R. Mosbaugh, Anglo-Canadian Leather Co., Huntsville, Ont., Can.; Guy T. Creese, Creese & Cook Co., Danvers, Mass; Henry W. Healy, Central Leather Co., New York; H. B. Hommon, Cincinnati, Ohio; Charles R. Delaney, J. S. Young & Co., Hanover, Pa.; A. S. Ross, M. D., Camden, N. J.; F. C. Stout, Philadelphia; R. Boehringer, Newark, N. J.; George H. Shaw, Washington; M. Dorset, Washington; Jerome S. Rogers, Leather and Paper Laboratory, Bureau of Chemistry, Washington; E. A. Prosser, Borne-Scrymser Co., New York; P. F. Reilly, F. S. Walton Co., Philadelphia; F. J. Norris, Keystone Leather Co., Camden, N. J.; Douglas McCandlish, A. F. Gallun & Sons, Milwaukee; R. E. Porter, Ashland Leather Co., Ashland, Ky.; H. C. Reed, Reed Laboratories, New York; Robert W. Griffith, Champion Fibre Co., Canton, N. C.; Thomas Blackadder, Smethport Extract Co., Inc., Damascus, Va.; J. W. Bogle, Helburn Thompson Co., Salem, Mass.; F. H. Small, Graton & Knight Mfg. Co., Worcester, Mass.; J. J. Kelly, American Oak Leather Co., Cincinnati, Ohio; C. H. Reumann, Philadelphia Drying Machinery Co., Philadelphia; John Arthur Wilson, A. F. Gallun and Sons, Milwaukee; Lloyd Balderston, Elk Tanning Co., Ridgway, Pa.; M. S. Smith, Salem Oil & Grease Co., Salem, Mass.; W. H. Teas, Marion Extract Co., Marion, Va.; Frank S. Hunt, Peabody, Mass.; Edmundo Piazza, Azul, Argentina; Fred W. Moseley, St. Hyacinthe, Can.; J. E. Breithaupt, Kitchener, Can.; Sig. Saxe, Marden, Orth and Hastings Co., New York; Charles R. Oberfell, England, Walton & Co., Philadelphia; A. P. Tanberg, E. I. Dupont de Nemours Co., Wilmington, Del.; C. Lee Peck, The Dorr Co., New York; S. S. Sadtler, Samuel P. Sadtler and Son, Philadelphia; Reinhold Lang, Lang Tanning Co., Ltd., Kitchener, Ont., Can.; W. K. Alsop, Elk Tanning Co., Ridgway, Pa.; John S. Downing and George V. Downing, J. E. Rhoads and Sons, Wilmington, Del.; R. W. Hickman, Bureau of Animal Industry, Washington, D. C.; J. W. Keller, Philadelphia, Pa.; T. A. Faust, Yocum-Faust, London, Ont., Can.; Samuel A. Faust, Ambler, Pa.; Allen Rogers, Pratt Institute, Brooklyn, N. Y.; C. E. Heald, J. H. Heald & Co., Lynchburg, Va.; H. T. Thornhill, J. H. Heald & Co., Lynchburg, Va.; Philip S. Tilden and John P. Allen, Harrisons, Inc., Philadelphia; John H. Yocum, Newark, N. J.; F. A. Loveland, J. W. and A. P. Howard Co., Corry, Pa.; Aug. H. Vogel, Pfister & Vogel Co., Milwaukee; V. A. Wallin, Wallin Leather Co., Grand Rapids, Mich.; A. M. Buswell and Arthur W. Thomas, Columbia University; Dr. A. Parker Hichens, H. K. Mulford Co., Philadelphia; G. E. Gallun, A. F. Gallun and Sons, Milwaukee; E. J. Haley, Haley-Hammond Co., New York.

The President's address appears elsewhere in this issue.

The Secretary, Mr. H. C. Reed, next gave his report. There were 163 active members on May 1, 1916. Since that time 17 have been elected and 2 transferred from associate to active membership; total gain of 9. Active members resigned, 3; dropped for non-payment of dues or other cause, 14; total losses, 17; net gain in active membership, 2. Associate members, May 1, 1916, 164. Elections, 58; resigned, 9; died, 1; transferred to active list, 2; dropped for non-payment of dues or other cause, 10; total deductions, 22; net gain, 36. Membership, May 1, 1917, active, 165; associate, 200; total, 365.

The Treasurer's report showed on account of the JOURNAL, receipts from advertisers, subscriptions, bound volumes and back numbers, $1737.45; expenses on all accounts, $1,749.78. Accounts payable from advertisers, for bound volumes and back numbers, and unpaid dues amounted to $652.67. It will thus be seen that if amounts due on JOURNAL account were paid the receipts would be in excess of expenditures. On general account, the following items were included: Cash, May 1, 1916, $1,643.86; dues received, $1,702.37; interest, $34.18; total, $3,380.41. Expenses: Annual meeting, $131.02; Council meetings, $115.19; committee expenses, $64.22; printing, postage, etc., $382.26; Secretary's expenses, $249.96. The cash balance, May 1, 1917, was $2,425.43.

After reading his report, Mr. Reed suggested that it might be well for the Association to invest $1,000 in a Liberty Bond. A motion authorizing the Council to make such an investment was passed. The Council was also directed by motion to pay over $200, or more if they deemed it advisable, to the American Red Cross. The President requested all present to register on the adjournment of the session.

The next item of business was the report of the Committee on Comparative Analysis, by R. H. Wisdom, Chairman. Several members expressed themselves in favor of continuing this Committee, so that we may have each year a test of the way our method of tannin analysis is working. (Mr. Wisdom's report was printed in the May JOURNAL.)

The report of the Committee on Solubility of Hide in Salt Solution, which appeared in the May JOURNAL, was presented and called forth some discussion. F. H. Small said that one point which had been discussed in this connection was whether it was safe to use soaks a second time, the salt carried into the soak from the first pack of hides being looked upon by some observers as likely to cause solution of hide. Judging from the results of this work, there seems no reason why soaks should not be used a second time, so far as loss of hide substance is concerned.

A report on "Specifications for Kaolin" was called for from Mr. R. W. Frey. Mr. Frey was not present, but F. P. Veitch reported that some work had been done on the subject, though no formal report was ready. (In a later issue the report of Mr. Veitch and discussion following will be presented.)

C. R. Oberfell now gave his committee report on "Determination of Free Sulphuric Acid in Leather." This report and an abstract of the discussion will be found elsewhere in this number. Adjourned to 2 P. M.

AFTERNOON SESSION, THURSDAY, JUNE 7.

The first item was the presentation of Mr. Guy T. Creese's committee report on Dye-Testing, which was printed in the June JOURNAL. Mr. Creese passed around some samples of dyed yarns, and a considerable discussion followed, which will be published later in the JOURNAL.

Mr. Alsop's report on "Sulphonated Oil Analysis," printed in the June JOURNAL, was next considered. This also called out much discussion, which will be printed in a future issue.

Mr. H. B. Hommon, of Cincinnati, sanitary chemist in the Public Health Service next read a paper on the "Purification of Tannery Wastes," which appears elsewhere in this issue, together with an abstract of the discussion which followed it.

The last paper of the afternoon was by C. H. Reumann on "Modern Methods of Drying Hair." This paper also appears in this number.

MORNING SESSION, FRIDAY, JUNE 8.

This session was a symposium on anthrax. The first paper was by Dr. A. S. Ross, of Camden, N. J., on "Anthrax." The next, on "Practice and Theory in the Treatment and Diagnosis of Anthrax," by Dr. H. Z. Frisbie, of Elkland, Pa., was read by Mr. C. Lee Peck. Dr. A. Parker Hichens, of the H. K. Mulford Co., spoke on the "Nature of Anthrax, and Anti-Anthrax Serum." Mr. A. M. Buswell presented his paper on "Disinfection of Tannery Wastes," published in the June JOURNAL, passing around reprints of the paper, summarizing his results, and adding some data obtained since the paper was written. President Oberfell read a newspaper clipping about anthrax surgery at Bellevue Hospital.

Mr. Van A. Wallin read a paper on "Anthrax and Disinfection of Hides." Mr. F. H. Small real a paper sent by Alfred Seymour-Jones entitled "The Future of Hide Supply," dealing largely with the matter of disinfection. Discussion was postponed until the afternoon session.

FRIDAY AFTERNOON, JUNE 8.

The first paper of the afternoon was by Dr. J. Merritt Matthews on "Nigrosines." This paper and an abstract of the discussion which followed will appear in a future issue.

The discussion on anthrax was introduced by Dr. R. W. Hickman, of the U. S. Bureau of Animal Industry, followed by Dr. Dorset of the same Bureau. After some general discussion, Mr. S. S. Sadtler presented a report on some experiments in disinfecting effluent from Camden morocco factories. Mr. C. Lee Peck, of the Dorr Company, New York, reported on experiments in treatment of sewage from the tannery of the Proctor-Ellison Company at Elkland, Pa. Those present were invited to inspect the experimental unit at Elkland, which will remain in service until the first week in July, when it is to be torn out to make room for a larger installation.

It is the intention of the editors to publish the papers and discussion on anthrax in the August number of the JOURNAL.

Mr. J. S. Rogers read a paper describing experiments in testing the wear resistance of sole leathers. This paper and the data obtained in the experiments are not yet ready for publication. Some discussion followed.

"Drum Tannage" was the subject of Oskar Riethof's paper, which he now presented. This, and an abstract of the discussion following are to be found in another part of this number.

SATURDAY, JUNE 9.

H. L. Harris read a paper on "Borax and Boric Acid in the Tannery and Currying Shop," which will be printed later.

T. A. Faust presented his report of the work of the Committee on Effect of Hard Water on Tannin, which was followed by some discussion. Publication of report and discussion is deferred, probably until September.

The next feature on the program was a discussion on theories of leather chemistry, in which the following gentlemen participated: J. A. Wilson, Dr. A. W. Thomas, L. Balderston, Dr. William Klaber, and R. W. Griffith. This discussion will appear in a future issue of the JOURNAL.

Mr. Yocum criticised the Government specifications for sole leather.

Mr. Guy T. Creese made a motion that the Council be instructed to telegraph to the United States Government offering the services of the Association in any capacity in which they can be used. Mr. Wilson seconded the motion. In answer to a question, Mr. Creese accepted an amendment placing the matter of whether the offer should be made to the President or to the Council of National Defence at the discretion of the Council of the A. L. C. A. After a long discussion, an amendment offered by Mr. Kadish was adopted, directing the Council to specify what services this Association is prepared to offer. The amended motion was carried, and the Council so directed.

Instead of holding the business session over till afternoon, it was decided to remain in session long enough to finish the election and other items. Mr. Kadish and Mr. Seltzer were appointed tellers, and while they were counting the votes, F. H. Small read correspondence which he as Secretary of the American Section of the International Association had had with Professor Procter in relation to the organization of that Association. The matter was referred, on motion, to the Council, who are to report a plan of action.

J. S. Rogers proposed the preparation of a ten-year index of the JOURNAL. After some discussion the matter was referred to the Council, with power to act.

The report of the tellers showed that J. H. Yocum and F. H. Small had been elected members of Council.

The proposal to amend Section 7 of the By-Laws so as to admit associate members to the right to vote except on matters affecting changes in methods was lost. That to amend Section 20 was adopted. The amended section is printed in this issue. Adjournment was reached at 1.30 P. M.

COUNCIL MEETINGS.

A meeting of the Council was held at the Marlborough-Blenheim on Wednesday evening, June 6. No report of this meeting has been received by the JOURNAL.

Immediately on the adjournment of the annual meeting, the new Council met. Present: Messrs. Oberfell, Reed, Veitch, Alsop, Small and Yocum. F. H. Small was authorized to correspond further with Professor Procter and the Secretary was instructed to have copies of the correspondence which was read at the meeting made and sent to each member of Council, so that at the next Council meeting some progress might be made in deciding what had better be done.

The Secretary was instructed to write to President Wilson, transmitting the resolution of Mr. Creese, and telling in what ways the members of the Association might be of service.

A number of new members were elected.

The Secretary presented a proposal from J. A. Wilson to amend article 2 of the By-Laws to read as follows: "The objects of this Association are, (*a*) to devise and perfect methods for the analysis of leathers and of all materials used in their manufacture; (*b*) to promote the advancement of chemistry, especially in regard to its application to problems confronting the leather industries; (*c*) to publish the results of investigations and researches dealing with the above subjects."

The matter of standard methods for water penetration tests was discussed, but no action was taken.

The Editor was instructed to find out the probable cost of printing a ten-year index of the JOURNAL, to report to the Council.

Mr. Oberfell and Mr. Veitch were appointed to draw up a provisional method for the determination of magnesia in leather ash.

The Treasurer was authorized to invest $1,000 in Liberty Bonds and to pay $200 to the American Red Cross.

PRESIDENT'S ADDRESS.

By Charles R. Oberfell.

The past two years have witnessed a long overdue awakening of the public mind to the advantages which chemistry is offering in the economic life of this nation. This is a condition which will react not only to the advantage of the trained chemist, but in addition its beneficial effect will be felt by the population as a whole. A popular appreciation of the true worth of the role played by chemistry in the industries will result in increased and more economical production, in this way contributing to commerce in general which will mean continued prosperity for the masses after the close of this war.

This nation has too long thought of chemistry in terms of the university laboratory, the apothecary's shop and the compounder of special formulae. What is needed is an appreciation of the fact that chemistry has its largest and most useful application in the industries of the country. The fact that certain chemical substances, such as synthetic dyes and medicinal products have become scarce and also that other substances are used as munitions of war has brought the subject home to the average citizen. He is as a result showing some signs of grasping the idea that the manufacturing of dyes and explosives, fertilizers and steel are chemical processes. The press is showing some indication of awakening and are offering for public consumption material bearing upon the industrial phases of chemistry which a year ago would have been passed over completely. As industrial chemists to-day let us for the common good encourage this form of popular instruction.

To-day we should be proud of the part which we are destined to play in the greatest history-making epoch of all time. The

American Chemical Society after offering its services to the President has co-operated with the Director of the Bureau of Mines in preparing a census of chemists and metallurgists. From this are being prepared lists of men best fitted by experience and training to aid in the solution of various problems with which the industries of the country will be confronted in prosecuting the war to a victorious end. Not only this but further, in conjunction with the National Academy of Sciences the research ability of the nation is being organized for the purpose of attacking any original problem which needs solution. The Government has often keenly felt the need of expert advice in scientific matters and is taking the necessary steps to make this advice available. I am informed that in the two enterprises just named 10,000 chemists and metallurgists are enrolled for whatever duties may be required of them.

The A. L. C. A. has co-operated in this great work. Our services as a body were offered to the Council of National Defense. As a result of the action taken, in which you co-operated, the Federal Government should now be in possession of information which will enable it to place its hands on those of us who are best equipped to aid in any problem relative to the preparation of tanning materials and the production of leather which is one of the most essential of the munitions of war. We should in consequence hold ourselves in readiness to serve out Government in whatever form is most desirable, no matter what the sacrifice.

Prior to the war we were importing from all parts of the world vast quantities of various tanning materials, which were used in one way or another to augment our native supply. These importations have in large measure been cut off so that our tanners have been compelled to depend on domestic materials. In this connection as leather chemists we are rendering valuable service in giving advice, and in these endeavors let us carry in mind one fine idea: to produce for the use of our soldiers who will risk their lives for the preservation of those great principles on which our nation is founded the highest quality of products that is within human attainment. Quality is the great word, and let us not be satisfied until we have spent our best efforts in its behalf. Let our influence with our employers and our work in the plant be not making of the greatest profits but rather the making of the best leather that will insure comfort, health and strength to our gallant troops. Let us join with the National Association of Tanners, who at their recent meeting in Boston adopted the following resolution, "Be it resolved by the National Association of Tanners, that we extend to the Government our full co-operation in supplying the highest quality of military leathers that can be produced, at fair prices, and offer our further assistance in any capacity that may be of service," and make this patriotic resolution our motto.

I have a most practical thought to bring to your attention. Your President, acting in a personal capacity, has been for some weeks in touch with certain Army officials in the drawing of specifications by which sole leather for Army shoes may be purchased free from adulterants and weighting materials. The importance of this cannot be overestimated, as you all know, and I am pleased to say that these specifications have received the approval of the producers of sole leather and that they have been adopted by the Quarter Master General in Washington.

Sole leather will be purchased and Army shoes will be manufactured under the observation of inspectors who will find it necessary in order to insure the object for which the specifications were designed, to have made a great many analyses of sole leather. In view of the fact that many millions of shoes are to be made there do not exist Government laboratory facilities sufficient for this purpose and to have this work done by commercial laboratories would involve the spending of large sums of money which can be avoided. It seems to me that here is an opportunity for us as leather chemists to perform a patriotic duty and to volunteer to do this work. My suggestion is that we offer our services for the analysis of sole leather such as is necessary for the successful procuring of this product according to the official specifications.

These specifications call for the determination, according to the official methods of analysis of this Association, of water soluble material, total sugars as glucose, ash, Epsom salts and oil. The practical working out of this suggestion can be obtained by preparing a list of our members who volunteer their services, and to these samples taken by the inspection department can be sent for analysis in such order that the burden may be evenly distributed. If we are willing to give our time, our employers or the owners of the laboratories will certainly permit of their use. From our membership I estimate that 75 men in 50 different laboratories can be enlisted for this work, which figures speak for themselves. This meeting should be the place for the beginning of this voluntary service and it can then by official direction be organized for the work to be done.

Let us turn from problems and thoughts of war to the early days and aims of this Association. I am impelled to this by a persual of the subjects which will constitute the program of this meeting. I refer to the fact that we will here consider a number of subjects intimately connected with the application of our science to the manufacturing problems of the leather industry.

The objects of the A. L. C. A. as contained in our by-laws are as follows: "(*a*) To investigate the methods of analysis of tanning materials, and all other materials connected with the manufacture of leather, with intent of perfecting or improving such methods. (*b*) To publish all papers and information on matters above mentioned in such manner as may be deemed advisable. (*c*) To do all other things in any way connected with the accomplishment of the objects above mentioned." We thus note that in the beginning we were limited to the consideration of the development of methods of analysis. President Teas in his address before the second annual meeting of this Association at Washington in November, 1905, said: "The object of the A. L. C. A. is solely the advancement and standardization of methods of analysis; we are not organized for the purpose of solving manufacturing problems, nor to inquire into methods of manufacture."

Since that time our stated objects have not been altered, but we have grown perhaps subconsciously, far from this limited field of activity. Who will venture to say that this growth has not been wise and for the best interests of the leather industry and that it does not promise great achievement for the future? Our program to-day is worth the time and attention of the manufacturer, and it is in direct answer to his support to us by his associate membership in our organization. We only hope for his increased presence at our annual gatherings.

In thus passing quickly over the analytical objects which consumed our early attention we may be permitted to stop and view the result with some satisfaction. Our official methods for the analysis of tannins have been adopted, with slight variations due to local conditions, elsewhere until they are the recognized standard and universally used all over the world.

In closing may I express the hope that our efforts in the field of applied chemistry to the manufacture of leather will be equally successful.

PURIFICATION OF TANNERY WASTES.

By Harry B. Hommon,

Sanitary Chemist, United States Public Health Service, Cincinnati, Ohio.

The rapid growth of large cities upon the watersheds of the interstate rivers during recent years has placed a burden upon the purifying powers of the rivers to such an extent that Congress was prevailed upon to pass a law in August, 1912, empowering the Public Health Service to study "The Pollution, Direct or Indirect, of the Navigable Rivers of the United States."

In carrying out the instructions contained in this law the Potomac and Ohio Rivers were selected for a detailed intensive study of the extent and effect of the pollution received at all points along the watersheds.

The interest aroused among the authorities of the cities and the owners of large manufacturing plants on the watersheds led to a request, especially from the manufacturers of small towns, that the Government go further than make a survey, and work up methods for purifying industrial wastes. In many cases law suits were threatened and everywhere the states were threatening to pass laws prohibiting the discharging of waste liquors from manufacturing plants into the rivers or small streams emptying into the rivers.

In the absence of available data whereby manufacturers could comply with such laws if passed, the Government began the study of methods of purifying industrial wastes from plants that were representative of different industries producing liquid wastes. It was realized that all the industries of one class might not produce liquid wastes of exactly the same character, but it is well within reason to expect these wastes to be similar enough to enable sanitary engineers to make a comparison between those of a company wishing to purify their wastes and those studied at the different factories. The importance of securing a disposal plant that will properly perform its work will warrant any company retaining a competent sanitary engineer to work up the proper design for their disposal plant even when the plans are to be based upon results obtained from the operation of small testing units.

A testing station was started in operation at the Deford Leather Company's plant, Luray, Virginia, in September, 1914, and the tests completed August 9, 1916. Another testing station was constructed at the Haffner Brothers tannery, Cincinnati, in April, 1916, and is now in operation to determine whether there is a variation in the volume and character of the wastes from different tanneries using the same raw material and practically the same method of manufacturing but making a different kind of product and to learn what modifications of design would be required to meet the varying character of the wastes.

TESTING STATION AT LURAY, VIRGINIA.

The Deford Company make butts for belting leather from cattle hides and sole leather from the heads and bellies. Tan liquor leached from oak bark at the plant is used in tanning the butts and some chestnut extract for tanning the heads and bellies. No other chemicals are used except a small amount of alkali and acid in bleaching the heads and bellies. There is no bating and the liming process is the ordinary procedure of most all tanneries. The unhairing is done entirely by machinery and the fleshing almost entirely by machines.

The favorable situation of the outlets from the Deford tannery whereby a gravity flow through the test units could be obtained and the interest taken in the work by the owners of the tannery were the factors that determined the location of the testing station at Luray. Every process in the tannery producing liquid wastes had a separate accessible outlet and advantage was taken of this favorable situation to study each waste separately at first and later to bring them all together in the proportion in which they were discharged from the tannery.

Settling tanks and filters were installed on each of the four principal outlets in the early part of the tests and the volume from each outlet and the effect of the treatment studied for one year. The wastes from each outlet may be described as follows: First, those from the beam house, including the spent lime waters, washings from the beam house floors and the alkali and acid waters from the bleaching vats. This waste computed on a basis of flow through the entire tests was 65,500 gallons per day. Second, the water used in washing the lime out of the hair removed by the unhairing machine. This was 23,500 gallons per day. Third, the spent tan liquors from the rocker pits and the wash water resulting from rinsing the hides when removed from the lay-away yard. These wastes were, in volume, 7,000 gallons from the rocker pits and 7,000 from the hide washing. Fourth, a small amount of dilute liquor from a revolving drum in which the heads were rinsed, and the water wrung out of the heads and bellies by centrifugal machine after bleaching.

The Government is interested not only in developing methods of purification, but in assisting the manufacturers in saving material escaping in their liquid wastes and making actual demonstration of the fertilizing value of the solids removed by the settling tanks. Therefore, during the early part of the tests each waste was studied separately but later when the volume and chemical composition of each had been determined a portion of each one was delivered to a central point where the principal devices were located and the tests continued by mixing the different components and treating them in various combinations of settling tanks and filters.

The early studies had proven that the spent tan liquors were too concentrated to permit of purification by filters operated at economical rates, and it was necessary to utilize the reaction between the tannic acid and the excess lime in the beam house and hair washing wastes to obtain a mixture that would be suitable for treatment on filters. Even this combination, however, required rates of filtration too slow to be practical for a permanent plant. Further studies at this time developed the fact that by treating the spent tan with sludge from the lime vats its concentration could be reduced about one-half, and the strength of the combined beam house and hair washing wastes could be considerably reduced by treatment with iron (copperas or ferrous sulphate) at a rate of 10 grains per gallon. The combination of these wastes thus modified admitted of purification in a plant that will be within the financial limits of the average tannery.

The plant that was operated during the latter part of the tests included the following tanks and filters: First, a storage tank for the spent tan liquor, 7 feet by 8 feet in plan and 2 feet deep. In this tank the spent tan was treated with lime sludge, the mixture allowed to settle and the supernatant added to the beam house and hair washing wastes. Second, a small storage tank of about 10 cubic feet capacity for the copperas solution. Third, two settling tanks connected in series, each 7 feet in diameter and 14 feet deep. The first of these two was of the Dortmund and the second of the Imhoff type. In these tanks the solids were removed. Fourth, two cinder filters, both 5 feet square and containing 7 feet and 5 feet of cinders respectively. Fifth, a coke filter 2 feet 9 inches square containing 5 feet of coke. Sixth, four sand filters, one 5 feet square containing 5 feet of sand, one 3 feet square containing 3½ feet of sand and two, 1 foot in diameter, containing 2 feet of sand.

Lime sludge from the unhairing vats was mixed with the spent tan liquor until it was neutral and the supernatant mixed with the other wastes in the proportions as discharged from the tannery. A solution of copperas (ferrous sulphate) was previously added to the other wastes at the rate of 10 grains per gallon, and the composite passed into settling tanks where it was retained for four hours. Here the solids in suspension were settled out and the supernatant applied to the cinder and coke filters, and the effluents from these were distributed over the sand beds.

ANALYSES OF THE RAW AND TREATED WASTES AT THE TANNERY OF THE DEFORD LEATHER COMPANY, LURAY, VA.

		Nitrogen as			
Source	Susp. solids	Organic and Free Am.	Nitrites	Nitrates	Oxygen consumed 30′—96°C.
Beam house	850	—	—	—	600
Hair wash	900	—	—	—	200
Spent tan liquor	1,100	—	—	—	13,000
Composite	1,200	70	—	—	900
Effluent set. tank	450	55	—	—	530
Effluent cinder filter	160	30	0.29	6.0	205
Effluent sand filter	30	25	0.17	23.0	55

The results given in the above table show average analyses of each waste taken separately; of the composite consisting of the different wastes previously treated as already described and mixed in proportion to their respective volumes; and analyses of the settling tank and filter effluents.

The effluent from the coke filter is not included as the results obtained by it were practically the same as those from the cinder filter. There was no additional absorption of color or any other advantage found in the coke to justify the additional cost of the material. The sand filters also gave such similar results in spite of the differences in depth that the one given in the table is thoroughly representative.

Under suspended matter it will be observed that the amount in the composite waste is greater than that in any of the individual wastes. This is due to the fact the copperas which was added formed precipitates by its reaction with the various wastes and thus increased the suspended matter. Under the oxygen consumed column it will also be noticed that the analysis of the composite mixture shows a lower result than would be expected considering the ratio in which the different wastes were mixed. This is due to the fact the analysis given for the spent tan liquor in the table was obtained from the average of samples as discharged from the tannery while the spent tan liquor mixed with the other wastes was treated with lime sludge which reduced the concentration from 30 to 50 per cent.

The analysis of the sand filter effluent shows that by the treatment as a whole the suspended matter was reduced from 1,200 in the composite mixture to 30 parts per 1,000,000, the nitrogen from 70 to 25, the oxygen consumed from 900 to 55 and nitrification developed to the extent of 23 parts per 1,000,000. The rates corresponding to the period covered by the table were 250,000 and 200,000 gallons per acre per day for the cinder and sand filters, respectively. No odors developed in the samples after storage in a warm room for 10 days, there was only a slight color and fish (minnows and sunfish) were able to live in it for more than a month.

The sludge or the solids that accumulated in the settling tank was made up from the suspended matter that came from the tannery through the beam house and hair washing outlets, together with the iron precipitate resulting from the reaction of the copperas added to the various wastes. To this must also be added the sludge resulting from the reaction between the spent tan liquor and the lime sludge. It was black in color, had but little odor, contained some hair, was finely divided and flowed readily through a 4-inch pipe. It dried out to a spadable condition in about 10 days when applied to a depth of 10 inches over a bed of fine cinders 1 foot deep. The amount of dry sludge (100° C.) was 7.3 tons per 1,000,000 gallons of waste or 82 cubic yards per 1,000,000 gallons with 90 per cent. water as drawn from the tanks.

The fertilizing ingredients on a dry basis (100° C.) consisted mainly of the nitrogen, 2 per cent., and lime as calcium oxide, 18 per cent. The other constituents ordinarily found in fertilizer were: Potassium as K_2O, 0.3 per cent.; phosphates as P_2O_5, 0.53 per cent. Grease (ether soluble matter) constituted 1.4 per cent. From the figures given above it is obvious that the nitrogen and lime are the only compounds of any particular value as a fertilizer although the entire mixture had a tendency to loosen up heavy soil and form humus and to that extent would be valuable to the soil. Tests carried out using this material on corn planted in clay ground showed decidedly better growth in the fertilized hills and the same was true with oats, wheat and beans, but the test plots were small and located in unfavorable places so that the grain did not mature. The Deford Company has used the solids from the beam house and hair washing wastes removed by a pond in which these are settled for several years in fertilizing the land on their farm and the results have been very satisfactory as they are now raising better and more grain on their land than is grown on any other land adjoining. The sludge from the settling tank of the testing station was a better fertilizer than that collected in the settling pond as it was well digested, better mixed, and more finely divided.

TESTING STATION AT HAFFNER BROS. TANNERY, CINCINNATI, OHIO.

At the Haffner Bros. Tannery harness leather is made from cow hides. The process of tanning is similar to the method used at the Deford Company, both companies using the extract from oak bark leached out at the tanneries. At both places a small amount of commercial extract is used but the quantity is small compared to the total amount of tan liquor required. A small amount of bate is used at Haffner Bros. and there are other minor differences in the process of tanning at this tannery not employed at Luray, but the essential features are the same, particularly as they refer to the wastes produced. While the same raw products are used at the two tanneries and the process of manufacturing is practically the same, the impression among tanners is that more water is required in making harness leather and that the tannic acid in the liquors can be used up to a greater extent than is practical in making belting or sole leather. The data obtained on these points, as given later on in this paper would tend to bear out this impression regarding the spent tan liquors, but the other wastes were practically the same at both tanneries.

As already stated the purpose of making the study in Cincinnati was to learn whether tanneries in different localities using the same kind of raw material and essentially the same method of manufacture but turning out different kinds of leather, produce wastes of different character, and, if so, what changes in the design of the purification plants would be required. The testing station, therefore, that was designed for this study was a duplicate of the plant operated at Luray, Virginia, during the latter part of the work when a satisfactory effluent was obtained.

A 5-horse-power gas engine direct connected to a 2½-inch centrifugal pump was installed for raising the wastes to the measuring boxes. The spent tan liquor was discharged in the morning before the other wastes began to flow so that a storage tank 14 feet by 2 feet by 4 feet deep for the tan liquors was required. Two settling tanks, each 6 feet by 12 feet deep were designed to study different periods of sedimentation and there were four filters, two primary, one of cinders and one of coke, and two sand filters, one to receive the effluent from the coke and the other from the cinders. All of the filters were 5 feet deep. The cinders and coke were washed to remove the dirt and fine particles and the sand was the ordinary river sand used in the city for concrete work. It was fairly coarse, free of clay or loam and of good hard material.

The spent tan liquor was measured in the tannery while being discharged from the vats and a portion pumped to the storage tank to be discharged into the settling tank with the other wastes in the same proportion the volume of this waste bore to the other wastes. The general wastes were measured every 30 minutes by a weir placed on the main outlet sewer from the tannery.

TABLE SHOWING THE NUMBER OF GALLONS OF WASTE DISCHARGED PER DAY AND PER HIDE FROM THE DIFFERENT SOURCES AT THE TWO TANNERIES.

Type of waste	Deford Leather Co. Luray, Va.	Haffner Bros. Cincinnati Ohio
Gallons per Day.		
Beam house	65,500	52,700
Hair wash	23,500	Do not wash hair
Spent tan	14,000	2,800
Total	103,000	55,500
Gallons per Hide.		
Beam house	240	316
Hair wash	85	Do not wash hair
Spent tan	51	17
Total	376	333

In the above table are given the volumes of wastes produced by the various operations in the two tanneries studied, first, on a daily basis and, second, on the basis of the number of hides tanned. At the Deford Company's plant where the average number of hides tanned per day was 275 and the hair was washed, the average total flow was 103,000 gallons and the amount per hide was 376 gallons. At Haffner Bros. where 167 hides were tanned per day and there were no hair washing wastes except from the dehairing machine the total amount discharged per day was 55,500 gallons and the amount per hide 333 gallons. Deducting the hair washing wastes from the Luray totals and those from the deheairing machine, which are included in the beam house wastes, from the Haffner Bros. results, the volume of beam house and spent tan wastes per hide becomes 291 gallons and 289 gallons for the Luray and Cincinnati tanneries, respectively. The amount of tan liquor used per hide at the latter place was only 17 gallons, while at Luray it was 51 gallons. In a survey made by engineers of the United States Public Health Service it was found that for six large tanneries the total wastes discharged per hide tanned was 270 gallons and the amount of spent tan 20 gallons.

In the operation of the test units the spent tar liquor was pumped to the storage tank in the morning at the time when it was discharged from the tannery. From this tank it was added in proper proportion to the beam house waste which was pumped continuously throughout the day to a weir box in which the volume to be treated in the tanks was controlled. The mixed wastes leaving the weir box received the copperas and passed through the two settling tanks, the first of the Dortmund and the second of the Imhoff type. These tanks afforded a computed detention period, based on total displacement of 4 hours to 30 minutes.

From the tanks a portion of the wastes was taken to an orifice box above the filters and the excess wasted. The cinder and coke filters received measured volumes from this orifice box and the effluents from these filters were applied to the two sand filters, each one receiving the entire effluent from one of the primary filters.

TABLE SHOWING ANALYSES OF RAW AND TREATED WASTES AT THE HAFFNER BROS. TANNERY, CINCINNATI, OHIO.

Source	Susp. solids	Nitrogen as			Oxygen Consumed 30'—96° C.
		Organic and free Am.	Nitrites	Nitrates	
Beam house	1,450	100	—	—	800
Spent tan liquor	900	60	—	—	3,900
Composite	1,430	100	—	—	1,000
Effluent set. tank	380	75	—	—	700
Effluent cinder filter	120	30	—	—	300
Effluent sand filter	15	13	0.4	10	85

The suspended solids do not show the same variation in the composite sample as was pointed out in the discussion of this determination in the results from the Deford Tannery. This was due to the fact that the spent tan liquors were practically neutral when discharged and it was unnecessary to add lime sludge to them and the iron added combined with the small amount of tannic acid, forming iron tannate which was not removed by the method of determining the suspended matter. As the spent tan liquors were not treated before entering the other wastes the oxygen consumed value for the composite sample is the same as that computed from the analysis of the separate wastes.

As in the test at Luray, it was found that the cinder and coke filters gave practically identical results, and for this reason the results from only the one set of filters are recorded. Under the circumstances the cinders are the logical filtering media. The effluent from the sand filter was practically free from suspended solids. The nitrogen and oxygen consumed were reduced to 13 and 85 parts per million respectively and nitrification developed to 10 parts per million. During the period covered the rates on both filters were 200,000 gallons per acre per day. No odors developed in samples of the effluent of the sand filter after a 10-day storage at 20° C., the color was reduced to that of weak tea, and fish life was supported for over two months.

The suspended matter removed from the wastes by the settling tanks and referred to in the text and tables as sludge was considerably more at Luray than at Haffner Bros. This was due to the large amount of solids precipitated by the reaction between the spent tan liquor and lime sludge, which has been included in the table. This treatment it will be remembered was not used at Haffner Bros. The following table gives the volumes and analyses of the sludge accumulated at the two tanneries and for comparison and analysis of horse manure.

Table Showing Volume and Composition of Sludge from Mixed Tannery Wastes, and an Analysis of Horse Manure.

	Beford Leather Co. Luray, Va.	Haffner Bros. Cin., O.	Horse Manure
Cu. yd. per mil. gal. at 90 per cent. moist	82.0	63.0	—
Tons per mil. gal. dry solids............	7.3	5.5	—
Total organic nitrogen—per cent.........	2.1	1.8	0.70
Ether soluble matter (fats)—per cent....	1.4	1.0	—
Phosphates as P_2O_5—per cent............	0.53	1.0	0.11
Potassium as K_2O—per cent.............	0.29	0.32	0.63
Calcium as CaO—per cent...............	18.0	26.0	—

With the exception of the phosphates which was about twice as high at Haffner Bros. as at Luray, the sludges at the two tanneries analyze about the same. The nitrogen and fats are slightly higher at Luray and the calcium higher at Haffner Bros., but the differences are not great. As compared with the horse manure the sludges from both tanneries contain more of each fertilizing ingredient with the exception of the one constituent, potassium.

Disposal of Sludge.

The same method for drying the sludge was adopted at both the testing stations. Shallow filter beds were excavated with the bottom sloping to a central drain and filled with 1 foot of cinders with a 4-inch layer of sand on the surface. When the sludge was applied in quantities not to exceed 12 inches in depth over the surface the sludge dried to a spadable condition in about 10 days of clear warm weather. During very wet and very cold weather the time required for drying was longer but at the extremes not more than one month was required. There was no offensive odor near the beds and there was no difficulty in removing the sludge with shovels. After accumulating in large piles when removed from the beds the sludge did not become offensive, did not become soaked up with water after heavy rains and there was no reasons why it could not be stored in piles near the filter beds until it would be convenient to haul it away either to be used as a fertilizer or for filling low ground.

No field tests were made to determine the fertilizing qualities of the sludge from the Haffner Bros. Tannery. However, from the analyses and the results obtained by the Deford Company using the solids from their settling ponds in increasing the fertility of their land, there can be no doubt that this material has considerable fertilizing value, particularly for land deficient in lime. Since it is profitable to ship manure from the cities to the country for fertilizing land, tannery sludge with the lime present and containing twice as much nitrogen as manure ought to be worth at least as much as manure and there ought to be no difficulty in disposing of this sludge for fertilizer.

If it is necessary to dispose of the dried sludge for filling in low ground it will probably be advisable to mix the cinders from the boilers with the sludge to facilitate further drying. Underdrainage should also be provided to prevent the storage of rain water in the sludge.

Conclusions.

It is the policy of the Government in conducting these tests to continue the investigations up to the point where there is reasonable assurance that a solution has been developed and then to co-operate with the company where the tests are conducted, or with an association of companies, in building much larger units than those tested but not a full capacity plant, the company or companies paying for the construction and the Government making the plans and supervising the operation.

As a result of the tests at Luray three tanneries in Virginia, the Deford Company of Luray, the Leas & McVitty Company of Salem, and Cover and Sons of Elkton, were sufficiently interested in the purification of their wastes to contribute enough money to build a plant to test out on a large scale the results obtained in the smaller units. Plans were prepared for this plant, and construction was started March 5th which should be completed in time to start operation by June 15th.

This plant will treat 10,000 gallons per day and in its design advantage was taken not only of the information gathered at the testing station operated at Luray, but also the further experience gained from the tests conducted at Cincinnati.

The conclusions reached in these tests and their practical adaptation in this larger unit may be briefly summarized as follows: First, a storage tank for spent tan liquor to be used, also for treatment of this liquor with lime sludge if it is strongly acid. As it is customary to discharge tan liquor intermittently or but once a day, this tank is required to distribute the flow throughout the day. For the 10,000 gallon plant at Luray duplicate tanks each 10 feet by 6 ft. in plan and 3½ feet deep with dosing appliances are provided. Second, solution tank for the ferrous sulphate (copperas) solution. These tanks are in duplicate, each 1½ feet by 2½ feet in plan and 2 feet deep and have the necessary regulating devices. Third, a settling tank of sufficient capacity to allow a minimum detention period of 2 hours computed on the displacement basis. The tank for this purpose at Luray is 20 feet long by 8 feet wide by 11 feet deep and contains baffles and scum boards for holding back the scum. Fourth, cinder filters having a total depth of 5 feet of cinders or 4 feet exclusive of the underdrains. At Luray this is 42 feet by 30 feet. Fifth, sand filters. As good results were obtained with a depth of sand of 2 feet as of 5, the sand filter at Luray 42 by 30 feet is divided into three sections having 2, 3 and 4 feet of sand laid over underdrains which occupy a maximum of 1 foot sloping to zero at the sides. Separate outlets are provided for each section for taking samples and provisions were made to increase the depth of the shallow sections if it becomes necessary. These filters as well as the cinder filters will operate at a rate of 200,000 gallons per acre per day. Sixth, sludge beds with sloping bottoms containing 1 foot of cinders overlaid with 4 inches of sand. For a 10,000 gallon unit treating the type of wastes produced at Luray an area of about 600 square feet is required.

In the operation of the testing units it was found that better results were obtained by operating the filters at low rates throughout the 24 hours, rather than applying the entire dose for a given rate during the working day. In the permanent unit the settling tank is designed to store enough wastes during the day to operate the filters during the 14 hours the tannery is not in operation. During the latter part of the tests sand filters 2 feet deep gave as satisfactory results as the deeper filters, but these filters were only 1 foot in diameter and the results were not directly comparable. It seemed advisable, however, to construct the larger filter in the permanent unit of three different depths to definitely decide this point.

It is recognized that a testing station operated under the constant supervision of a technical man may produce better results than can be obtained from the operation of a large plant under the control of an unskilled operator. It is also appreciated that small units like those operated in the tests may be more readily adjusted to temperature changes and other unfavorable conditions affecting the results. It was to learn how far the results obtained from the operation of the testing units could be duplicated in a large plant that recommendations were made to the tanners interested that they build and operate a large unit.

The plant now under construction at Luray is to be under the general supervision of the Government but this will extend only to making analyses of samples sent to the Government laboratory and to occasional visits for the purpose of suggesting changes in construction and operation.

The data given in this paper are but a brief summary of the results obtained from the operation of the two testing stations. A detailed report will be published in the near future containing a complete description of the plants and the results obtained and a progress report will be published giving the results from the operation of the permanent unit.

DISCUSSION.

Mr. Victor H. Kadish inquired whether Mr. Hommon had tried the activated sludge process.

Mr. Hommon replied that it had been tried on a small scale both at Luray and at Cincinnati, but with negative results. The organisms necessary to the success of that process seemed not to be able to live in the presence of any considerable amounts of tan liquor.

Mr. V. H. Kadish spoke of experiments tried in Milwaukee, in connection with the disposal plant being installed there. Nearly all the tanning there is done with chrome, so the effect of spent tan liquors does not have to be considered. Classification of tannery wastes is an important matter. In Milwaukee a large proportion of tannery effluent, perhaps 70 per cent., is practically clear water which could go into the city sewers and be treated at the disposal plant without difficulty. The remaining 30 per cent. could be treated at the tanneries, and these liquors are rich in nitrogen. The treatment of the soaks and other wastes should yield a salable product and thus pay for itself. The activated sludge process has been experimented on at Milwaukee. It works well for soaks, and would probably work for sulphide liquors if they were not too concentrated. One of the men connected with the disposal plant, Mr. Nordell, has designed a new porous plate system for air supply in the activated sludge process. Instead of pipes with holes or "filtros" plates, he uses basswood sections in the bottom of the tank. The air is thus distributed in much finer bubbles than by any other method that has been tried, and the quantity of air necessary to do the work is thus reduced by something like 75 per cent. The reduction in cost thus effected makes the activated sludge process look very promising. It yields a sludge with high fertilizing value.

Mr. Hommon remarked that in using filter processes it is necessary to have all the wash water and other comparatively clean effluent mixed with the more concentrated liquids in order to dilute them sufficiently to make it possible to get them through the filters.

Mr. Norman C. Hertz said that the Lackawanna Leather Company, Hackettstown, N. J., pump all the waste from their tannery out onto a bed of limestone, which absorbs the water, and the sludge is collected and sold at a good price for fertilizer. The Company own enough land to enable them to do this without creating a nuisance. At first they had to give away the sludge, but when its value became known it found a ready market.

Mr. Yocum explained that the neighborhood in question has a deep bed of glacial drift which makes an excellent natural filter.

Mr. Veitch referred to experiments on sludge utilization carried out some years ago which demonstrated that such material can be used to good advantage if the tannery is situated in a truck-raising neighborhood or in any region where there is a constant demand for fertilizers of this character.

Mr. Riethof described the method used in a European country for disposing of sludge containing sodium sulphide. It was allowed to lie for three years and then worked over and allowed to lie three years more, by which time it was in condition to bring a good price as a fertilizer. This long time is necessary for the chemical changes to be completed which result in rendering the sulphide useful instead of harmful to the soil.

Mr. Sydney Davis asked Mr. Hommon if he could give figures on the cost of an installation to handle half a million gallons a day.

Mr. Hommon replied that it would be very difficult to make any estimate without knowing local conditions. For 30 miles outside of Cincinnati cinders can be had for 35 cents per cubic yard on the switch. If they had to be shipped far the cost would be much greater. With the cost of cinders and sand known, the problem could be solved approximately. The details of the experiments described in the paper will be published by the Government soon, it is hoped this summer, and data for cost estimates will be included.

DRUM TANNAGE.

By Oskar Riethof.

In all branches of industrial activity the last decades have witnessed radical changes in manufacturing processes and it is not surprising that the tanning industry has kept pace with the time, improving the old way of making vegetable tanned leather, besides inventing and developing entirely new methods. It may be true that many tanners of the old school made changes, not because they were enthusiastic about the newer methods of their competitors, but because they had to choose between keeping abreast of the time or dropping out.

When we have opportunity to compare the modern process of making vegetable tanned sole belting and harness leather, as established in countries with well developed leather industries, we are surprised to find that not all countries took the same course in the way of modernizing. All new tanning processes have two common features; they require less time and use stronger liquors. But otherwise they differ quite distinctly. We can be sure that these differences in development are not a matter of chance, but were due to special conditions in the different countries, making it advisable to use certain tanning materials and to produce leather of certain qualities in order to satisfy trade demands.

The United States undoubtedly were and still are favored by nature with a big supply of hemlock, oak bark and chestnut wood, and these three materials are still the main materials employed in the tanning of heavy leather in this country. But as the supply of native barks is diminishing and cannot fill the demands or satisfy the rapidly growing tanning industry, foreign materials in ever increasing quantities must be imported. With respect to tanning materials, this country will be confronted in the near future with conditions similar to those in England about the middle of the last century and in most countries of Continental Europe about 20 years ago.

Before the war oak bark in Germany and Austria-Hungary cost at the tannery from $14 to $20 per ton. This bark contains on the average 10 per cent. tannin. When we figure 8 per cent. as available, the tan unit, without the expense of leaching, costs from 9 to 12½ cents.

The high price of oak bark in Continental Europe is not a matter of demand and supply, but is caused by the excessive cost of peeling and handling. The 'Schaelwaldbesitzer' or owner of an oak forest has to get the price or must clear the land for other purposes.

On fir bark the conditions are a little better. In fact, fir bark is generally the cheapest tanning material at the disposal of the European tanner, costing about $13 per ton or about 7 cents per unit available tannin. But this material is not much of a filler and is mostly used in combination with other materials. You may be surprised that I give the cost of peeling as a reason for the high bark price, because wages in Europe are low. In fact, laborers in Hungary are earning only about 50 to 75 cents per day. But when you consider that the European oak and fir barks are only one-quarter to one-half inch thick, you will agree with me as to the cost of peeling as compared with the heavy American oak and hemlock bark.

In comparing the development of the tanning process in different countries it seems to me that the tanners in the U. S. and England, as a rule, used strong liquors long before the European tanner. The sole leather turned out in Europe about 20 to 30 years ago with weak liquors gave a low yield, but had good wearing qualities. To get the necessary firmness it had to be rolled down hard and dried in a rather hot room. It was therefore thin, considering the weight of the hides used. So it is easy to understand why the plump and well filled American and English sole leather could find, in years gone by, a ready market on the European continent and was able to compete successfully with the domestic product, even when handicapped with a high import duty.

About 1890 Durio came out with his first successful process for drum tannage, followed in quick succession by others, all using strong liquors and the movement in a drum to accelerate the tanning process. When men owning processes for drum tannage came to a sole leather tanner in Germany, Austria, France, Italy, etc., who tanned his leather in one to two years, making from 50 to 60 per cent. yield on salt weight and told him that he could tan his stock in four weeks, making at least 60 per cent. yield on butcher weight, corresponding to about 72 per cent. on salt weight, you could not blame him for listening to the proposition. At that time the average sole leather tannery was rather small because the steadily increasing hide prices combined with the slow return made it imperative to the tanner to operate carefully in order to be able to meet obligations.

About 1900 many European tanners shifted to drum tannage and it must be said, most of them with considerable success. It cannot be denied that at first many turned out a very poor quality, but they profited by experience, often at a very high expense. The first patents used the drum exclusively, but as early as 1894 Eitner predicted that the future would belong to a combination of vat and drum tannage, because an efficient drum tanning process must fulfil the following requirements:

(1) The tan liquor must be exhausted.
(2) The process must progress fast enough to justify the expended power.

We see to-day that all hides to be tanned in drums are first tanned in handlers or rockers, until they are more or less struck through. Then they are brought into the drum where they come in contact with heavy liquors. I do not want to say that drum tanned leather on the average was better than the good old oak sole leather, but it satisfied the customer, because it was cheap and it satisfied the tanner, because he made money on it.

About the same time as in Europe the drum proposition was brought before the American tanner, but not with the same result. Some of the biggest tanners in this country tried it out, in fact used the process for a time, but with a few exceptions came back to their layer vats. One objection I heard mentioned was that the yield was lower than with the standard methods, that is, oak, union and hemlock. And here we have the reason: The European tanner changed to drum tannage because he was able to get a better yield than with his weak liquors; meanwhile the English and American tanners objected on account of getting lower yield.

I do not want to impart the impression that all sole leather in Europe is drum tanned, but the percentage of it is very high and seems to be increasing all the time. Nevertheless we still find a great number of generally smaller tanneries producing vat tanned leather. Besides we find all kinds of combinations of vat and drum, some using the drum first and later giving a layer of some kind, others doing the reverse.

What I say about sole leather will apply to harness and belting leather too. In fact I believe that drum tannage is specially adapted for them. My experience is, as I shall explain later, that for a successful drum tannage the stock before entering the drum must be pliable, therefore not too plump. Such conditions are ideal for belting and harness leather, because we want the finished product pliable and the fiber not too much swollen and must leave enough space between the fibers for the different oils and greases used in currying. What we expect from belting and harness leather is toughness and breaking strength, and in this respect drum tannage gives as good results as vat tannage, when the tanning process is conducted properly.

Professor Paessler[1] made many tests of the tensile strength of belting leather of different tannages and came to the conclusion that the kind of tannage, or in other words, the time of the process does not seem to be of noticeable influence.

Professor Procter carried out many experiments on a similar line, showing that a very high percentage of combined tannin (degree of tannage) actually reduces the breaking resistance.

If it may be allowed to give my own experience, I want to mention that in one tannery I was connected with for some years we tanned belting leather principally with oak bark, the process requiring from six months to one year, depending on the weight of the hides. It seemed advisable to add a cheaper grade to the production, so we started to make drum tanned belting leather. As we had our own belting department, I could follow up both tannages through the entire process and further on to the ultimate customer, and I was surprised to find that the consumer was as well satisfied with belts made from drum tanned stock as he was with oak tannage. I, myself, made many tests, comparing breaking resistance, stretch, etc., without being able to find any notable difference. I might add that the men in the belt shop who handled the leather for years, were unable to differentiate between the two tannages. The same is true of harness leather. In fact I do not believe there are many tanners left in Austria-Hungary who are tanning harness leather in layers.

Previous to the war the military authorities in Europe spec-

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[1] Abstract, this J., 1909, pages 84 and 109.

ified oak bark tannage for all leather, but this was merely a matter of conservatism and fear that leather tanned with other materials may deteriorate during the many years that shoes and harness are stored away in arsenals.

Let us now consider the practical side of drum tannage. At first I will try to give you a general outline of a drum tanning process. It may seem superfluous to do so, because many of the gentlemen present know well how to tan leather in drums, but for the sake of completeness it may not be amiss.

The hides from the beamhouse enter a handler system of about twelve vats. The head liquor registers about 29° Bk., and is worked down, running ultimately into the sewer. Rockers are unknown to the European tanner and he would be afraid to use them. The liquor for the handlers is made up either entirely from extract used in the drum, where it loses its astringent character, or partly from liquor from the leach-house, where all kinds of suitable domestic and foreign tanning materials are used. When the stock comes from the handlers ,it is generally pretty well struck through. It either goes directly to the drum, or is first given a kind of extract layer in exhausted liquor from the drum, registering about 6° Bé. or 45° Bk. The starting liquor in the drum registers about 60° Bk. and is strengthened in intervals to about 90° to 110° Bk.

In some tanneries the stock is tanned out in one wheel, in others the tanning is done in a system of three wheels, so that the exhausted liquor from the first one goes to the handlers and to the above mentioned extract layer. Forty-eight to seventy-two hours in the drum will complete the tanning. It is customary to let the leather lie in pile for about 24 hours to solidify the tannin before it enters a tempering vat, where the excess tannin is removed. From there on the process is more similar to our American methods. In some cases no bleach whatever is used, but most tanners employ some kind of bleach, either wet or dry. In case of wet bleach the stock passes through a wringer, is usually hand oiled and hung up to be in right condition for setting, which is done by machine or by hand. Rolling is done in much the same way as in this country, but many long rollers with heavy pressure are in use.

This is certainly a simple process, but nevertheless it has to be worked through intelligently, if satisfactory results are to be obtained.

I will try to outline some of the reasons why so many tanners had poor results with drum tannage. The principal thing is the matter of plumping. You will agree with me, when I say that the degree of swelling is very important for any vat tannage, but still more so for drum tannage. To explain this more thoroughly, I will have to treat this subject from a theoretical standpoint. What is the effect of plumping hide? It is an intimate penetration of water within the fiber, enveloping each particle. We know that water itself is readily taken up by hide fiber and are making use of it in our soaking process. We further know that either alkalies or acids increase the effect of soaking and swelling in such a way, as to accelerate the absorption process of water by the fiber. We are speaking of an alkaline plumpness in our limes and of acid plumpness in our yard. Gelatine in its chemical constitution is undoubtedly closely related to hide substance and was used by Procter for very interesting experiments on the comparative plumping effect of water, different salts and acids. He measured the plumpness by the increase in weight on account of more or less absorption of water, because the small amounts of acids and salts absorbed can be neglected or simply deducted.

The plumped fiber naturally offers a greater surface to the cording to this consideration we should try to plump as much as tannin, will accelerate the process and increase the yield. Ac- possible in order to tan quickly. But this is true only to certain limits in the different tanning methods and especially so in drum tanning. We must not forget that by swelling we are not only increasing the thickness of the hide, but are reducing at the same time the space between the single fibers, therefore making the felt-like texture of the pelt or partly tanned hide more close, hard and less pliable. If we bring then a such prepared hide into a drum half filled with extract, the hide will not bend, it will swim in the extract without folding and unfolding and the penetration will be a slow one, specially when we consider that between the swollen fibers there is not much space left for the extract to reach the inner portion of the fiber bundles. The result will be slow tannage and low yield. We have a similar experience in our extract wheels. If we are bringing hard leather into them, it is a pretty hard proposition to get the extract into the stock. The idea in drum tanning therefore should be not to overplump the stock and to keep it soft and pliable through the whole process.

In drum tannage, the liquors, generally speaking, have not much time for fermentation and the acidity will therefore not increase very much. But I have found that in most cases the natural acidity and the natural plumping effect of the extract is great enough to make and keep the stock plump. It would be futile to try to give you figures as to the percentage of acid the liquors ought to contain. We chemists have to admit that our present methods for the estimation of acidity in tan liquors are very poor. They are of benefit to check up the acidity in one certain plant at different times, but when it comes to comparing different plants, the results will often be misleading. We know that some acids like gallic acids have hardly any plumping effect whatever, but still if they are contained in a liquor, they may be found in the acid figure, depending on the indicator used for titration. We know that the general character of sole leather, turned out in a certain yard, will depend to a great extent upon the water used for the different operations. Salts of strong acids and strong alkalies, like common salt, reduce the plumping effect of acids, so that water and liquors containing considerable quantities of them, may not plump well, even if the analysis indicates high acidity. On the other hand we know that salts of strong acids and weak bases, like calcium and magnesium sulphate have an excellent plumping effect, but we have no way of expressing it in the acid figure. To what extent salt is able to counteract the plumping effect of acids on account of reducing the ionization, is best shown in our pickling process, preceding in most cases our chrome tannage. Here we are using an acid liquor of 1 to 2 per cent., but by adding salt in sufficient quantities, we are able to prevent swelling.

I want to show you by an experience I had in Europe with two tanneries, located only two miles apart, how much the character of the water influences the plumpness of the stock and the final appearance and yield. The tanneries were built some 60 years ago by two brothers. Both were using the same class hides, the same tanning material—fir bark—and the same process, making so-called 'Fichtenterzen.' One of them turned out a plump firm leather with good yield, the other one a mellow leather with a yield about five points behind. The low yield made the production to the second mentioned brother unprofitable and after intensive study to overcome this trouble he, or in fact his son, decided to change over to belting leather and he did this with splendid success, because his water was better suited for it. Such questions as the adaptability of a certain water for tanning purposes and of a good and simple method of determining the plumping effect of salts and acids in our tan liquors, were investigated by some of our best men, but still a great amount of research work will have to be done on these and similar lines.

An other very important question for the drum tanner is the regulation of the temperature in the drum. We know that the plumping effect is in opposite relation to the temperature. We notice this in estimating the white weight; the higher the temperature of the water in our water pools, the lower the white weight will be, a fact very well known, but still often forgotten. We notice the same in the above mentioned pickling process for chrome leather. As we increase the temperature of the pickle, we can reduce the percentage of salt and still hold down the plumping effect of the acid. If we bring the partly tanned hide into our drum and allow the temperature to rise too high, we reduce the plumpness or in other words- drive water out of the fiber before we have fixed the swelling by tannin. The result will be flat leather and low yield. The rule should be to keep the temperature in the drum down, until the stock is well struck through. After this heat will be beneficial, as it will accelerate the process and give firmness, plumpness and weight to the stock.

An other very interesting chapter in drum tanning is the kind of extract used. Here we will have first to decide, what kind of leather we want to make in order to make the right choice. We cannot expect the tannin to penetrate rapidly, if we prevent it from doing so by closing the pores with a coat of sediment. In this respect the highly clarifield French product, as used in Europe is superior to our standard chestnut extract, so very well adapted for vat tannage.

If I advocate clear liquors, it does not necessarily mean low insolubles in our analysis. We have to remember, that in the last drum we are using extracts of 90° Bk. or more at about 110° F., and under such conditions a considerable part of what we in our analysis call "insolubles," will be in solution and readily absorbed by the hide. The so-called cold-soluble bisulphited quebracho extracts are clear in all concentrations, but their treatment changes the chemical constitution of the tannin molecule. Such highly sulphited extracts tan very rapidly, but do not give high yield. This is the reason why special quebracho extracts, like "Triumph" from Dr. Albert Redlich and similar products from Renner & Co. and others are used extensively in Europe, where a clear extract is desired, which at the same time gives good weight. These products are cold soluble, but not sulphited.

The benefit of using liquors of high purity is apparent. Non-tannins will dilute extract and retard the reaction between the fiber and the tannin molecule. I do not want to minimize the importance of non-tannis, because they are acid forming and under certain circumstances likely to be absorbed by the hide, but in drum tanning they undoubtly retard the process.

The wood tannins, like quebracho, chestnut and oak wood penetrate rapidly and are the principal materials used on the European continent. The last mentioned—oak wood extract—is of special interest. It has very good qualities, gives good color and weight, makes firm leather and tans very rapidly. In fact the speed with which it is absorbed by hide is so great, that its effect has cost many tanners who were not aware of the danger, a great deal of money. When fresh oak wood extract is brought in contact with hide in the first stage of the tanning process, whether vat or drum tannage—the oak wood tannin will be precipitated in the outer parts of the hide section in such quantities, as to prevent the tannin during the rest of the process from reaching the center of the hide. The result will be a raw streak in the leather. It therefore should be a rule, not to use oak wood extract except in the last stage of the process. Here it will be very beneficial on account of its great affinity to the fiber, as it will combine even when other materials have no further tanning action.

I do not intend to say much about the finishing of drum tanned leather, but it is my experience that the American methods of running scrubhouse, rolling room and dry loft are very well adapted. On the Continent and specially in England great care is taken in the finishing of sole leather. It is set out carefully by machines and often by hand, nailed on sticks, so as to hang flat and special attention paid in rolling in order to avoid bagginess. I find that in the U. S. the percentage of sole leather suitable for machine work is very high. This is different in Europe. There the machine has not yet such an important place in shoemaking and the shoe manufacturer, working in the old-fashioned way, prefers a hard sole, which has to be soaked in water, in order to be workable. The rising number of European shoe manufacturers, using the latest type machines, have often a hard time to secure suitable leather for their purpose, because many tanners do not know how to make leather which combines weight, firmness and pliability. If you take the average Continental or English sole leather tanner and explain to him that you desire leather which can be bent sharp without chacking, he will think it strange and will not understand that sole leather should be given a more severe bending test than that obtained in the actual wear.

It may be in place to say a few words on the comparative analysis of leather by the vat and drum process. Years ago when I was asked, if a certain leather was vat or drum tanned, I made an analysis and if the percentage of water solubles was above ten per cent. I was pretty sure of drum tannage. Thuau in 1909 gave the requirements of the Belgian Government for sole leather as following: Ash below 1 per cent., hide substance 48 to 50 per cent., water solubles maximum 8 per cent. Kohnstein gives as average of a large number of analyses the water solubles of oak and pine vat tannage with 3.5 per cent to 8 per cent., of drum tannage with 14 to 15 per cent. In the typical American and English sole leather we find normally around twenty per cent. water solubles and it is significant, that since the beginning of the war the English Government had to increase the limit of water solubles in army sole leather from 20 to 25 per cent. I might add that the new army regulations of this country, just published, limit the water solubles of sole leather to 26 per cent. American and English tannages and in fact all modern vat tanning methods cannot therefore be told from drum tannage by the percentage of water solubles.

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[1] Le Cuir 1909, No. 22-24.

[2] Allgen. Gesberzeitung, No. 9, 1912.

Some chemists believe they can tell from the "degree of tannage," whether a certain sample is vat or drum tanned. They claim that the degree of tannage, that is parts tannin combined with one hundred parts hide substance, is lower in rapid tannage than in vat tannage. To see to what extent this is true, I collected all the leather analyses possible and made up the accompanying tables, showing the "Degree of Tannage" and the percentage hide substance in different tannages. Those figures are taken not only from my own results, but I have also used analyses published by Veitch, Parker, Thuau, Yocum, Meunier and others. It may be surprising that the limits are so far apart, but the exceedingly high and low figures are to be found in relatively few samples, so that they do not alter the average to a great extent.

As very well known, the results differ somewhat depending upon the part of the hide from which the sample is taken. The loose parts of the hide tan faster and more thoroughly than the butt, therefore the degree of tannage will be higher in the belly. Another fact we have to consider is that some of the samples analyzed may not have been tanned thoroughly and naturally will show a low degree of tannage. We further have to remember that we are getting the percentage of combined tannin by difference. We add moisture, insolubles ash, soluble solids and hide substance and report the difference to 100 per cent. as combined tannins. But it really consists of organic matters, insoluble under the conditions, under which we are extracting the solubles. It includes therefore the bloom and all difficulty soluble and insoluble tannin we were able to carry into the leather by different means as heat, milling, etc. But even if we make reservations for those shortcomings in our analytic methods, the table should tell us quite interesting facts. We find our four American standard tannages leading, together with North German sole and Austrian terze, the last two named plumped with acids and tanned by a slow process principally with strong tanning materials. In French oak sole leather (time over one year) with exceedingly low degree of tannage and high percentage of hide substance we see the result of weak liquors. Further down in the table we find all kinds of mixed tannages, that is tannage in vats with a mixture of different tanning materials and generally stronger liquors and in shorter time than the old tannages like French oak.

The second table gives the analyses of drum tanned leather. I did not have at my disposal as many analyses as of hemlock or union, but it still shows that the Degree of Tannage is lower than in most vat tannages. The reason in my opinion is not so much the short time of the process, but to a greater extent in some cases the lack of sufficient swelling of the fiber on account of low acidity. I said before that great plumpness and rapid tannage in the drum are two factors, difficult to combine. Without going deeper into the theory of the tanning process I will say that it is my opinion that tannin will penetrate the swelled fiber filled with water molecules more thoroughly than a less plump fiber, assuming that sufficient tannin is applied in right concentration. The single fiber tanned with sweet liquors in the beginning of the process and therefore not well plumped, will not be so very thoroughly struck through by the tannin molecules and the result must be a lower percentage of combined tannin. This is confirming the results of investigations carried out by Eitner.* He found that Rhenish oak sole leather, which is tanned by a slow vat process with rather sour liquors, gives no glue by boiling with water, while sweet tanned leather swells, yielding glue.

TABLE SHOWING DEGREE OF TANNAGE AND PER CENT. HIDE SUBSTANCE IN DIFFERENT STANDARD TANNAGES.

	Degree of tannage			Hide substance per cent.			No. of
Kind	Aveage	Lowest	Highest	Average	Lowest	Highest	Anal.
Vat Tannages:							
American oak sole........	80.0	44.6	98.0	40.5	31.5	43.4	41
American Union sole......	80.6	53.0	104.0	37.2	30.3	46.2	58
American hemlock sole....	77.5	60.0	107.0	36.2	30.2	43.1	20
California oak sole........	84.6	65.4	94.6	34.0	33.3	35.3	3
English oak sole..........	70.7	53.0	83.5	36.3	34.9	38.6	8
North German sole........	82.9	82.4	83.3	39.4	39.1	39.7	2
Austrian Terze	80.4	—	—	36.5	—	—	1
French oak sole...........	68.7	65.7	73.1	44.2	42.6	45.4	6
English sole (mix. tannage)	73.6	64.1	85.3	36.1	34.7	37.3	7
French sole (mix. tannage)	73.7	63.0	76.6	38.4	35.6	40.9	5
Italian sole (mix. tannage)	62.1	61.9	62.3	36.7	35.6	37.8	2
Spanish sole (mix. tannage)	68.6	68.1	69.2	40.4	40.2	40.5	2
Venezuela sole	57.1	—	—	48.0	—	—	1
Drum Tannages:							
American drum tannage...	70.0	53.0	79.0	38.1	33.3	49.0	10
English drum tannage.....	47.8	36.3	59.2	39.6	35.8	43.3	2
French drum tannage.....	80.0	—	—	39.8	—	—	1
German drum tannage.....	63.6	—	—	34.4	—	—	1
Belgian drum tannage.....	62.1	54.2	70.1	34.0	33.8	34.2	2
Dutch drum tannage......	65.8	—	—	41.2	—	—	1
Austrian drum tannage....	72.0	—	—	39.5	—	—	1

[1] Gerber, 1912, No. 38. Abst. this Jonrnal, 1912, pp. 281-2-3.

Up to the present time with out limited knowledge of the theory of the tanning process we do not know whether there is a theoretical "Degree of Tannage," or in other words, whether fiber and tannin combine according to chemical equivalents. We must therefore be very careful in condemning leather for the single reason that its degree of tannage is rather low.

To come back to our table, it may be interesting to compare the percentage of hide substance of the various tannages. As this figure is in opposite relation to the yield, it allows us to make comparisons in this respect. We will not be surprised to see California Oak giving the best yield, followed by Hemlock, Union and Oak in the order named. Both English vat tannages show good yield, equal to our Hemlock leather.

In the second table we find two drum tannages with very low percentage of hide substance, therefore very high yield, in spite of a comparatively low degree of tannage. In such cases the weight is given by high water solubles, or with other words by filling up with extracts or other substances.

There is no doubt and confirms my experience, that it is possible to get with drum tannage as high yield as with any other method.

I am sorry to be unable of stating in this table the specific gravity of the leathers tanned by the different processes. The degree of tannage, percentage hide substance and the specific gravity are according to my opinion the most useful factors in the analysis of leather. The degree of tannage tells us the extent of the tannage, the percentage of hide substance, the yield and the specific gravity, the cutting value. In a former paper dealing with specific gravity I spoke at length about the importance of combining high yield with low specific gravity in order that a certain sole leather might have good cutting results. The specific gravity will depend upon the extent of plumping and filling and finally upon the conditions, under which the leather is rolled and dried. Sweet tanned leather seems to have as a rule a slightly higher specific gravity than leather tanned with sour liquors.

RICHWOOD, W. VA., June, 1917.

DISCUSSION.

Mr. Yocum said that the process of Durio Brothers had been installed by the Howells at Newark, N. J., in the early nineties, the leather had broken grain, and the venture was not a success. One reason for the troubles encountered was that the extracts available in this country were not suited to the process.

Mr. S. H. Frank said that the firm of S. H. Frank and Co., had tried out the Durio process years ago without success. At the present time the Durio Brothers are making leather for the Italian Government, using a drum process and taking about 21 days from start to finish. Mr. Piazza, who was present, was mentioned as a representative of the Durios. Recently a cablegram had been received from them suggesting that the U. S. Government might be induced to buy their process; Durio Brothers not realizing that the U. S. Government are not tanning their own leather, as the Italian Government appears to be doing. Mr. Frank had received samples of the Durio leather, and it seemed very good. The process is in use in South America, especially Argentina.

Mr. Riethof had never found that a properly managed drum process produced leather with damaged grain. He believed that the process which had not succeeded, referred to by Mr. Yocum and Mr. Frank, was one in which the whole tannage was done in the drum. The Durios are now using a process beginning with handlers and finishing in the drum, it is understood. A principal difficulty with the Continetal processes of drum tannage, from the point of view of the American shoe manufacturer, is that the product is hard and brittle.

Mr. C. M. Morrison had used many makes of tanning drum. He described the Allen drum as having the hides pinned around frames. One tanner who had put in an expensive plant for the Allen process is no longer using it. Good leather is being made by processes in which a part of the tannage is done in the drum. The tumbling drum is not satisfactory because a part of the hides are sure to be damaged by the tumbling.

Mr. S. Saxe stated that a large sole leather tanner is now tanning large quantities of leather by a drum process in which the time from the beamhouse to the dry loft is five days. The quality of the leather is good.

Mr. W. H. Dickerson: One of the first men to try drum tannage in this country was John Grant. He made some tests in Jersey City, and afterward installed a set of drums in a tannery at Woodstock, Canada. This tannery ran for some time exclusively on the drum process, and the American Oak Leather Company afterward tried it.

Mr. C. M. Morrison: The American Oak Leather Company are not now using the Grant process. Every sole leather tanner to-day is using drums, or ought to be, and each may work out the problem of their use to suit his own conditions.

Mr. Joseph Daoust, of Montreal, introduced himself to the convention and said that he had used in his shoe factory leather made by the Durios. It was in bends, and was satisfactory in every respect except price, which was prohibitive.

Mr. J. A. Wilson asked Mr. Riethof in regard to the effect of rise of temperature on the plumpness of product, questioning the statement made in his paper that at a higher temperature the plumpness was less.

Mr, Riethof reaffirmed the statement in the paper, saying also that in a pickling process rise of temperature represses plumping.

Mr. Edmundo Piazza had travelled with Mr. Durio in France, where the Durio system is in use, as well as in England and Spain.

Mr. S. H. Frank invited any who were interested in the Durio leather to call at the Frank warehouse in New York or write him there if they wished to see some sides made by that process.

CHEMICAL CONTROL.

By T. G. Greaves.

In spite of the remarkable growth of American chemical industries in the past two years, the serious shortage of chemicals and chemical apparatus has come home to the thinking public and expressed itself by giving chemical control a place in the popular press alongside of efficiency engineering, salesmanship and how to invest money. This suggests that, to keep the ideas of the public on the subject conservative, chemists themselves should make a statement of what they mean by chemical control. The main object, however, is, that being once stated a start is made towards a definite formulation of ideas, which when adapted, improved and disseminated by other chemists and manufacturers, may lead the backward companies to that system and spirit that has enabled some to grow where others have failed.

As one person's view of any idea is necessarily limited, and as so general a subject cannot be covered in detail because of the differences of the problems in the various industries, this sketch will necessarily be incomplete and only general in character. It is also unavoidable that most of it will seem very self-evident to manufacturers.

Secrecy in manufacturing is giving place to co-operation, as is shown by the large number of trade and scientific journals. This is partly due to the advent of the chemists into business and the consequent putting of trade secrets and rules, originally, perhaps, found out by experience, on a scientific basis, or rediscovering them, and removing the dictates of the expert from the realms of mystery to the light of facts that can be demonstrated and explained and repeated. Whether or not this is an advantage to the manufacturer, it undoubtedly is to the public, because it brings business into the light and makes it a valuable servant instead of a hated oppressor. Manufacturing is now regarded in a broader way than formerly. Now it represents an investment, not of dollars only but of the life work of a group of men. It represents service to humanity. Every improvement helps to keep down the cost of living and puts more in reach of the poor.

Chemical control is not a matter of startling discoveries, for when a discovery is made the discoverer probably doesn't know it will be important or else meets with no success in its use or marketing. As there are now many men of approximately the same training thinking over the important industrial problems, progress in discoveries is usually divided among many and often over a long time. The making of grain alcohol from wood sounds like a startling discovery but it is 98 years old and has barely reached the point where, under the best conditions and management, it is a paying industry. It has many years of the work and discouragement of many men and many failures to its discredit.

Few industries have had such a discouraging time as this one, but big changes and corrections are now less than ever likely to be made all at once, because the important processes have, for some time, been under detailed study. Almost all have now reached a point where only small developments have to be made either as the market requires them or a little sooner. The possibilities and peculiarities of the market are, of course, a guide to the manufacturing staff, which should keep in close touch with the customers. Besides this, knowing the products better, they can guide the demand to the most practical material for any given purpose and so help the salesman and the customer.

Chemical control concerns itself particularly with the small corrections and changes and with the regular operation. It depends on chemical and other tests, but, as they are only valuable to the extent to which they are used, one of the chief requirements is to direct the taking of the samples so that the results of the tests will give the maximum information of the kind that is the most useful at that particular time. The samples, of course, must be taken so as to represent accurately the material to be tested.

Some substances are susceptible of accurate analysis based on chemical activity in definite proportions, while other substances react so indefinitely that they have to be tested by some arbitrary method based on the observance of exactly the same rules in different laboratories, or they are tested in the way in which they are to be used. Chemical manufacturing businesses are liable to the same general classification. In some which deal with the more indefinite products it seems that the more detailed work is done the more indefinite and uncertain everything becomes. As an illustration of this point, it has often been remarked that it is much harder to get a definite bacteriological report from one of the bacteriologists, who has given up his life to thinking and working on nothing else, than from a general practitioner or a college student. The realization of the difficulties and limitations, as well as the possibilities, has a practical value in every-day factory operation, although it may not be readily apparent.

Chemical control is not a matter of inspiration or of things being so and so because someone said they were, but it is the study of cause and effect by means of careful work that considers every condition that could influence the results before drawing a conclusion. The consideration of physical laws and the chemical relations of the different forms of matter gives a definite conception of a product in any particular stage of manufacture and sometimes suggests relationships. It also explains otherwise obscure changes.

One of the big objects is to keep the product uniform. To accomplish this the process must be carefully standardized so that the mill will run uniformly. This is universally recognized but in very few plants is the standard method committed to writing and available to all who are connected in any way with its execution. The advantages of having such a written guide are: (1) there is less chance of mistakes being made by new men due to misunderstandings or forgetting; (2) more attention will be paid to the details; (3) variations are more likely to be reported; (4) if it is not in black and white the foremen of the different shifts will have different ways of operating and feel that a change is an affront to their management, and so the spirit of the work may be hurt or the system may not be uniform or readily available for improvement.

The well known advantages of the standardized process are: the foreman will be more free, except in case of emergency, to replace weak machinery, keep supplies and repair parts on hand without keeping too large a stock, see that the same emergencies or mistakes do not keep on occuring, put in small improvements, and develop themselves.

It is evident that conditions sometimes arise that require disregard of instructions. Common sense must meet emergencies; experience and inventive ability must sometimes make the best of a bad job. These occurrences should always be reported to all whose work they affect. Then the laboratory will know what to look out for and irregular results can be interpreted. Special samples can also be taken from the part of the product which is most affected so as to bring out the variation and by noting cause and effect add to the experience of the company. This seems a better system than regarding the laboratory as a detective trying to find out when the plant is run differently or somebody makes a mistake.

Another misuse of the laboratory is to be too quick to make complaints on differences in the analyses of buyer and seller or about variations in quality between different lots. As irritating as these may be, it is best to deal with them only when necessary and where good can result. The manufacturer wants to make a good, uniform product, and the buyer wants a good, uniform product; so complaints, between reputable firms, are only a means of bringing the organizations together for mutual help and understanding. Satisfactory results are easier to obtain by a visit than by letter.

Probably the most interesting feature of manufacturing is the yield. The possible yield is figured from the analysis of a daily sample made up by mixing an average sample for each charge. The most profitable yield, however, is not the highest yield but depends on the cost of obtaining each successive portion compared with its value. In practice it is almost always more economical to leave some of the possible yield in the spent materials. Yield is usually expressed as a certain per cent. of the difference between the possible yield and the portion left in the spent, based on some particular raw material. The difference between this and 100 represents the per cent. lost in manufacturing which can be lessened by eliminating chemical errors, leaks of liquid or dust, and decomposition. A simple way to increase the yield on the fuel basis is to improve the combustion by attention to the type of furnace, by firing so as to make a good, even fire bed, by stopping the excess of cold drafts, by proper insulation, by utilization of waste heat, and by reducing the mechanical friction.

The spent material is put through a recovery process and used over again or used as it is in some other operation. The daily analysis of the composite sample of the spent shows the amount of yield left behind and is used in figuring the yield of the recovery process, if there is one. It also throws light on other questions.

As the cost enters as a factor in the question of how much of the possible yield should be obtained, it is evident that the cost of the different steps in the process and of running the machines used in each step should be known as nearly as possible. This is also necessary in figuring the profit or price on the different products and the different forms in which they can be sold.

In processes where a definite chemical reaction is involved the ratio between the raw materials is an important factor in the yield and requires many tests to establish. For example, in the manufacture of nitroglycerine there is a certain best ratio between the nitric acid and glycerine. Then the water formed along with the nitroglycerine stops its formation. So there has to be a definite best ratio between the water already in the acids plus that which will be formed and a material which is added to take up the water. The conditions of heat, etc., are of like importance. When the process is only one of leaching, the ratio and conditions need only be determined approximately in the manner suggested in the consideration of what yield is most economical.

Where the process is well standardized the individual parts can be tested. In one of the largest chemical plants in the country the ratios and conditions were frequently changed. A certain per cent. yield and a certain strength spent were regularly obtained by the typewritten method so the effect of the changes could be studied as large scale tests. Small experimental plants are sometimes built to supplement the laboratory in this way. This is especially the case where the lack of homogenity of raw materials prevents accurate sampling, or where the process cannot be well standardized. Such demonstrations are more convincing than laboratory tests and figures, and sometimes mill conditions cannot be duplicated in the laboratory.

The lots of finished product are, of course, tested in some way to see that they are all right before leaving the factory or else for valuation. With some simple, well standardized processes this test together with that of the spents may be considered as a sufficient analysis of the raw materials. Where ratios have to be definite, analyses of the raw materials are used in figuring the proportions.

It is important to accumulate information bearing on all the uncertain and little understood features of the process. A large part of such information will be negative results but these have their place in constructive work.

Among some of the other problems met with are the substitution of better suited or cheaper materials[1], the consideration of adding new products, better ways to use the spent material, improving the quality, keeping up with new ideas and adapting them to different uses, the recovery of runs spoiled by accident, making up some of the materials used, etc.

There is no reason to segregate chemical control to any part of the organization nor is it practical to recognize works management as a field with a different point of view because of the extent to which the boundaries would overlap. Those who are not chemists can carry out chemical control, all except the tests, and, if the organization is good, the standards of the firm and its aims and problems can hold all, even the new men, loyal and working harmoniously together, each man realizing that it is his business to look out for the company in his particular station and that the company will then look out for him personally and for his best interests.

Efficiency engineering, which only works on the surface and when applied to men often does more harm than good, may be made unnecessary by chemical control. A good organization is the prime requisite. The men should not only be proud of doing their work as well as it can be done and so keeping their department as good as the same department in any other company, but they should also be kept bigger than their jobs and capable of promotion. This is accomplished in part by hiring, even for the most humble positions, only those who are essentially honorable and able and willing to develop the spirit of cooperation both in obedience and in taking responsibility. They are then given a definite place and slowly developed and kept open minded.

It gives a man more self respect to work under a fixed system

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[1] Some firms are using high-priced grades or classes of materials where cheaper ones would do as well.

and know what will guide his future than to be merely an employee in Mr. So & So's business. There is no loss of elasticity in having every man know what his jurisdiction is, who his boss is, and exactly what is wanted of him, nor his having only one boss whenever possible. This gives a good man opportunity for steady development and advancement, while an indefinite system gives a more unworthy man a chance for rapid advancement by pushing himself forward. Sound growth is slow. Unworthy men should be discharged during their first year. The apparent danger of a man leaving and taking trade secrets with him is not serious, because a man who is trained in one organization and put down in the midst of another finds different ideas, customs and systems, and there are now few secrets of such obvious merit as to be taken up from a new man. Besides a man doesn't want to leave a good organization after several years of growing into its spirit.

Among the various expedients used to keep the employees open-minded the underlying principle followed by some progressive firms is to keep them together in their off time and promote a free and friendly exchange of ideas between them, especially those who carry responsibility, and also between the employees and that part of the outside world which is interested in the same business. They are often taught the various phases of the business by moving them from one department to another, giving them a well rounded development and thus strengthening and balancing the firm and getting more men's ideas on each part.

Organization is economy and power whether it is in an artificial dye industry or a chain of cigar stores. The late Charles Wheelan, founder of the United Cigar Stores, said that he hadn't built up his business but that his men had done it, he only giving them opportunity, and that there are no wise men and few fools but that opportunity is the only thing that counts. The intelligence of the men is sometimes an unused resource but a good foreman in a good organization will bring it to bear on the work and the incidental problems and possible improvements. The development and training of the men is another available asset that is worth many times the trouble and planning which it requires of the executives.

Chemical control is not a scrap of science tacked on to somebody's business but it is an atmosphere which is conservative in giving to every man his due, both officially and personally and progressive in being alive to the finding, judging, and fullest use of facts and theories. It operates in good organizations.

LABORATORY OF J. H. HEALD & CO.,
Lynchburg, Va.

FREE SULPHURIC ACID IN LEATHER.

Committee Report, 1917.

By C. R. Oberfell.

The importance of this subject and the need for a reliable method is so well known that further comment along this line is unnecessary. The demand for such a method, however, is increasing since our Government is insisting on a mineral acid specification for military leathers.

The object of this investigation was to determine the accuracy of the Wuensch method. This method is as follows:

Wuensch Method for Free Sulphuric Acid in Leather.—Weigh 5 grams of the sample into a 400 cc. beaker, moisten the leather with water and then add 50 cc. fuming nitric acid. Evaporate the solution with barium chloride and hydrochloric acid to drive off the nitric acid. Filter and wash the residue with hydrochloric and weigh as barium sulphate. To the filtrate sulphuric acid is added to precipitate the excess of barium chloride and convert all bases into sulphates. The solution is filtered, evaporated to dryness, ignited and smoked off with ammonium carbonate to decompose the bisulphates and after acidifying with hydrochloric acid the sulphates are estimated with barium chloride. This represents the total sulphuric acid which the bases are capable of neutralizing. The first estimation less the second gives the amount of free sulphuric acid.

The description of this method is due largely to H. R. Procter. An effort was made to locate the original description by Wuensch, but without avail in this country.

Samples of leather were prepared as follows:

Sample D is a blank, that is, it is a straight tanned, unadulterated, nonacid leather.

Sample C is the same as D to which 3.58 per cent. sulphuric acid was added.

Sample B is the same as D to which 8 per cent Epsom salts was added.

Sample A is the same as D to which 7.5 per cent. Epsom salts and 2.80 per cent. sulphuric acid was added.

For a basis of comparison these samples were analyzed by both the Wuensch and the better known Procter-Searle Method. The results are far from complete as only half of the committee contributed data. As far as the results go they indicate that the Wuensch method is unreliable and breaks down completely in the presence of magnesium sulphate.

TABLE I.

Sample A—Wuensch Method.

		Sulfuric Acid					
	Moisture per cent.	1 per cent.	2 per cent.	Average per cent.	Calculated acid per cent.	Added epsom salts per cent	Error per cent.
C. R. Oberfell	7.10	4.56	4.38	4.47	3.22	7.5	1.25
J. S. Rogers	7.16	4.18	—	4.18	2.80	7.5	1.38
Sample A—Procter-Searle Method.							
C. R. Oberfell	7.10	2.96	3.08	3.02	3.12	7.5	0.10
J. S. Rogers	7.16	3.01	2.99	3.00	2.99	7.5	0.01
Sample B—Weunsch Method.							
C. R. Oberfell	6.90	0.55	1.43	0.99	0.42	8.0	0.57
J. S. Rogers	7.04	0.68	—	0.68	0.00	8.0	0.68
Sample B—Procter-Searle Method.							
C. R. Oberfell	6.90	0.29	0.51	0.40	0.32	8.0	0.08
J. S. Rogers	7.04	0.55	0.56	0.55	0.19	8.0	0.36
Sample C—Weunsch Method.							
C. R. Oberfell	8.40	3.94	3.99	3.97	4.00	—	0.03
J. S. Rogers	8.40	2.79	—	2.79	3.58	—	0.79
Sample C—Procter-Searle Method.							
C. R. Oberfell	8.40	3.87	3.82	3.85	3.90	—	0.05
J. S. Rogers	8.40	3.78	3.71	3.75	3.77	—	0.02
Sample D—Wuensch Method.							
C. R. Oberfell	6.90	0.37	0.47	0.42	—	—	0.00
J. S. Rogers	6.84	0.00	0.00	0.00	—	—	0.00
Sample D—Procter-Searle Method.							
C. R. Oberfell	6.90	0.32	0.32	0.32	—	—	0.00
J. S. Rogers	6.84	0.26	0.11	0.19	—	—	0.00

There are two inherent sources of error in the Wuensch method. One is the precipitation of barium sulphate in a highly complex organic solution. Under ideal conditions errors creep into this operation so that in a solution of leather anything aside from approximate results can not be expected. It is certain, however, that the sample must be degreased thoroughly before solution is attempted. The second source of error is due to the fact that the presence of ammonium carbonate does not prevent the reduction of sulphates to lower order during the ignition to destroy the organic matter in the second phase of the operations.

TABLE II.

Wuensch Method.

Sample	Found	Calculated
C. R. Oberfell—Summary.		
A	4.47	3.22
B	0.99	0.42
C	3.97	4.00
D	0.42	0.42
J. S. Rogers—Summary.		
A	4.18	2.80
B	0.68	0.00
C	2.79	3.58
D	0.00	0.00

Procter-Searle Method.

Sample	Found	Calculated
C. R. Oberfell—Summary.		
A	3.02	3.12
B	0.40	0.32
C	3.85	3.90
D	0.32	0.32
J. S. Rogers—Summary.		
A	3.00	2.99
B	0.55	0.19
C	3.75	3.77
D	0.19	0.19

The results by the Procter-Searle method are better than expected, and indicate that good agreement can be obtained between different operators. They also indicate that magnesium sulphate has no apparent effect on it. This should not be taken too hopefully, however, for it is known that this method does not give reliable results in the presence of Fe, Al, NH_3, and Cr salts.

It is probable that it breaks down under other unknown conditions.

The recommendation from the work is that the Wuensch method be not further considered as an official method for this purpose.

Discussion.

Mr. J. S. Rogers said that one point in regard to the Wuensch method not mentioned in the report is that it fails in the presence of chlorides. He regards the Procter-Searle as the best now available, but a better one is urgently needed.

Mr. Oberfell mentioned cases in which leathers had been rejected on account of free sulphuric acid although no acid had been used in making them. The method used was the Procter-Searle.

Mr. F. P. Veitch had often found low results by the Procter-Searle method but never high ones.

Mr. Oberfell cited the case of a grain split tanned without the use of mineral acid and bleached with tin crystals and sumac. He blamed the positive test for sulphuric acid on the tin crystals. In other cases leathers containing Epsom salts gave high results for sulphuric acid, and he had credited that to the Epsom salts, but the committee results indicated that such an opinion was not warranted.

Several members remarked that leather which had been bleached with tin chloride would have some free hydrochloric acid, but no explanation of the positive tests for sulphuric acid was forthcoming.

MODERN METHODS OF DRYING HAIR.

By C. H. Reumann.

The drying of hair is perhaps as old as the tanning industry itself, but in spite of this fact, very little has been written on the subject. Furthermore, the subject of the proper preparation of hair has not until recently been given the attention that it really deserves. Many of the smaller tanneries have been inclined to consider this product a form of waste and to neglect its commercial possibilities almost entirely.

The steadily increasing value of hair has caused increased attention to be paid to this department and has converted this form of waste into an extremely valuable by-product. It has also led to the development of more and more efficient and economical methods of drying and to improved methods of handling, so that the methods and the machinery in use in a modern hair plant bear but slight resemblance to those in use fifteen or twenty years ago.

Even to-day there is much room for improvement, especially in many of the smaller tanneries. This was illustrated a short time ago when a hair salesman showed me two samples of stock. Both were of about the same grade as regards the hair itself, but one sample contained so much lime and foreign material that it had the appearance of a very inferior grade. This salesman said "Had this tannery used the proper washing and preparing methods, the poorer looking sample would have brought at least six cents more a pound than it did." To get the most out of your product no matter whether it is leather or simply a by-product such as hair, you must treat it in the most efficient manner possible so that it will produce the largest net returns.

The subject of unhairing and preparation of hair is so broad that there will not be time to consider the different methods of unhairing so we will have to be content with first a summary of the methods of washing and handling of the hair preparatory to drying and second to a summary of the development of drying machinery and of the types of drying machines now most commonly used.

WASHING MACHINERY.

Many of the earlier types of washers were built on the paddle principle and although they were fairly efficient, the hair had to be shovelled into the tanks and removed in the same cumbersome manner. More recently the development has been along the lines of a continuous system of handling in order to eliminate as much of the labor as possible. The types developed were still of the paddle wheel type, but the process was made continuous. One system consisted of a set of three machines working in tandem. The hair from the first paddle was thrown on a traveling conveyor by means of a revolving fork and delivered on a conveyor apron to the next unit.

A system now used quite extensively consists of a long cast iron bowl with a series of paddle wheels and provided with a perforated plate screen. The hair is worked along by means of the paddles and is subjected at the same time to a spray of water and is finally forked on to a traveling conveyor and delivered from the washer.

One of the most efficient types of hair washers yet developed is the cylindrical type. This has been perfected in some of the Philadelphia hair plants and has been successfully used by some of them for a number of years. It consists essentially of a tapering cylinder about 6 to 8 feet long mounted over a semi-cylindrical perforated plate or wire screen. The cylinder itself is provided with lugs set in spiral form at intervals around its circumference. The hair is introduced into the washer through a hopper at one end of this cylinder and as the cylinder revolves, the spirally set lugs force the hair along the semi-cylindrical screen in much the same way as any material is conveyed on a spiral conveyor. At the same time the spray of water directed along parallel to the axis of the cylinder helps to remove the lime. Smaller particles of lime drop through the perforations in the screen whereas the larger particles along with the cuticle and other foreign materials drop to the bottom of the tank at the end of the cylinder. The hair itself floats to the surface where a forked conveyor carries it along a sloping perforated plate screen. During this stage of travel, it is still further subjected to the cleansing action of a finely divided spray of water and when finally delivered from the conveyor, the hair is in a very clean condition.

A machine of this kind will deliver from 2,000 to 4,000 lbs.

of clean dry hair per day of ten hours, depending of course upon the nature and character of the hair. Where larger quantities than this are desired, the units are placed in tandem and speeded up so that the hair receives only a partial washing in passing through the first unit and is more thoroughly cleaned during its passage through the second machine. In this case the action is made automatic so that there is no handling of the material from the conveyor of the second unit. One of the most essential features of this type of washer is an abundant water supply so that sufficient quantities of water may be sprayed on the hair at all times in that way give a very effective washing.

Hair as delivered from the washer will contain anywhere from six to eight times its own weight of water and cannot be delivered directly into a drying machine in this form. It is far more economical to eliminate the greater portion of this moisture by mechanical means than to endeavor to remove it with steam during the drying. The very oldest method consisted of allowing the hair to drain overnight on a slatted platform and then to dry it the next day or after a sufficient period of time had elapsed. This was effective in so far as the top layers of hair were concerned, but the hair at the bottom of the pile usually contained a much greater quantity of water than was desirable. One hundred pounds of limed hair yields only from 8 to 20 pounds of clean dry hair.

Centrifugal machines, more commonly known as hydro-extractors, have been used very successfully in the hair trade for the removal of the extra water from the hair. The hair had to be shoveled into these extractors and the material whirled around at high speed for approximately five minutes to remove the excess water. With good extracting it is possible to remove water to such an extent that there would be less than 50 pounds of water to 100 pounds of wet stock. Good average practice gives about 65 pounds of water to 100 pounds of dry hair.

The hydro-extractor although a very efficient means of removing the excess moisture from the stock meant a break in the continuous chain so that many concerns have been content with removing as much moisture as was possible by passing the hair through squeeze rolls. By this method it is not possible to get the moisture content down any closer than about 60 per cent. or approximately 125 to 150 pounds of water per every 100 pounds of dry hair but many plants prefer to place this extra burden on the drying machines for the sake of having a continuous system of handling the material.

More recently still, a Milwaukee firm have announced a new type of wringer which works automatically and removes 50 per cent. of the moisture. They claim that this will receive hair from the washer and deliver it to the dryer without any extra labor.

In plants where squeeze rolls are used, it is possible to convey the hair automatically from the washers to the wringer and then from the wringer to the feed of the dryer by means of apron conveyors. Where extractors are used, however, the conveying of the stock has usually been accomplished by means of a blower system, the stock being placed in the hopper of the blower as it is removed from the extractor and then blown right into the feed hopper of the dryer.

Drying Machinery.—The very earliest forms of dryers were very crude affairs and were called table dryers, receiving their name from the fact that they were mere wire screens or tables. The hair was spread to a thickness of about a foot or so and heated air delivered by a blower at one end was forced up through the stock. It required a very long time to dry by this method, six to seven hours, depending on the grade and the kind of hair. The hair had to be turned over by hand several times to insure uniform drying. Three serious disadvantages: The blowers required a considerable amount of power to move the air. The system was wasteful of heat as the heated air was blown up through and then wasted. Thirdly, it required a large amount of labor since all the stock had to be placed on the screens, turned over occasionally and had to be removed in the same way.

The advent of the modern automatic dryer was a distinct step in advance as it cut down the labor item and was also much more economical of steam, labor and floor space. The whole system was made automatic in that the hair was dumped into a feed hopper and delivered in a uniform layer to a traveling apron which passed through the dryer, where it was subjected to the circulation of heated air and emerged from the dryer about 15 to 20 minutes later thoroughly and uniformly dried.

The first machines were of wood construction and for that reason a dryer was a great fire hazard. Fan bearings were inside and this together with the high heat caused frequent fires through overheated bearings and were responsible for a very high rate of insurance where these dryers were used. The dryer industry is greatly indebted to the hair plants for much of the development of drying machinery, for they were among the first to insist on machines with all bearings outside of the dryer enclosure and away from the heat and also on a more permanent and fire-proof housing. This led to the development of the modern type of dryer, with a structural iron frame work, steel panels, with asbestos lining to prevent the radiation of heat with no danger from fire from an overheated bearing. As built today, the machines are as near fire-proof as it is possible to build them, no wood whatever enters into the construction and in addition they are supplied with a fire extinguisher system inside of the machine which can be connected directly to the mill fire extinguisher system.

There are a number of efficient dryers of this type on the market to-day including the Sargent Dryer, the Proctor Dryer, the Hunter Dryer and the "Hurricane" Automatic Dryer manufactured by our Company, the Philadelphia Drying Machinery Company.

The "Hurricane" machine is usually arranged with an automatic feed. This is provided with a hopper to contain several hundred pounds of hair and an inclined spiked slatted apron carries the hair from the hopper and delivers it in a uniform layer to the apron of the dryer. A revolving beater placed in front of this feed apron regulates the amount carried on the spikes. The thickness of hair on the apron varies from five to eight inches depending on the nature of the stock. The time required to pass through the machine may also be varied by means of a cone drive on the apron. The time necessary to dry the stock will vary from 10 minutes to 20 or 25 minutes.

The dryer itself is divided into two longtiudinal compartments. One serves to carry the wire cloth conveyor and the other for the housing of the steam heating coils. These two compartments are separated by a steel partition which does not reach entirely to the floor, and contains in the upper portion a series of openings in which are placed the fans for the recirculation of air.

The air is drawn over the heating coils, blown through the hair and passing under the partition is again drawn through the coils where it is reheated. A certain portion of the moist air is removed near the feed end by means of an exhaust fan. At the same time fresh air is drawn in through an opening at the delivery end of the machine. In this way the air in addition to being continuously recirculated is drawn up through the machine in a spiral manner gradually absorbing more moisture until it is finally discharged. This recirculation system has proven extremely efficient and has been the greatest single factor in bringing the modern dryer to its present high state of efficiency.

The steam coils are arranged so as to reduce the heating surface as the drying proceeds. In this way a gradual reduction in temperature is accomplished, the hair being subjected to a lower and lower temperature. The most recent developments have been along the line of increasing the amount of air circulated and in that way lowering the temperature of drying and preserving the quality of the dried product. Exhaust steam may be used. As regards capacity, the machines are built in standard sections and with conveying aprons from 4 feet to 9 feet in width. The apron width usually depends on conditions in individual plants. The capacities of course vary with the length and run from 2,000 pounds of dry hair per day to 10,000 pounds. Since the sections are of standard length, a machine can be lengthened out at any future time to increase its drying capacity.

Hair, although it dries quite readily, has a tendency to matt if subjected to the continual air circulation in one direction, for this reason it is necessary to agitate the hair on the apron at intervals. This is done by means of a series of revolving kickers which open up the hair and present new surface. Another way this is sometimes done is to use a blower and blow part of the air through the hair so that it is blown off of the apron and in that way opened up.

With the increasing cost of factory construction and consequent greater value of floor space, there has been a demand for a machine to turn out a greater capacity for a given floor area. To meet this demand the multiple apron type of dryer has been developed. Three aprons are usually used, the hair dropping from the top apron to the one next below it. This gives a considerably greater capacity for the same length with about the same expenditure of steam and power.

Conditioning.—As ordinarily delivered from a dryer, hair contains about 5 per cent. of moisture. This is considerably below the normal amount. For this reason the hair after being baled will pick up moisture and in that way increase in weight. Many commission merchants will store the bales in damp warehouses or even sprinkle the floors to have the hair pick up this moisture. But even at best this is a poor way to condition as the hair at the centre of the bale is drier than the rest. In buying hair you should insist on a moisture test or buy it on the basis of conditioned weight, otherwise you may be paying for water instead of hair and water at 30 cents a pound is a pretty expensive item.

Considerable work has been done on the development of conditioning machinery for yarn and other textile materials, but as far as I know, but very little has been done to condition hair. The method employed on yarn for instance is to dry the yarn thoroughly during the first stage of the process, then cool it by circulating cool dry air and finally condition it by circulating very moist air in the last section of the machine. The yarn takes up a certain portion of this moisture and is delivered from the machine containing the normal percentage of moisture uniformly distributed. I look to see a further development along this line within the next year or so with the idea of being able to deliver hair with the normal amount of moisture, assuring more uniform and better quality of hair than is possible to-day.

ABSTRACTS.

Sole Leather versus Fiber Soles. *Leather Manufacturer,* June, 1917. Mention is made of experiments at the Leather and Paper Laboratory and the Bureau of Standards, and rumors are referred to which credit at least a dozen tanners with tests, but give no results. Extensive quotations are made from an address by F. P. Veitch before the Pennsylvania Shoe Retailers' Association. He states that the increase in leather prices is due at least in part to deficient supply of hides. One important service which science can render is the discovery of better methods of leather making, and the Leather and Paper Laboratory is engaged in the study of these problems. Experiments have also been conducted there in testing the wearing qualities of sole leather. The series of tests of various kinds of leather and substitutes which it is proposed to examine is outlined. Beside Mr. Veitch's remarks, the article includes an account of the Bureau of Standards machine, which was described in the *Scientific American* of May 19, as indicated in the following abstract.

Testing Leather for the United States Government. G. H. CLAUDY, *Scientific American,* May 19, 1917, p. 493. The apparatus developed at the Bureau of Standards by Mr. P. L. Wormley is described, with two cuts. It uses samples of leather about 2 by 8 inches in size, four of which are fastened to the circumference of a wheel which rotates in contact with a rotating concrete disk. The plane of the concrete disk is horizontal; that of the wheel carrying the samples vertical. The sample wheel is driven by a chain and sprocket, and the friction of the pieces of leather against the concrete causes the disk to revolve. The loss by wear in 40,000 revolutions ranged from 7 to 35 per cent., depending on the grade of leather. It is expected that the concrete disk will be replaced by one of carborundum, which may be made in any type desired, and duplicated with accuracy.

The Composition of Menhaden Oil Fatty Acids. E. TWITCHELL. *Jour. Ind. Eng. Chem.,* June, 1917, pp. 581-4. A purpose of this investigation was to test the use of the author's melting-point method of determining fatty acid mixtures, as well as to investigate the composition of the fatty acids of menhaden oil. The method in question is as follows: A measured quantity of the mixture to be analyzed is added to a solvent consisting of a pure fatty acid of the kind to be determined. The melting point of the new mixture is determined, and from this the lowering of the melting point of the solvent. This depression is caused by all the acids in the mixture except the one sought, which, being identical with the solvent, would have no effect on it. Assuming that the other acids, singly or in mixture, produce a lowering of the melting point of the solvent proportional to their total concentration and independent of the kind of acid, the amount of other acids can be calculated, and the one sought obtained by difference. The assumption that the lowering of the melting point of the solvent acid is proportional to the percentage of other acids present is very nearly true in most cases up to 20 per cent., though, if the solvent is an acid of unusually low melting point compared to the dissolved acid, the depression beyond 10 per cent. is greater than normal. The assumption that all acids produce the same lowering of melting point is for this purpose near enough the truth where the more common fats were concerned, which do not differ greatly in molecular weight. The author has in most cases assumed that 20 per cent. of one acid dissolved in 80 per cent. of another will lower the melting point of the latter 4° C. Hydrogenation converts unsaturated fatty acids into saturated ones having the same number of carbon atoms. Fusion with caustic potash decomposes members of the oleic series with the production of saturated acids having two less atoms of carbon. It may be assumed that those of the linolic series by the same process yield saturated acids with four less carbon atoms, those having three double linkages (linolenic), six less, etc. The author in a previous paper has described the results of investigating the acids of menhaden oil, using the hydrogenation process. He found palmitic acid, 22.7 per cent.; other saturated solid acids, 11.8 per cent.;; unsaturated acids with 16 carbon atoms, none; with 18, 26.7 per cent.; with 22, 20.3 per cent.; other unsaturated acids, 18.6 per cent. The incompleteness of this analysis was due to lack of the necessary pure acids for comparison. The preparation of myristic and arachidic acids is described. The acids of hydrogenated menhaden oil were separated by fractional distillation. In the first fraction the presence of myristic acid was established as follows: 20 parts of the purified fatty acids of the first fraction were melted with 80 parts of pure myristic acid. The melting point of pure myristic acid is 53.76°, that of the mixture was 51.60°. It is fairly certain that acids other than myristic in the fraction consist chiefly of palmitic, and the melting point of myristc acid is lowered by 20 per cent. palmitic to the extent of 4.53°. Using this figure it is easy to calculate the percentage of myristic acid in the first fraction. Whether the myristic acid was present in the original oil or was a product of hydrogenation remained to be determined. Fractions 15 and 16 of the distillate had a combining weight of 308.5 (average) and were the most likely to contain arachidic acid. Behenic acid (molecular weight 340) had been shown to be present in the oil, and was almost certainly in this fraction. A process similar to that just described for myristic acid indicated about 49 per cent. arachidic acid in fractions 15 and 16 of the hydrogenated oil. A similar determination in which the total fatty acids of the hydrogenated oil, not distilled, were used, gave 22 per cent. as the probable amount of arachidic acid in the whole. The solid fatty acids from the original oil were separated and found to make up 31 per cent. of the total fatty acids of the menhaden oil. The proportion of myristic acid found in this mixture of solid acids was 29.6 per cent., or 9.2 per cent. of the total fatty acids of the oil. A similar test for arachidic acid gave a negative result. The arachidic acid found in the hydrogenated oil was therefore due to the hydrogenation of some unsaturated acid with 20 carbon atoms. From the iodine value of the solid acids (9.44), the percentage of oleic acid was calculated as 10.5 per cent. Palmitic and stearic acid were determined in the same manner as the myristic acid, being 52.9 and 5.7 per cent. respectively of the solid fatty acids of the oil. The previous result as to the percentages of various constituents in the fatty acids of menhaden oil may therefore be extended thus: palmitic, 22.7 per cent.; myristic, 9.2 per cent.; stearic, 1.8 per cent.; unsaturated acids. with 16 carbon atoms, none; with 18 carbon atoms, 24.9 per cent.; with 20, 22.2 per cent., and with 22, 20.2 per cent. A sample of the menhaden oil was fused with caustic potash and little or no arachidic acid found in the product, indicating the absence of erucic acid.

Tannery Troubles Caused by Water. ANONYMOUS in *S. and L. Rep.*, June 21. If limed hides are put to soak in water of high temporary hardness, lime blast results, through the precipitation of calcium carbonate in the hide. This may be avoided by adding a small amount of clear lime water to the water in the vat, stirring it up and allowing the precipitated carbonate of lime to settle before putting in the hides. Lime blast is also caused by exposure to the air, particularly where there is a draft, since the carbon dioxide of the air is sufficient to produce a layer of calcium carbonate on the hide if it is long exposed. If lime blast has been suffered by skins, it may be removed by pickling. In the case of heavy hides, the natural acids of the first liquors are generally sufficient to remove it. Pickled skins may be seriously damaged by coming in contact with fresh water, as the water removes some of the salt and the acid remaining in the skin causes excessive swelling. The same damage may result from contact of pickled skins with liquor not containing salt. The addition of salt to the liquors in which pickled skins are to be tanned should be based on the amount of liquor, not on the amount of skin, since the object is to prevent the salt from diffusing out of the skin, and the rate of diffusion depends not on the weight of salt in the liquor, but on its concentration.

Running Spent Tan Liquor Over the Leaches—The Folly of It. J. R. BLOCKEY. *S. and L. Rep.*, May 17, 1917. Two reasons are assigned for running spent liquor over the leaches, to clarify muddy liquors, and to avoid throwing away the tannin in the spent liquors. If the muddy appearance of the liquor is due to really insoluble matter, "bloom," it has no tendency to darken the color of the leather. If it is due, as in the case of quebracho, to difficultly soluble materials, while the color of the leather may be improved by filtering the liquors, it is better to buy extracts which have been clarified. The reason why some tanners have been misled in regard to the tannin content of spent liquors, is that they suppose the barkometer reading to be an index of tannin content. If a liquor has started at 80° barkometer and been sapped to 20°, instead of having one-fourth of the original amount of tannin, it has more nearly one-twentieth, since the tannins are absorbed much more rapidly than the non-tannins. One serious difficulty which sometimes arises from running spent liquors over the leaches is that the accumulation of calcium lactate and other mineral salts in the liquors interferes with penetration of tannin and injures the quality of the leather.

PATENTS.

Process of Repairing Enameled Leather. U. S. Patent 1,226,146. A. M. TOWLE, Augusta Me. and G. M. TOWLE, Hallowell, Me.

Hide-working Machine. U. S. Patent 1,227,780. CHARLES J. GLASEL, New York.

Process for Tanning and Impregnating Materials by Means of Electricity. U. S. Patent 1,229,150. B. SCHWERIN, Franefort, Germany.

Artificial Leather. U. S. Patent 1,228,848. S. TSCHOUMAKOFF, Petrograd, Russia. Birch bark is cemented to a textile fabric.

Process for Treating Leather for Gloves. U. S. Patent 1,230,358 ALBERT AARON and GEORGE M. JONES, Gloversville, N. Y., assignors to Meyers and Son, N. Y. After tannage the leather is buffed with a dry wheel on both sides before dyeing.

Process for Tanning Fish Skins or the Like. U. S. Patent 1,230,266. K. BENDIXEN, Copenhagen, Denmark.

Process of Manufacturing Leather. U. S. Patent 1,230,667. OMA CARR, New York. The hides are placed in a chamber in which a partial vacuum is maintained. The tanning liquor which is introduced into this chamber is alkaline, and is kept warm. The leather is acidulated before removal from the chamber.

Tanning. British Patent 17,350. E. W. MERRY, Sheffield. A combination of alum and sodium pyrophosphate, with or without coloring by means of gambier, quebracho or other tan.

Leather Oil. British Patent 103,688. O. RÖHM, Darmstadt. Castor oil sulphurized just enough to remain soluble after neutralization.

Tanning. British Patent 103,827. O. RÖHM, Darmstadt. Relates particularly to iron tanning, but is also applicable to chrome and such like metal tanning processes. Simultaneously with, or previous to, the treatment with iron salts, the tanning is assisted by treatment with an aldehyde, such as formaldehyde. This tanning may also be combined with tanning by phenols, naphthols, aromatic carboxylic acids, or vegetable tanning-media. Other materials may also be used, such as soap, sulphides, etc.

Treating Sewage. British Patent 17,463. E. B. MARTIN, Eccles, Lancashire. An arrangement of tanks for the activated sludge method of treatment.

Process for the Utilization of Waste Sulphite Liquor. U. S. Patent 1,218,638. A. D. FEST, Chicago, Ill. The liquors are dried, the residue calcined, and the sulphurous vapors used to produce a fresh quantity of bisulphite liquor.

Process for Manufacturing Leather. U. S. Patent 1,221,929. F. W. WEBER, Perth Amboy, N. J., assignor to the Roessler and Hasslacher Chemical Co. The process consists in adding to a one-bath chrome liquor a salt of zinc, and in neutralizing with a phosphate.

Buffing Leather. British Patent 102,986. S. T. THRING and others. The grain is made brittle by treatment with a caustic, and after drying may be ground off.

Softening Skins. British Patent 5,814. OTTO RÖHM, Darmstadt. Enzymes from the pancreas, in aqueous solution and rendered alkaline, are employed.

Tanning. British Patent 103,295. OTTO RÖHM, Darmstadt. Iron is used in connection with tannin, a phenol or an aromatic carboxylic acid. Such a solution may be made with 10 parts iron alum, 10 parts of tannin and 3 parts of salt in 100 parts of water.

Tanning. British Patent 17,137. A. T. HOUGH, London. Compounds or derivatives of silicon are employed for tanning. A solution of sodium silicate to which dilute HCl and salt have been added is a typical liquor.

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CORRECTIONS.

In the May number, page 185, Hemlock Extract, results by C. C. Smoot, III, and L. E. Stacey, the non-tannin figure should be 15.80, making the tannin 17.66.

In the July number, page 327, lines 14 and 15 from bottom should be transposed. Page 331, line 15, for "chacking" read cracking. (For additional correction, see p. 434.)

REPORT OF COMMITTEE ON EFFECT OF HARD WATER ON TANNIN.*

T. A. Faust, Chairman.

The only exhaustive investigation conducted on this subject is that by Nihoul and Martinez in 1901. Their paper was entitled "Influence of the Nature of the Water used in the Extraction of Tannin," and as this paper has never been published in the JOURNAL of the A. L. C. A., it was thought proper to preface the report of this committee by an abstract of this paper. Messrs. Nihoul and Martinez selected five Belgian waters, each of special characteristics for their work. One water marked "somewhat hard" consisting of one-half permanent and one-half temporary hardness, another water marked "hard," a third water marked "very hard," a fourth marked "rich in sulphates," and a fifth marked "rich in chlorides."

The tanning materials used were oak bark, pine bark, sumac, and valonia. Extractions were made both hot and cold. They state as follows:

"No great difference in rapidity of extraction was observed between the different waters, but the color of the extracts varied considerably. The water rich in sulphates intensified the red color of the pine bark extract and produced a strong dirty green shade in the sumac liquor. Both changes were still more marked with the water rich in chlorides, an observation of considerable importance to extract makers, in view of the different shades yielded by the same extract when sold to different tanneries. Water marked "hard" and "very hard" also give deep colored

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* Report given at the Atlantic City Convention, June 9, 1917.

solutions and produced so turbid a liquor with the sumac, that filtration through a second filter paper became necessary.

The most important conclusions to be drawn from the figures are:

(*a*) That there is always a marked and in some cases, a very serious loss of tannin, if natural waters are used instead of distilled water.

(*b*) That in all cases the nontannin is increased.

(*c*) That the hide absorbs some portion of the mineral constituents of the water, *i. e.*, a slight natural "weighting" is produced by natural waters.

The authors have chosen the total hardness (in German degrees) as the most useful criterion of the nature of the waters, and plotted these values, with the percentage losses, into curves, which show at a glance how the suitability of a water that is to be used for preparing tan liquors, depends on its hardness. The curves bring out the following points:

"*Hot Extraction.*—Chlorides present in the water used for making tan liquors cause a serious waste of tannin in the case of oak, sumac and pine, but not in the case of valonia.

"Hard waters cause a sensible loss of tannin in the four materials examined, and an extreme loss in the case of sumac.

"*Cold Extraction.*—Whilst the amount of tannin extracted is several percent. less than when heat is employed, the composition of the water has less influence on the yield. Thus is very hard waters only are available, extraction may be conducted as profitably by the cold as by the hot method and with greater advantage in the extreme case of sumac."

It was thought advisable to confine the work of this committee to hot extractions only, and to approximate working conditions in the tannery as closely as possible. The chairman had a considerable amount of data on dissolving extracts for analysis in hard water and in distilled water, and in most cases the extract dissolved in hard water showed lower tannin. It was not thought, however, that this procedure was analagous to tannery practice, and the following directions were therefore drawn up and mailed to the members of the committee.

DIRECTIONS FOR COLLABORATIVE WORK ON HARD WATER COMMITTEE.

Experiment No. 1. Take several hundred grams of ground bark and nuts; divide into two equal portions and extract one with hard water and the other with distilled water, running experiments side by side so as to insure uniformity.

It is suggested that the bark be placed in a 1-liter beaker, 350 cc. of water added, and kept one hour at a temperature of 135° F. The liquor is then poured off, and the bark given two additional waters of 350 cc. each, heating the second to 180° for one hour, and the third to 200° for one hour.

The liquor can be decanted into a 1-liter flask, preferably filtering through cloth, so as not to lose any of the bark. This will give a rather weak leach house liquor. Take barkometer, dilute accordingly and run per official method, using distilled water in making the necessary dilutions. Calculate the tannin found back to the basis of the bark started with.

Experiment No. 2. Dilute 100 grams of mixed extracts, the analysis of which you know, with 200 cc. hard water, and make another mixture diluting 100 grams extract with 200 cc. distilled water; heat both side by side to 110° F. for two hours, stirring occasionally. This will approximate the general methods of dissolving extracts in the tannery. The mixture should be made in weighed beakers, so that the water evaporated during the heating can be replaced.

Take the barkometer of the two samples and analyze by official methods as liquors. Calculate the tannin found to basis extracts started with, and compare (1) whether the tannin found in the mixture made with distilled water agrees with the theoretical, and (2) the difference between the two waters on the same extract.

Kindly give the temporary hardness of the water used (Hehner Method), and also determine the total solids. You probably have access to about 3 liters of hard water, either from some well in the neighborhood, or possibly you may have a sample in the laboratory.

The chairman has a considerable number of analyses made by dissolving extracts in hard water instead of distilled water in making the dilution required for analysis; these analyses generally show a considerable loss.

You will note that in this work the actual analyses are all made with distilled water, as the chairman believes this to give more nearly the actual facts, but your opinion on the matter is desired.

It is requested that if convenient, the results be in by April 1.

CRUDE TANNING MATERIALS.

All Water Analyses are Reported in Parts per 100,000.
H. W. = Hard Water.

BLACKADDER.

Hemlock Bark.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
1.34	1.20	0.14	0.31	0.89	66.3	Distilled
1.48	1.34	0.14	0.33	1.01	68.8	H. W. containing 13 parts lime

Oak Bark.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
2.65	2.47	0.18	0.82	1.65	62.2	Distilled
2.72	2.52	0.21	0.90	1.72	63.2	H. W. containing 13 parts lime

Hemlock and Oak.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
1.88	1.77	0.11	0.54	1.23	65.4	Distilled
2.08	1.90	0.18	0.56	1.34	64.4	H. W. containing 13 parts lime
2.07	1.91	0.16	0.55	1.36	65.7	H. W. containing 130 parts lime

PORTER.

Mixed Barks.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
6.84	6.25	0.59	2.99	3.26	52.2	Distilled
6.85	6.24	0.61	3.13	3.11	49.8	H. W. containing 40 parts T. S., 21 parts Perm. Hard., 5 parts Temp. Hard.

BALDERSTON.

Oak Bark.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
1.42	1.25	0.17	0.54	0.71	50.0	Distilled
1.77	1.66	0.11	0.86	0.80	45.1	H. W. containing 43.5 parts cal. carb.

Hemlock Bark.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
1.44	1.29	0.15	0.44	0.85	59.0	Distilled
1.57	1.45	0.12	0.64	0.81	51.5	H. W. containing 43.5 parts cal. carb.

Oak Bark.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
1.24	1.04	0.20	0.50	0.54	43.5	Distilled
1.39	1.36	0.03	0.66	0.70	50.3	H. W. containing 41 parts cal. carb.

Divi Divi.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
9.58	9.09	0.49	2.93	6.16	64.3	Distilled
9.73	9.20	0.53	3.17	6.03	61.9	H. W. containing 41 parts cal. carb.

Kernahan.

Bark.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
5.75	5.43	0.32	1.50	3.93	68.3	Distilled; tan extracted 15.72
6.09	5.76	0.33	1.88	3.88	63.7	H. W.; tan extracted 15.52 7½ parts Temp. Hard., 377 parts T. S.
Seltzer and Marshall.						
Half Hemlock and Half Oak.						
1.99	1.88	0.11	0.79	1.09	54.7	Distilled; tan extracted 7.33, lost 0.64 per cent.
2.05	1.94	0.11	0.86	1.08	52.6	H. W.; tannin extracted 7.27, lost 1.18 per cent.
Fresh Bark.						
2.18	2.03	0.15	0.72	1.31	60.0	Distilled; tan extracted 8.81, lost 0.93 per cent.
2.22	2.08	0.14	0.76	1.32	59.4	H. W.; tannin extracted 8.88, lost 0.93 per cent.; containing 58 parts T. S. and 24.25 Temp. Hard.
McLaughlin.						
New Bark.						
On Basis of Bark.						
				15.71	60.7	Distilled water
				11.17	43.75	H. W. containing 77 parts salt and 25 Temp. Hard.
				15.25	58.69	H. W. containing 8 parts salt and 8½ Temp. Hard.
				15.33	58.96	H. W. containing 11 parts salt and 8 Temp. Hard.
				14.93	50.61	H. W. containing 77 parts salt and 6 Temp. Hard.
				14.73	52.83	H. W. containing 77 parts salt and 6 Temp. Hard.
				14.75	54.81	H. W. containing 30 parts salt and 14 Temp. Hard.
T. A. Faust.						
Bark and Nuts.						
4.02	3.84	0.18	1.41	2.43	60.5	Distilled; total tannin extracted 24.30
3.11	3.94	0.17	1.56	2.38	57.9	H. W. containing 30 parts Temp. Hard.; total tannin extracted 23.80
Smoot and Stacey.						
Oak Bark.						
2.36	2.22	0.14	0.94	1.28	54.3	Distilled; theoretical tan 1.62
2.54	2.39	0.15	0.93	1.46	57.5	H. W. containing 5 parts Temp. Hard.

EXTRACTS.

All Water Analyses are Reported in Parts per 100,000.
H. W. = Hard Water.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
BLACKADDER.						
Blended Extract A.						
42.59	39.44	3.15	13.90	25.54	59.96	Distilled
42.59	40.40	2.19	14.13	26.27	61.47	H. W. containing 13 parts lime
42.59	40.35	2.24	13.47	26.88	61.36	H. W. containing 130 parts lime
42.59	39.70	2.89	13.71	25.99	60.10	H. W. containing 13 parts lime 1 part salt
Quebracho and Hemlock.						
36.95	32.76	4.19	8.32	24.44	66.14	Distilled
37.00	33.04	3.96	8.36	24.68	66.70	H. W. containing 13 parts lime
37.00	33.24	3.76	8.47	24.77	66.91	H. W. containing 130 parts lime
37.00	32.53	4.47	7.82	24.71	65.46	H. W. containing 13 parts lime 1 part salt
PORTER.						
Mixed Extracts. Calculated to basis original extract.						
42.40	41.10	1.30	14.30	26.80	63.20	Distilled; theoretical tan 26.45
42.55	41.00	1.55	14.25	26.75	62.86	H. W.—40.15 parts T. S. 21.50 parts Perm. Hard. 5.00 parts Temp. Hard.
BALDERSTON.						
Chestnut.						
16.27	15.82	0.45	5.35	10.47	64.35	Distilled—theoretical tan 10.50 theoretical purity 64.5
16.43	15.93	0.50	5.62	10.31	62.75	H. W. containing 41 parts calcium carbonate
KERNAHAN.						
14.13	13.24	0.89	4.59	8.65	61.21	Distilled; theoretical tan 8.92
14.64	13.50	1.14	5.04	8.46	57.78	H. W.; 377 parts T. S., 7½ Temp. Hard.
SELTZER AND MARSHALL.						
One-half Chestnut and One-half Quebracho.						
14.84	14.52	0.32	4.54	9.98	67.2	Distilled; theoretical tan 10.35
14.87	14.56	0.32	4.51	10.05	67.5	H. W.—58 parts T. S. 25 parts Temp. Hard.
Extract No. 2.						
14.80	14.43	0.34	4.36	10.07	68.0	Distilled; theoretical tan 10.34
14.87	14.53	0.34	4.40	10.13	67.4	H. W.—58 parts T. S. 25 parts Temp. Hard.

HOLMAN AND FREY.

T. S.	S. S.	Insol.	N. T.	Tan	Purity	Remarks
Chestnut.						
41.12	38.68		13.96	24.72	60.1	Distilled; theoretical tan 25.47
41.10	38.79		14.05	24.74	60.1	H. W., Potomac tap; 7 parts T. S. no Temp. Hard.
Sumac.						
44.37	42.25		19.26	22.99	51.81	Distilled; theoretical tan 23.08
44.44	42.15		19.35	22.80	51.30	H. W., Potomac tap water
Sumac. Heating five hours at 185 degrees.						
44.30	42.35		19.86	22.49	50.83	Distilled
44.34	42.26		19.82	22.44	50.60	H. W., Potomac tap; theoretical tan 23.08
T. A. FAUST.						
Mixture One-third Chestnut, One-third Hemlock and One-third Quebracho						
15.45	14.21	1.24	4.77	9.44	61.1	Distilled; theoretical tan 9.84 theoretical purity 63.7
15.32	14.19	1.13	4.79	9.40	61.4	H. W., 30 parts Temp. Hard.
Chestnut Extract.						
12.35	11.82	0.83	3.72	8.10	65.6	Distilled
12.56	11.95	0.61	3.89	8.06	64.1	H.W. containing 30 parts Temp. Hard.
SMOOT AND STACEY.						
Mixture Three-fifths Chestnut and Two-fifths Quebracho.						
17.80	16.90	0.90	6.38	10.52	59.0	Distilled; theoretical tan 10.76 per cent.
17.86	16.90	0.96	6.37	10.53	58.9	H. W. containing 5 parts Temp. Hard.

ABSTRACT OF REMARKS OF COLLABORATORS AS TO THEIR EXPERIMENTS.

BLACKADDER.—Instead of leaching the bark in beakers, used an old fashioned extractor consisting of copper cylinder set in jacket and having a drain cock at the bottom. As no hard water was available some was prepared by taking 100 cc. of saturated lime water, making up to 1 liter and adding distilled water; and on some experiments the quantity of lime was made ten times as strong, and another experiment 10 parts of salt per 1,000,000 was added.

PORTER.—The water used is very low in temporary hardness, hence very little difference on extracts is noted and only a slight difference on barks.

BALDERSTON.—The liquor extracted from oak bark with hard water showed higher tannin; probably due to the solublizing effect of hard water on the insolubles of the oak. The result for hemlock bark indicates no difference but whether the liquor extracted with hard water will work as well in the yard as regards the quality of the leather produced is another question. I do not believe hard water shows any real disadvantage with Divi.

KERNAHAN.—The water used contained a very high quantity of salt and considerable sulphates and seems to have affected the extracts more than the bark.

SELTZER AND MARSHALL.—The hard water produced a considerable loss in case of the bark, but a rather low loss in the other case, these figures being based on analysis of the spent tan, the liquor and original materials which gives the amount not accounted for. In the case of the extracts the hard water showed a smaller amount of tannin not accounted for than distilled water. The liquors made from the two samples of extract showed 0.36 per cent. acetic acid in both hard water and distilled water solutions and it is our opinion that no tannin is destroyed by temporary hardness until all the acids are neutralized. The fact that the hard water solution showed more tannin than distilled water in some cases we believe is due to the fact that the hide powder absorbs not only tannin but salts. However, some of the differences in results are due no doubt to the fact that the original materials are treated with larger amounts of hide powder than the resulting liquors in that less hide powder is called for by the methods.

MCLAUGHLIN.—Based on considerable work done along these lines I think the suggested procedure is unsatisfactory as the bark in one case may retain more liquor than the other, also hardness is only destructive at a high sustained temperature. The method used in results reported was to extract in regular extractor one-half outside and the remainder refluxed, which method is not unlike practical leaching, as the strongest liquor is not boiled.

HOLMAN AND FREY.—The Potomac tap water would normally be considered pure and results on the extracts differ slightly in the theoretical percentages. A modified experiment was carried out, heating the extract for 5 hours at 185° F., which shows a still greater variation on the theoretical percentage but no considerable difference between distilled water and Potomac.

OPINION OF INDIVIDUAL MEMBERS OF COMMITTEE AS TO CONCLUSIONS TO BE DRAWN FROM THE TABULATED RESULTS.

BALDERSTON.—It seems to me that so far as raw materials are concerned, these results indicate that hard water has no effect on the amount of tannin extracted for most materials tested. Mr. McLaughlin's figures are exceptional, and it must be either that salt has a deleterious effect or that the material he used behaves very differently from those used by the other collaborators. I am disposed to think the salt is responsible, and we do not consider salt a constituent of hard waters in this part of the world. The waters he used should, I think, be called salt waters rather than hard waters.

As to the effect of hard water used in the dissolving of extracts there is no doubt that in some cases hard water has seemed to cause loss of tannin but these results do not seem to bear out such a conclusion.

KERNAHAN.—In looking these over it is pretty hard to form any opinion as to the effect of hard water on tannin. Some of the collaborators have used their own method of digestion, and others have used a water of practically no hardness and no total solids.

I believe, however, that the total solids in water have a greater effect on the tannin than does the temporary hardness. This is borne out by the water which I used, which contained practically no hardness compared with its total solids. The hardness, however, will probably precipitate more tannin when used in dissolving extracts than it will when used in leaching barks, as the water going on the tail leach is generally up around 200° F., and at this temperature the bicarbonate in a temporarily hard water will be driven off, and the calcium or magnesium carbonate will be precipitated where it will do the least harm. Mr. Yocum thinks that the total solids are of more importance than the temporary hardness.

SELTZER AND MARSHALL.—We notice that you should have specified the analysis of spent bark and that our results are the only ones which show the actual amount of tannin lost. We feel that there is not much more to add concerning this matter as we believe it difficult to draw a conclusion from the analysis of the bark liquor and state what will take place in practical operation, as the leaching in this experiment was not as thorough as that usually done in actual practice, however, taking into consideration the analysis of liquors by leaching with soft and hard water on bark the average tendency appears to be a slight loss of tannin in the liquor which will probably show up still higher when taking into consideration the analysis of the spent bark which was not thoroughly leached. Considering the action of hard water in the leach house the extra non-tannin will be added to the liquors giving the yard a lower purity than if water with lower solids was used. The best plan would be to properly soften the temporary hardness in the water with lime in a suitable water softening apparatus. This apparatus could be used for softening the water for the entire tannery which would be an ideal condition. In this connection it must be remembered that soft water aids acid formation and hard water hinders the formation of acid. This is further evidence that hard water will first attack the acid in preference to the tannin and we believe that only when the hard water meets the neutral tannin solution will there be a destruction of tannin.

Taking up the matter of dissolving extracts in hard water the result of the experiments of most operators seems to show a slight destruction of tannin. We believe no destruction of tannin will take place if the extract is acid.

MCLAUGHLIN.—As far as the work done goes it indicates little difference between hard and soft water in leaching, in respect to tannin destruction. As mentioned before, however, hardness seems to actually destroy tannin only through sustained boiling. As this long boiling does not occur in leaching house operation, it is a fair assumption that hard water will destroy little tannin.

But when you come to the effect of mineral salt in the leached liquor as regards the plumping and tanning of the hide, a different and a complicated problem presents itself. I believe it will be found that those tanneries producing the plumpest, best and most thoroughly tanned leather have a soft and pure water supply.

VEITCH AND FREY.—The results, with the possible exception of those by Mr. Laughlin do not show or even indicate a loss in tannin by the use of hard water. Mr. McLaughlin, however, did not conform to the prescribed procedure and this undoubtedly, as is to be expected, would account partly at least for the losses indicated by his work. It is believed that the procedure used in the work was not suited to occasional losses of tannin. The temperature was not sufficiently high and the extraction of raw materials was not sufficiently complete to give reliable indications. It is believed that further work should be done and that no attempt should be made at this time to draw conclusions from the work so far completed.

It is suggested that boiling water be used in some future experiments and that among the materials experimented with should be those which are very low in insolubles since insolubles themselves often occasion material differences between operators' results.

In addition to the use of natural hard water, it is suggested that each operator also conduct his experiments using distilled water to which a definite quantity of certain salts have been added.

SMOOT.—While we note practically no variations in either the bark or the extract due to the use of hard water, so far as the percentage of the insolubles and total tannin is concerned, we do notice that the solutions are darker and we cannot help but believe that the prolonged use of hard water in the beam shop or yard would ultimately show depreciatory results in tannin and available liquors.

P. M. C. ARMSTRONG.—It would seem from the figures submitted that the assumption that hard water did not destroy tannin in practice is correct. The Seltzer and Marshall analysis of mixed barks appears to show some loss, but on the other hand, there is much contradictory evidence.

It would seem to me that in dealing with such small percentages some volumetric method might yield more uniform results, and perhaps a permanganate titration would be more satisfactory.

Mr. Balderston suggests that the quality of the leather might be affected, but it seems to me that in a process in which so much lime is deliberately introduced into the hide could scarcely be affected by a small percentage in water itself. Under the best of conditions the quantity of calcium carbonate free in the hide after slight deliming is far in excess of the amount in any water, however hard. We have quite hard water here (Detroit River) and have no trouble in securing a flexible grain. The natural precipitation of phlobaphenes may be accelerated by the presence of lime, however, and this might be made the subject of investigation.

BLACKADDER.—It seems to me that there is a lack of concordance in the results of various members of the committee resulting probably from the fact that each used a different hard water. This is, however, not to be regretted for it serves to drive home, what seems to be an evident fact, namely, that there are at least two contrary factors in the natural hard waters. Firstly, there is a solubilising factor, due to the alkali under which we would include temporary hardness, and secondly, a precipitating factor due to the salts present in the permanent hardness. In my own experiments I was struck by the fact that the use of a saturated lime water solution in diluting extracts caused an actual gain in tannin, which gain was immediately reduced by the use of a water containing a minute amount of sodium chloride in addition to the lime. I am aware that such a water as I used would not occur in practice but it serves to show the action of the two factors mentioned. I would suggest that the work of the committee be continued and that all members use a similar water in their experiments. Further I would suggest that a typical hard water be taken an analyzed and the action of each component be studied singly and then possibly in various combinations.

PORTER.—The general results seem to indicate that hard water as a rule has a solubilizing effect on tannin, especially as applied to the extraction of raw materials. Also that this solubilizing effect is due largely to the permanent hardness and to the alkalinity of the water. The fact that the loss in tannins, whenever that occurs, seem to be largely due to the temporary hardness would lead one to believe that, whereas bicarbonates are alkaline towards mineral acids and the stronger organic acids, it is acid in reaction towards tannic acid.

SUMMARY.

Owing to the nature of the work and the wide diversity of the materials used by the various collaborators, the analytical results are somewhat lacking in definitiveness; furthermore, the chairman neglected to specify the analysis of spent tan, which would have added to the completeness of the results on crude tanning materials. The general consensus of opinion by the individual members of the committee, as to the conclusions to be drawn from the tabulated results, indicates a very serious doubt as to any considerable destruction of tannin by hard water. It was shown, however, that salt had considerable effect on tannin, and the point was also raised, that total solids are of more importance than temporary hardness.

The points brought up by Messrs. Seltzer and Marshall are worthy of note, *viz.:* that soft water aids acid formation, and hard water hinders this formation, indicating that hard water will first attack the acid, and that no destruction of tannin can take place, as long as any acid is in the liquor.

Several collaborators call attention to the fact that the solutions are darker and that their experience has been that an inferior color, and a less plump leather is produced by the use of hard water.

Messrs. Porter and Blackadder brought up a point which seems to explain to a large extent the rather peculiar results obtained in this work, *viz.:* that the hard water produces a solubilizing effect on tannin which compensates for any precipitating action due to sulphates or chlorides.

The chairman believes that the work done indicates no considerable destruction of tannin by hard waters, but does believe there to be some loss from waters rich in sulphates or chlorides. The fact that analysis show no loss in tannin is probably due to the solubilizing effect mentioned above, which will naturally lower the insolubles and increase the soluble solids, and which will counteract the increase of nontannins, due either to any conversion of tannin to nontannin by the constituents of the waters, and in addition the increase due to the combination of the hide powder with the mineral salts of the water. It is believed, however, that the work has proven that a considerable decrease in purity results from the use of hard water, and that a difference in color of the leather is evident.

In order to throw some further information on the subject, the chairman went to considerable trouble and expense to build an experimental leach house on exactly the same principle as the ordinary tannery leach house. A battery of six tubs, which held 60 pounds of bark each, was built complete with a heater box equipped with brass piping, etc. To accentuate any possible differences, the high tannin content materials were used for these experiments, using a mixture of mangrove bark, myrobolans, and divi divi. The water was put on the tail leach at about 180° and off the head at 110° to 115° and all general working conditions were maintained as closely as possible to actual working procedures in a regular leach house. Unfortunately, however, there was a slight amount of leakage, necessitating taking the results of this work with some reserve, but even so it is believed that the figures appended below are of some value.

	Soft water		Hard water	
	Liquor	Spent	Liquor	Spent
Pounds liquor	623		544	
Total solids	13.63%		17.36%	
Soluble solids	12.63		15.73	
Insoluble solids	1.01%		1.63%	
Non-tannins	4.87		6.69	
Tannin	7.76	7.54% basis air dry new bark	9.04	8.57 basis air dry bark
Purity	56.9		52.1	
Pounds tannin	48.35	27.14	49.18	30.9
Pounds tannin in new barks	129.5		129.5	
Pounds tannin lost	54		49.4	

The above results show actually more pounds of tannin lost by soft water than by hard, but this may be due as explained above to leakage, but the chairman is quite satisfied that there cannot be any considerable actual destruction of tannin by the hard water used for this work. This hard water contained 60 parts of total solids, of which 30 parts was temporary hardness. The purity however shows a large decrease, and the color test made on sheep skins indicated more of a red color with the hard water than with soft. This is probably due to the hard water extracting more of the coloring matter than the soft water.

DISCUSSION.

Mr. Reithof remarked that in practice most of the temporary hardness would be removed from water used for leaching on account of the high temperature involved.

Mr. Smoot said that in a certain tannery it was found that 20 per cent. more bark was necessary to tan a given quantity of hides when the leaching was done with hard well water than when soft river water was used.

Mr. Faust mentioned a tanner of splits who had much trouble with his drum tannage, using hard water. When he changed to soft water the trouble ceased.

ANTHRAX.*

By Dr. A. S. Ross, Camden, N. J.

In discussing this disease I hope you will not think me verbose when I tell you the term Anthrax is derived from the Greek word **ανθρας**, meaning coal, and that these ancients applied this term to the disease because the blood in the bodies dead of this infection turned black.

When I was asked to speak to you upon this subject, I felt it would be a task to gather anything very interesting upon this malady, which I thought was so rarely seen, but after I investigated I found it has importance commercially, and hence economically. In the province of Novgorod, Russia, alone, in a period of four years, 56,000 cattle and 528 men died of this disease. It is a disease found in many parts of the world, but is most rampant in Russia, Asia Minor, China, Argentina,

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* Read at the Atlantic City Meeting A. L. C. A., June 8, 1917.

Italy and also in the United States. Switzerland and Germany are exempt to a degree, due to advanced sanitation.

That it is increasing rapidly in the United States, cannot be denied, due to the vast importations of raw skins from these infected areas. It is an infectious disease, caused by the *Bacillus anthracis,* a rod-shaped, large spore bearing organism. Its means of transmission are various. It may be transmitted as an occupational disease through the medium of carcasses, hides, wool, hair, or any animal by-product. The spores are almost indestructible, and resist antiseptics and heat to an unbelievable degree. The United States Government report shows one case of a groom developing a malignant pustule on the back of his hand from being chafed by the leather band attached to a curry comb which had gone through all the many processes of tanning.

The persistence of the life of the spore within the earth is of great importance due to the fact that this causes the outbreak after each rainy season, because during the dry spell the earth loses its moisture and the earth worm burrows deeper in search for water, and returns to the surface during the wet season and deposits on the grass the spore which again infects the grazing cattle.

I myself, cannot believe these sensational paper reports of inoculation, through the medium of finished products, such as gloves, furs, shoes, etc. From my own investigations which cover years of records, I have failed to find a single case which occurred as a result of contact with a skin, after passing through the bating process. The cases which I have seen were those which came in contact with raws, or skins with hair attached. I recently made cultures of hair in the waste liquors, which showed one positive anthrax culture in nine taken.

At this time it is apropos for me to cite a case which was treated in Cooper Hospital, where after the patient was removed from the contagious building, an interesting experiment was carried out which consisted in suspending gelatinized threads in the infected room for twelve hours after each formaldehyde fumigation of twenty-four hours, and twelve hours of airing. The threads gave cultures of anthrax each time until the fifth fumigation. This continuous experiment consumed nine and one-half days, showing the great vitality of the spore.

Animals become infected by inoculation, *i. e.*, by direct contact, or indirectly by wounding their lips and gums on the short grass and stubble, which contains the spore, or through infected food or water, causing internal anthrax, or by inhaling the dried infected sputa, causing pulmonary anthrax. The fields thus become infected, hence the bodies of infected animals should be destroyed by incineration, fields should be quarantined, and all animals in the vicinity should be immunized by protective vaccines. This immunity lasts about one year.

I hesitate in arraying before you numbers of men who have tried to work out the problem of immunity, but I cannot pass by Tuissant, Pasteur and Sclavo, three men through whose untiring efforts has come the curative serum for man and the protective inoculation for animals; for it was Tuissant who discovered that by heating infected sheep's blood 55° C. for ten minutes and injecting this into other animals he caused a temporary immunity. Pasteur improved the crude methods of Tuissant, and produced an attenuated culture by growing virulent anthrax cultures under high temperature. It then remained for Sclavo to add another important link when he found that serum of immunized animals gave temporary immunity to other animals, which was the discovery upon which he built his antianthrax serum which is used upon man.

In considering the symptomatology we find that the patient usually has the history of an abrasion or wound upon which appears a small pimple-like enlargement without pain or pus, which in from six to twelve hours develops a small bleb which is of a color varying from a light straw to a dark grape; this soon flattens and becomes depressed in the center and leathery, being sorrounded by a circumference of small pearly blebs. In from four to twelve hours the adjoining structures become swollen and oedematous without pain and the patient, (characteristic of this disease), is non-apprehensive.

After a short time the temperature rises to 103° or 104°, the pulse increases to 130 or 140 or more, and the victim is seized with pains in arms, legs and back; chills are prominent; delirium ensues, and we have a picture of a man battling for his life against odds so great that in another few hours, profound stupor supervenes and he is carried away, usually with a convulsion epileptic in character, or the scene closes with coma.

(1) The suddeness of the symptoms, (2) the painlessness of the swelling, (3) the absence of pus in the pustule or eschar, and the peculiar vesicular circumference of the dark depressed papule are all diagnostic of this fatal malady, and should lead one to make smears at once for corroboration.

I am speaking now of external anthrax, to which my experience has been limited, as death from internal anthrax is preceded by the same general symptoms without an external pustule, plus pulmonary or intestinal symptoms according to the region attacked. The period of life is much shorter, and as a rule is not diagnosed except we have a clear history of anthrax infection due to occupations which would necessarily show exposure.

Writers claim that 80 per cent. occur on the hands and arms, which does not agree with my experience, as a large percentage of cases occurred on the face and neck. I believe the hands and arms are more liable to be the place of infection, due to the prevalence of abrasions and cuts, as I believe anthrax only attacks at a point where the skin is broken.

The prognosis is more grave as the infection occurs nearer to the face or head, thus anthrax on the arm does not give so high mortality as that of the face. I saw one case involving the wrist, in which the patient had the characteristic swelling, but the systemic symptoms were not severe, and the most severe case I have ever seen, which lived, was one which involved the lower eyelid and cheek, and yet the only fatal case I have had was on the arm. The mortality of external anthrax before the new serum treatment, was about 40 per cent., and with serum treatment, about 6 per cent. Of course, internal anthrax has given. a mortality of 100 per cent., yet we looked forward to better results with the use of serum.

In passing from the prognosis, I approach the most important part of my subject when I consider the treatment; which should be divided into preventive and curative. In the prevention of the disease, we have the solution of it, for if we could pick out the various batches of skins or hair which were infected and destroy them, we could eliminate it as an occupational disease. There have been attempts made at disinfecting the skins and wool, but they have failed commercially, due to the great loss. In the past two years, I have been practising a prophylactic method. It consists of cauterizing with carbolic acid all wounds found on employees and then applying alcohol dressings. This rule is absolute on pain of discharge, and any employee found with a wound unattended, is given the choice of treatment or immediate discharge. By this method we have, I think, conquered the disease to a degree, but when you consider that about seven to nine million skins are handled in the raw state in Camden alone, there is always danger of an outbreak. I have come to the conclusion that if I am given the case in the first twelve hours, I can save the patient; hence, any carbuncle, boil or abscess is immediately reported to my dispensary assistant in each of the establishments by the foreman, and smears are made at once, temperature is taken, and the patient is observed closely and is removed from work at once.

During the handling of raw skins I have the men submerge their hands and arms in bichloride solution—1 : 1000—frequently during the day, and we now have a separate dining apartment for the workers so they do not contaminate the food. I believe the day is near at hand when vaccination will give an immunity for a year or two; this has been accomplished in the veterinary field. At this point it would be well to impress upon you the fact that if an injection of anti-anthrax serum be given to each man exposed, it might cause him immunity to the disease for a time.

In the curative treatment we must consider that in the pustule we have a centre that is throwing out large quantities of bacteria, spores, and, possibly but disputed, anthracin, the supposed toxin, and remember the disease is a rapid one. The period of inoculation is from one day to three, and twelve to twenty-four hours is the average time for the patient to become dangerously poisoned; consequently an immediate sterilization of the site of infection is imperative. There are three methods surgically which I will consider in their respective importance:

First: Complete excision and cauterization with carbolic acid. This is the best method to be used—one which I have carried out in a number of cases which I have treated. This sometimes is not feasible due to the pustule being situated in a part of the face which would produce irreparable scarring, yet I did it on the base of the lower lid and cheek, feeling that a life long scar was far preferable to the risk of a life for cosmetic reasons. This case lived, but has developed an ectropion, which Dr. Cramer saw, and thought could be remedied by subsequent operation. I make a sweeping incision which is deep, cauterize with carbolic acid, leave the wound open, and dress in alcohol. The objection to this excision is the claim made that you open the blood paths and break down the line of defence, which I believe to be only theoretically correct, but without foundation in practice.

Another method which deserves second place is a crucial incision deeply made and the use of pure carbolic acid as a cautery.

The next method which is an old one, consists in the injection of pure carbolic acid around and into the pustule.

I have seen the crucial incision and the carbolic acid injection methods, but in both cases the victory was not so decisive and quick as in the excision method, yet both cases recovered. Other methods have been used, but have mostly failed; one of which is most interesting, in which they discovered that the anthrax bacillus grows very poorly in the presence of *Bacillus pyocyaneus,* hence they injected these bacilli into the wound hoping to retard the growth. This has been a failure practically. At this point I wish to say that a precaution mentioned at this time will be opportune and if followed will probably save the surgeon's life in some future case to which he may be called. Always remember that you are handling the quickest and most deadly of all infections, and that to enter into a case of anthrax with an abrasion or open wound on the face, neck, or in fact any exposed part would bring to you what it has brought to many physicians throughout the world—death—Hence always wear gloves that are perfect, be gowned, and do your work quickly; all instruments should undergo fractional sterilization under steam and dressings should be burned.

After the discussion of the surgical treatment, we come to consider the serum treatment which is really the only safe method to pursue as it has brought the mortality down to six per cent. There are two sera which I have used, one is the genuine Sclavo's serum made from ass's blood; this serum comes in glass ampulae, 10 cubic centimeters each, and has to be given by means of an anti toxin syringe which makes it inconvenient. It is also difficult to purchase. The other serum is a horse serum put up by

H. K. Mulford and Co., which comes in convenient form 10 cubic centimeters in each barrel—two barrels to a dose. I have used both sera and have had equal results.

If I had the choice of treatment, I would choose the anti-anthrax serum without any excision rather than excision without serum, but when these two methods are combined, if the case is diagnosed early I believe the death rate would be small. You must bear in mind the fact that these cases as a rule are overlooked even in hospitals, and the case has advanced many hours before a diagnosis is made.

I remember a case which applied to another hospital for treatment and the surgeon in charge treated it for an "Infected face," but the patient was providentially guided into the Cooper Hospital dispensary, where the chief of clinic diagnosed it immediately, and referred it to the chief on duty who saved the man's life. I remember another case which had been seen by two physicians who thought it a carbuncle, but the patient's condition became so alarming that another physician was called, who arranged to meet me at the patient's house, but when we arrived, death had already ensued. This case covered only twenty-four hours from the time the patient was aware of the condition.

In the consideration of the serum treatment, Sclavo's method should be taken seriously as it is based on his own experience in Italy where it was conceived and first practised. He advises 40 cubic centimeters *i. e.,* 10 cubic centimeters given in various regions of the body, and if the condition shows no improvement in twenty-four hours, he repeats it. In very severe cases, he injects it into a vein on the dorsum of the hand. (Why this region is advised, I do not understand, unless it is an Italian method of intraveneous injection). I have used the serum in 20 cubic centimeter doses every four hours and have controlled the cases very nicely. From five cases I have found, I gave respectively 210, 200, 140, 120, 60 cubic centimeters and have come to the conclusion that the best results are attained by giving 20 or 30 cubic centimeters every three or four hours for forty-eight hours, and then giving about two doses the third day and no more, for if the patient has not reacted by the third day, any treatment is useless. It is well to remember that this serum can be given in any amounts, as it is harmless and every case is a law unto itself.

In closing my remarks, I wish to say that in spite of the seriousness of this disease and its highly infectious nature, I have never seen a case contracted from an infected person, regardless of the fact that the Camden authorities do not quarantine in any way, and even in one case, little children kissed the victim each night with utter disregard of the ground upon which they stood. Dishes were interchanged against my orders, and I believe in one case, a public funeral was held.

PRACTICE AND THEORY ON TREATMENT AND DIAGNOSIS OF ANTHRAX.*

By Dr. H. J. Frisbie.
Elkland, Pa.

The diagnosis of anthrax in man is not difficult, especially the cutaneous type. In tanneries, and factories handling hair, wool, bristles etc., every cutaneous carbuncle awakens suspicion of anthrax, and a diagnosis is readily made from a history of the case. Every small cut or pimple on a laborer in a tannery or factory using hair or bristles should be carefully watched.

The most frequent error in diagnosis seems to be confusion with simple carbuncle. This simple carbuncle is a circumscribed necrotic inflammation of the skin, in which a number of openings usually exist, and the intervening skin sloughs. Intense pain is nearly always present.

The anthrax carbuncle begins as a small, elevated vesicle, which early breaks, leaving a dark necrotic center, surrounded by a circle of vesicles, like a small circlet of pearls. The absence of pain in the anthrax pustule is a prominent symptom, and the black, dry, necrotic center surrounded by its ring of vesicles with the rapid swelling of the tissues involved is unlike any other cutaneous sore.

Very different is the diagnosis of intestinal anthrax—but here again the occupation of the patient is a great aid. The sudden onset of very severe gastrò-intestinal symptoms—diarrhoea, vomiting, cyanosis, convulsions, collapse, in a man who is working in a plant using dangerous hides or wool or bristles is an indi-

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* Read at the Atlantic City Meeting A. L. C. A., June 8, 1917.

cation for prompt microscopical examination of the feces and vomited matter. The intestinal type may show small carbuncles on the integument, and on the mucous membrane of the nose and mouth hemorrhagic spots and severe bleeding may develop.

Malignant anthrax oedema may first show as a slight swelling of the eyelids and a puffy condition of the face. The oedema spreads rapidly, and symptoms of general infection and collapse come on quickly. This type is very seldom seen, and may easily be mistaken or overlooked. Any swelling or puffiness in the face of any worker in hides or hair should be closely watched.

The pulmonary type of anthrax is due to the inhalation of infected air, and is not often seen. The writer has seen one case in which the early symptoms were those of a severe pneumonia. Symptoms of a very severe toxic condition rapidly developed with the raising of large quantities of a very dark, bloody fluid, unlike any sputum the writer had ever seen. The case died in convulsions on the seventh day. Pulmonary anthrax can be diagnosed early only by a microscopical examination of the blood and sputum, and this should be made early.

The treatment of anthrax has undergone few changes during the past centuries. The old Greek physicians treated their cases of anthrax carbuncle by excision and the application of healing ointments. From these earliest times the excision of the pustule has been practiced, and is the usual treatment of the present time. The writer has treated or seen treated cases by nearly every method, including the treatment by the use of ipecac as well as the use of caustics. One early case was seen which was being treated by the use of whiskey and poultices of fresh cow-manure. This case, unfortunately died.

The best treatment to-day would seem to be by excision of the pustule; cutting wide and deep—swab out the wound with tincture iodine and leave a pack of cotton saturated with tincture iodine in the wound for two hours, when this pack should be removed and a 1/2000 bichloride dressing applied. The patient is given 20 cubic centimeters Mulford's anti-anthrax serum intravenously and 20 grains of quinia sulphate in capsules, and put to bed. After waiting 6 hours he is given from 20 to 80 cubic centimeters anti-anthrax serum, according to his reaction from the primary dose. He is then given 10 grains quinia sulphate in capsule every 4 hours as needed. The writer has used this treatment in many cases without a death, and the patients are usually up and dressed in four or five days.

The use of serum in the treatment of anthrax is rather new, but certainly not "in the experimental stage," as stated recently.

The only treatment for intestinal and pulmonary anthrax is by massive doses of the anti-anthrax serum, and stimulation.

Very recently Penna and Kraus of Buenos Aires studied the action of normal beef serum in more than fifty cases of anthrax, and with surprising results. At first they used prepared immune serum, but later found just as good or better results with the normal serum. At first this serum was used intravenously, but later its use subcutaneously gave the same results. This treatment should be given trial, and prompt reports should be made. This report only emphasizes the fact that we should continue investigation along this line, as the writer believes the ideal treatment is to be found by such study.

In all the experimental work done with serums it seems that use has invariably been made of the blood of the domestic animals, and no effort has been made to utilize the blood of men suffering from this disease.

In all corners of the world to-day men are searching for a better serum—looking for some means by which immunity may be conferred upon the laborer in infected locations.

Would it not be worth while for your association to engage a man interested in this line of work and make it possible for him to study every case which develops among the employees in the plants with which you are associated? The results would certainly be interesting and might bring great benefit to mankind.

This line of investigation could be easily carried on and every case could be thoroughly studied. The wonderful results following the administration of the anti-anthrax serum in neglected cases prove it to be of great value, and if further investigation brings a positive cure, it would rob one of the world's greatest plagues of all its terrors and bring absolute safety to a great body of men who are daily exposed to its poison.

To summarize:—Anthrax can be easily diagnosed by careful watching of all employees exposed to its infection, and the use of the microscope, if needed. Watch every little cut and pimple, and have anthrax in mind at all times. The treatment by early and free excision of the pustule and the early and free use of antianthrax serum with the use of tincture iodine in the dressing of the wound following excision, will give splendid results. The study of the blood of patients suffering from anthrax might give a better serum than is known at present and could be easily undertaken.

THE NATURE OF ANTHRAX AND ANTIANTHRAX SERUM.*

By A. Parker Hitchens,

Director, Mulford Biological Laboratories, Glenolden, Pa.

Anthrax is a disease which enjoys the distinction of having been one of the first demonstrated beyond doubt to be caused by a microorganism. The anthrax bacillus was discovered in 1850 by Rayer and Davaine in the blood of a sheep dead of anthrax. The organism was noticed by others—notably by Pollender in 1855; by Brauell in 1857; and by Delafond in 1860. It remained, however, for Davaine in 1863 to point out the constant presence of this peculiar rod in the blood of animals affected with anthrax and he named the organism "bactéridie charbonneuse." Finally, Pasteur, with his pupils, demonstrated the specific character of the anthrax bacillus by reproducing the disease in animals through the inoculation of pure cultures.

Nature of the Infecting Organism.—The anthrax bacillus is one of the largest of the disease-producing bacteria. It is shaped like a rod with square ends, but in well stained preparations, the ends seem a trifle concave.

One of the most important characteristics of the anthrax bacillus is that when grown upon anything not extremely favorable to its development, it rapidly forms spores. Spores represent a stage in the life history of certain bacteria somewhat similar to hibernation. The vital part of the organism takes on an extremely resistant covering which is usually spherical or oval in shape. The spore produced by the anthrax bacillus is oval and develops at about the center of the rod. Relatively few of the

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* Address at the Atlantic City Meeting, A. L. C. A., June 8.

disease-producing bacteria form spores regularly—the anthrax bacillus, the tetanus bacillus and some of the organisms responsible for gas gangrene in war wounds are the most important. It is to this characteristic of spore formation that are to be attributed most of the problems concerned in the eradication of the disease; anthrax.

While anthrax bacilli, in their actively growing state, may be destroyed by a moderate degree of heat—60° C. for a few minutes—and by relatively weak solutions of chemical disinfectants, their spores are not destroyed much below the boiling point and they resist even high concentrations of disinfectants; furthermore, while nonspore-producing bacteria resist drying and live outside the animal body for only a short time, the anthrax bacillus by means of its spores may, and does, remain alive in the soil and in polluted fluids indefinitely.

It is easy to demonstrate the permanence of all the characteristics of an anthrax bacillus in the spore state. Disease-producing bacteria which do not produce spores easily succumb to an unfavorable environment, but even if kept alive in the laboratory by repeated transfer to fresh culture media, they gradually lose their power to produce disease.

The spore-producing bacteria undergo no such changes. In order to demonstrate this fact, 17 years ago, Dr. M. P. Ravenel, then associated with the Laboratory of the Pennsylvania Live Stock Sanitary Board, dried upon silk cords some anthrax bacilli whose disease-producing power had been carefully studied. A few days ago, D. M. J. Harkins of the Mulford Laboratories, made cultures from some of these silk cords and without difficulty obtained active germs. These cultures when injected into animals showed disease-producing power quite equal to that of the original cultures studied by Dr. Ravenel. For 17 years these anthrax spores had retained unchanged all the essential characteristics of the original culture. This experiment makes plain the reasons for the difficulties encountered in efforts to limit the spread of anthrax and to disinfect hides and other material from infected animals.

Nature of the Disease.—As a first essential to the production of disease, the infecting bacteria must have the ability to grow within the living tissues. In the process of growth the composition of the body fluids and tissues is altered and there results the production of substances foreign to the tissues—metabolic products of bacterial growth and products of tissue destruction. On the other hand, the tissues and other fluids in their efforts to overcome the infection, destroy large numbers of the bacteria, and the products resulting from this destruction—also foreign bodies—are set free within the tissues. It is thus evident what a complicated process an infectious disease must be and how much we must learn before we are able to understand thoroughly its intricate mechanism.

Considering the ubiquity of disease-producing bacteria, and the relative freedom of our bodies from their harmful activities, we must conclude that a germ which can overcome the natural defences of the animal body must be endowed with very special characteristics. The anthrax bacillus has these characteristics; that is, the ability to utilize living animal tissues and their fluids for its nourishment. But the anthrax bacillus possesses another characteristic to which is due the malignancy of the infections caused by it. When growing in the animal body, it may surround itself with a gelatinous coating, or capsule, which protects it from the activities of the body tissues which have to do with the limiting and eradication of infections. It is on account of this capsule that abscesses caused by the anthrax bacillus tend to be malignant and progressive. The ordinary pus-producing bacteria do not have the ability to surround themselves with capsules and for this reason infections caused by them are more easily resisted and limited by the tissues, and such infections respond more readily to treatment.

The anthrax pustule is a localized infection because the antagonistic forces of the body make an effort to keep the anthrax bacilli bottled up. When these defensive mechanisms are broken down, the germs get into the circulating blood, and when this occurs, the death of the patient usually ensues. It is only when the body tissues and the body fluids are greatly reinforced in their antagonistic powers against the anthrax bacillus that the animal can exhibit much resistance to infection.

The severity of any infection depends in a large measure upon the disease-producing capacity or virulence of the germ causing the infection. The longer a germ grows in the bodies of animals through transference from one infected animal to another, the greater power it acquires of living and growing in the animal body. Thus, we have increase of virulence. On the other hand, by certain methods of treatment the virulence of a culture may be greatly reduced so that it cannot produce a severe type of infection. It is such cultures as these that are used for vaccination.

Protective Vaccination.—An animal recovers from anthrax through the formation of substances within its tissues which antagonize the anthrax bacillus. The same resistance may be artifically acquired by man or by one of the lower animals through the process of vaccination. Vaccination consists merely in the injection of cultures which have been reduced in virulence to such an extent that the tissues can without great difficulty, produce sufficient antagonistic substances to overcome them. As a rule, this first process is reinforced by the injection of a second dose of vaccine considerably stronger than the first. The result of the second vaccination is such that the tissues and other fluids are so reinforced in their ability to prevent the growth of the anthrax bacillus that infection is impossible even by cultures of very high disease-producing power.

Antianthrax Serum.—In the process of rendering an animal resistant to infection, a large proportion of the antagonistic forces are probably stored up within the tissue cells, but a certain amount also escapes into the tissue fluids and into the circulating blood. Following the injection into an animal of any albuminous substance, there appear in the blood serum of this animal newly formed substances which have specific activity with regard to the material injected. These newly formed substances are called "antibodies." After an animal has been treated with certain bacteria over a period of some months, the ability of this animal to resist infection can be measured with a certain degree of accuracy by estimating the amount of antibodies in its blood serum.

The process by which antianthrax serum is prepared is based upon these facts. Horses are usually selected for the purpose, and they receive first the anthrax vaccine in the usual doses, and these injections are followed by subcutaneous doses of cultures of greater virulence. Finally, doses are given intravenously, and after a few months' treatment, a horse may withstand as a single injection, a dose sufficiently large to kill a thousand horses, if it were distributed equally among that number. When horses that have been under treatment for several months show the presence of large quantities of antibodies in their blood serum, they are bled, the watery part of the blood, which is the serum, is collected, it receives a small quantity of antiseptic to prevent contamination, and after extremely careful tests, which are made in duplicate to be certain that there are no harmful substances in it and no living bacteria present, it is ready for distribution and use.

Administration of the Serum.—Every physician has had considerable experience in the administration of diphtheria antitoxin, and the amount of serum necessary to be administered is well known. With less experience in the administration of antibacterial serums, such as antistreptococcus serum, antipneumococcus serum and antianthrax serum, it seems reasonable to suppose that since they belong to the same class, the same quantities should be used. Such doses, however, are not sufficient; the curative power of 10 cc. of diphtheria antitoxin is probably ten or twenty times as great as the curative power of the most potent antianthrax serum that can be prepared. For this reason, to get results, much larger doses are necessary and in order that the beneficial action of the serum may be immediately available to the tissues, it is advisable to give the serum intravenously. Intravenous doses may be from 50 to 100 cc., or more, and given every 8 hours, or according to indications. Following an injection, there is frequently a fall in the temperature and an amelioration of the local symptoms. When the temperature begins to go up again, another dose of serum is injected.

DISINFECTION OF TANNERY SEWAGE BY MEANS OF CHLORINE.*

MR. BUSWELL: Since the morning is rapidly advancing and we hope to have considerable discussion not on the printed program, and since copies of the paper have been distributed among you in printed form, I will only summarize the work which is here reported.

This investigation has covered a period of over two years, and for the last year of that time, a plant that is described herein has been in operation in a tannery, the effluent from which consisted of 500,000 gallons per day and our results have according to our test, been highly satisfactory in preventing the spread of anthrax from this source.

The history of anthrax and the relative prevalence of anthrax have been pretty well covered in the papers preceding. I might mention the data referred to on page 333 in connection with the extent of anthrax in this country. I have only data for New York State but you will find that in New York State for the last three or four years there have been from 100 to 200 deaths among cattle for a year of anthrax.

The previous work in the treatment of tannery effluents has consisted largely in improving the physical properties of the effluent so as not to cause nuisance, and comparatively little attention has been paid until rather recently to the prevention and spread of anthrax from this source.

The paper presented yesterday, together with other reports that have been printed in the literature, show that tannery waste can be treated by the various methods of sewage disposal, either mechanical or chemical or biochemical, sedimentation, slow sand filtration or intermittent sand filtration, or the various biological processes such as sprinkling filters and trickling filters, and work which has been carried on to an experimental extent only with activated sludge in our hands and in the hands of Copeland at Milwaukee, give fairly good results, but nothing definite can be said as to the efficiency of activated sludge at the present time.

The problem which we had to solve was somewhat different probably from the average tannery problem. The tannery sew-

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* Discussion at the Atlantic City Meeting, A. L. C. A., June 8, 1917.

age was entering the village sewer and a sewage disposal plant had already been built by the village to handle both the village sewage and the tannery effluent. At the village plant there was a sedimentation tank, a septic tank and trickling filters, so that the mechanical and biochemical processes of purification were well provided for. In view of this fact it did not seem advisable to install filters and extensive tank systems at the tannery itself. It hardly seemed justifiable to have available double tank space for this type of treatment. We therefore attempted simply to disinfect the tannery effluent to such an extent that it would not cause the spread of anthrax, leaving to the village disposal plant the purification of the sewage so as to prevent pollution of the stream and nuisance.

Laboratory experiments, as reported in the tables here, showed that liquid chlorine was by far the most efficient disinfectant that could be used. We found it very much more efficient than bleaching powder—calcium hypochlorite. It has been assumed by many investigators that bleaching powder or hypochlorite would be practically the same as chlorine, but we found in our experiments that the liquid chlorine itself or a saturated liquid chlorine solution as it is conveniently handled, was very much more effective in killing anthrax spores both in the presence and in the absence of considerable amounts of organic matter. Experiments showed that 50 parts per 1,000,000 of chlorine would kill the anthrax spores when suspended in the general effluent from the tannery, which had been allowed to settle for 20 minutes, removing the suspended solids, and we therefore installed a chlorinator to add this amount of chlorine to the tannery effluent. The question of sedimentation, however, did not seem advisable and we tried the effect of screening. We found that when anthrax spores were added to the effluent from Reinsch-Wurl screens which removed the larger particles, 50 parts per 1,000,000 did not kill all the anthrax spores; there were some of them which survived, but these spores seemed to be completely attenuated, at least they would not kill guinea pigs.

Our experiments were carried out as follows: One hundred cc. portions of the tannery effluents which had passed through the screens were sterilized in flasks and from 1,000 to 2,000 anthrax spores per cubic centimeter of the effluent were placed in these flasks; then the required amount of chlorine was added and an hour's contact period was allowed to intervene. Portions were then withdrawn and plated on Petri plates, and at the same time 1 cc. portion was injected into the guinea pigs. The petri plates showed that there were from three to sixty surviving spores per cubic centimeter, but the guinea pigs survived the inoculation, so that apparently these spores were attenuated. On the basis of this experimental evidence the plant was installed at the tannery to treat the effluent in this manner.

Now to those of you who are not familiar with the Reinsch-Wurl screen, a straw hat makes a pretty good illustration. A Reinsch-Wurl screen is built very much like a hat except that it has a circular appearance rather than an oval one and is placed at an angle in the sewer. The rim is perforated with slots, in this case a sixty-fourth and a thirty-second of an inch wide and 2 inches long, and in some cases the other portion of the screen is also slotted in a similar manner. The upper portion is slanted inward instead of at right angles as in the hat. This screen revolves in the sewer and the sewage flows through the slots, and the heavier material, such as chunks of hide and fleshings and hair, is pretty effectively removed from the sewage as the screen revolves. The height of sewage is regulated so that it covers about a half of the screen. At the upper portion of the screen or at the upper part of the screen is a sprocket wheel with brushes on the end of each sprocket which brush off this mat of hair and hide and fleshings, etc., dropping the screenings on a belt conveyor and the clean screen passes back down through the sewage. The brushes are ingeniously arranged so that each portion of the screen is swept three times before it passes back into the sewage again.

The screenings consisting of the hide and hair and fleshings, etc., the portions which are most likely to contain anthrax spores or anthrax spores in large clumps, are effectively removed by this screen. In this particular case, about four to six barrels a day of material is removed by the screens, four to six barrels from an effluent of 500,000 gallons per day. These screenings are placed in covered barrels, protected from flies and are transported to a fertilizer plant where the first process in treatment is subjecting the material to high temperature which would disinfect it and kill any anthrax spores which might be present, before the stuff is used as a fertilizer on the soil. The effluent from the screen having this material removed, passes down through a chamber to which a saturated chlorine solution is added by means of Wallace and Tiernan's device. This is simply a system of reducing so that the chlorine is dissolved in a very strong solution and run directly into the sewer. The sewage then passes out into the village sewer and down to the disposal plant.

Since the installation of this completed system, we have made a great many tests on the treated and raw effluent as summarized in the list of inoculations, and they may be summarized as follows:

The installation of the screens was not completed until March 1, 1916. Up to that time the tannery effluent was treated first by the addition of bleach and later with liquid chlorine to the extent of 50 parts per 1,000,000, indicated by "Cl_2" in the table under "Treatment." During this period 21 samples of the untreated tannery liquors were tested, in eight of which anthrax was found, and of 15 samples of treated effluent 8 showed the presence of anthrax in the sludge. Since the installation of the screens 16 samples of the untreated, and 4 samples of the screened but not chlorinated effluent have been tested, of which 7 contained anthrax. Anthrax was not found in any of the screened and chlorinated samples tested, of which there were 13 during this period.

Now in bacteriological work, the technique and method of testing samples has a great deal to do with the results so that it is only fair to state exactly how these samples were tested and to mention some results which did not agree exactly with these.

It has usually been conceded in the literature that spores would withstand a temperature of 80° C. It was our practice, therefore, to heat all samples to 80° to kill any bacteria which might be present which were not anthrax and which were not spore bearing organisms, such as streptococcus and various organisms which might cause blood infections. Our samples were heated to 80° for half an hour, then 1 cc. portion of the sludge which settled to the bottom of the sample were inoculated into guinea pigs. In some laboratories it is the practice to centrifuge and suspend the centrifuged sediment in saline solution and then inoculate guinea pigs. The amounts which are used in centrifuging and inoculating are not greater and are rarely as great as would correspond to the amount of material from which the sludge is removed by sedimentation and by our method. For instance, the sludge injected would correspond to the sludge from about 30 cc., and where centrifuging is used as a rule, not so large an amount as that is taken.

In one case where the effluent from this tannery was tested by the Bureau of Animal Industry, where the effluent was not heated to 80°, but heated only to 60°, anthrax was found in one out of three inoculations, I believe, from the same sample in the treated effluent, so that the anthrax was affected by the chlorine at least sufficiently so that it would not withstand a temperature of 80°, and we feel it probably was attenuated so that it would not withstand the other adverse effects of nature, such as the effect of antagonistic bacteria which would attack it in a septic tank, or the effect of sunlight and various other natural agents which work very deleteriously, as we know, on anthrax spores. This work was done by the Bureau of Animal Industry since our paper was prepared and submitted for publication, so it is not included in the present paper, but the question of the heating or the temperature to which anthrax spores or samples suspected of containing anthrax should be heated before inoculation is perhaps an open one although it was not so considered until these experiments by the Bureau of Animal Industry.

However, the cattle epidemic which had existed along the streams into which this tannery effluent was emptied has entirely been stopped since the application of this method of treatment so that from a practical standpoint, and from the results from the tests made, as we made them according to then standard methods, the method of treatment has been satisfactory in preventing the spread of anthrax from this source.

Dr. Klaber: I would like to ask one question of Mr. Buswell. In speaking of the treatment of the effluent of the sewage with 50 parts per 1,000,000 is it meant it will be a total of 50 parts per 1,000,000 or a total of 50 parts per 1,000,000 above the amount of chlorine necessary to combine with the organic matter?

Mr. Buswell: Two hundred and twenty-five pounds of chlorine per day are used for 500,000 gallons. Of that amount 50 per

1,000,000 is not sufficient in most cases to combine with all the organic matter.

MR. YOCUM: What is the cost of the chlorine per pound?

MR. BUSWELL: I hesitate to mention any price at the present time, if you will ask the chlorine manufacturer for the price of chlorine he asks you what you want it for. If you want it for manufacturing war materials it is in the neighborhood of 35 to 40 cents per pound, because he knows that at the end of the war you are no longer his customer. If you want it for disinfecting sewage, he will probably give it to you for as low as 10 cents, 15 cents and 18 cents a pound.

MR. YOCUM: I only asked because I had occasion to buy some and I had to pay 20 cents.

MR. PECK: What is the effect of your liquid chlorine on fish life in the stream in which it is discharged?

MR. BUSWELL: As I stated before, the chlorine 50 parts per 1,000,000 is not sufficient probably to combine with all the organic matter so that eventually all the chlorine is taken up, free chlorine cannot be detected in the effluent from the town plant at all.

MR. PECK: What was the cost of the Reinsch-Wurl screen?

MR. BUSWELL: Two screens 8 feet in diameter were installed in this case and the cost, I believe, was approximately $5,000 apiece.

MR. PECK: What would be the effect of this chlorine if injected as soak; what would be the effect on the hide?

MR. BUSWELL: We have tried the chlorine for disinfecting hides to rather high concentration and it does not seem to harm the hide much or harm the anthrax spores very much either; not as much as we had hoped it would. It has some effect, I think, so experiments that are not quite finished seem to show that it has greater effect than bichloride and I don't know whether it has greater effect than the Schattenfroh method or not.

MR. KADISH: I would like to ask if it is necessary to treat the entire tannery effluent or if only certain portions of it, say the beam house?

MR. BUSWELL: I believe Dr. Dorset will make some statements in that respect. Undoubtedly only the beam house effluent and the soak effluent would be the liquors to be treated if it were practicable to segregate them. In this particular case the engineering difficulties and the difficulties in getting a class of labor necessarily employed in tanneries, to conscientiously segregate these things and turn the valve in the right way made it seem better to us to let the whole stuff go down through the same sewer and treat it all. Furthermore, the other liquors do not have so high a chlorine absorptive power as do these soak liquors and beam house liquors, so they do not require a proportionately greater amount of chlorine for treatment.

MR. FAUST: What effect has temperature on the efficiency of chlorine, that is, very cold liquors in the winter time? Do they have the same bactericidal effect?

MR. BUSWELL: These samples were taken throughout the winter, although I don't believe the temperature in this particular case varies greatly the year around. They warm their soak water in this particular tannery; they are all housed in a comparatively warm building so that we have not observed any great lowering of the temperature. Temperature, of course, greatly increases the effect of any disinfectant. Frequently, the raising of the temperature 10° C. will double the effect of the disinfectant. We have made some calculations on the question of raising the temperatures of the effluent so as to cut down our cost of chlorine, but the cost of coal and the difficulties involved would be greater than the cost of chlorine.

MR. DICKERSON: I think the normal price of chlorine is about 7 cents. Bids were received as low as 5 cents a pound before the war. Chlorine could be shipped in tank cars and the cylinders filled from the cars so that 5 cents a pound where there are large quantities used might be a normal price for chlorine. It was a drug on the market before the war.

ANTHRAX AND HIDE DISINFECTION.*

By Van A. Wallin.

The experience of the tanners with the hide disinfection rules during the past year has not been a happy one. Expense, disappointment, irritation and serious loss have attended the introduction of the recent new rules issued by the Department of Agriculture; the tanners bearing the burden with as much grace as they could summon to the situation.

It is almost unnecessary to state that the rules were *not* created for the purpose of adding to the tanners' tribulations; those responsible had no malevolent intent. The tanners were merely unfortunate; they were not regarded as reprehensible, their sufferings are incidental to the cause of scientific interest in the welfare of the great American Farmer with a big F.

Indeed the administrators of government control, comprising scientists, chemists, pathologists, bacteriologists and other gentlemen of title, have freely accorded us the right of petition. They have gone further and extended us the privilege of consultation in the framing of the new rules, have courteously advised and investigated and, in my belief, have in every way done what they could to ameliorate the unhappy situation for the tanner, consistent with what they regarded as essential to the protection of the cattle industry.

Under the law, the quarantine regulations governing the importation of animal and vegetable products are written by the Secretary of Agriculture, issued by the Secretary of the Treasury and distributed abroad by the Secretary of State. This trinity of executive has not always fully co-operated and some of our troubles have been due to misunderstandings and blunders on the part of the Government.

The tanners have had to bear in mind that the authority vested by law in the Secretary of Agriculture is absolute. We find there can be autocracy within a democracy. Under the law the Secretary can entirely prevent the importation of hides, even all animals, plants or vegetables, if in his judgment it is wise to do so as a protection against the introduction of diseases. Indeed the wording of the law is that all such products are absolutely pro-

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* Read at the Atlantic City Meeting A. L. C. A., June 8, 1917.

hibited entry into this country, unless and until they are specifically permitted to enter under the regulations. As an Assistant Secretary of the Treasury once said to a committee when the subject was under discussion. "The Secretary of Agriculture has authority greater than that of the President and second only to that of the Almighty." So the tanners have not been in position to assert their rights; they have no rights under the law. The free importation of hides is not a right, it is a privilege, granted by the Secretary of Agriculture to those who conform to his regulations.

There are three diseases to which cattle are subject that are the object of the hide quarantine regulations, Anthrax, Foot and Mouth Disease and Rinderpest. They are all of serious importance and the government does well strictly to guard the cattle industry against them. I believe the tanners are willing to cooperate in this service, but ineffective and unnecessary regulation which does not afford practical help to the farmer and causes expense and damage to the tanner ought not to be. I hope to show that the present regulations may be with safety and justice "revised downwards."

Anthrax is a deadly disease; it attacks both cattle and men. In cattle it is always promptly fatal and, except where prompt and intelligent medical treatment is available, is equally fatal with man. Fortunately while it is infectious it is not seriously contagious and usually occurs in limited areas and numbers, generally in isolated cases. It could be readily stamped out of the country but for the fact that the germ is exceedingly tenacious of life, existing for years in dirt and dust, ready to assume its deadly occupation when placed under favorable environment. No germicide has yet been discovered that will positively destroy anthrax in hides (except under long continued treatment) that will not damage the hide. The Seymour-Jones method provided for treatment preferably at the point of shipment, involves an expense for plant and operation that makes it impossible of acceptance by any one buyer in competition with one who is not forced to use it. If all the nations who import hides should insist on the Seymour-Jones method of hide disinfection, it would seem as though it might be a practical working arrangement, the product itself bearing the cost. Immersion in a 1 to 5000 mercury solution immediately followed by the liming process is effective and, we believe, does no injury to the hide. Immersion in 1 to 1000 mercury solution without the limnig process seems to be equally effective but is found to damage the grain of the hide to such an extent as to make it impracticable. Therefore, there is at present no practicable method of efficient disinfection adapted to tanning under the sweat process. Inasmuch as a large proportion of the hides subject to disinfection are tanned in sweat tanneries, this leaves a very difficult situation which will, unless modified, force the American tanner out of some of the most important hide markets.

There has appeared recently in print a good deal of information, accurate and inaccurate, regarding anthrax. The subject had has a lot of newspaper space tending to mislead the public as to the serious importance of the disease. During the past twelve months several articles of value have been published in the American Leather Chemists' Association Journal and in the July issue will be found a report on the subject submitted by a committee to the last annual meeting.

A publication entitled "Anthrax as an Occupational Disease"* has just been issued by the United States Department of Labor. This volume, written by Dr. John B. Andrews, covers the subject of anthrax in a most comprehensive manner. It should be in the hands of all who are interested in the problem. A very valuable report on "Disinfection of Tannery Wastes" is in the last number of the American Leather Chemists' Association Journal. I understand this report is to be read to-day by the author at this meeting.

The evidence is conclusive that anthrax has been brought into this country from time to time on hides and skins for many years, probably for many decades; that it has never resulted in serious injury to the cattle industry and that where animals have died the tanner has paid the bill. Under these conditions it seems unjustifiable to enforce restrictions directed against anthrax so severe as, in many cases, to be prohibitive. The anthrax danger is not serious, considered as a subject for national regulation. A large part of this danger is overcome by using a 1

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* A review of this pamphlet will be found elsewhere in this number.

to 5000 mercury solution. This measure of safety should satisfy the Government.

"But what about foot and mouth disease?" the cattle men will ask.—"This trouble is serious, creates tremendous loss and when it appears is nothing short of a public calamity." This is true. Foot and mouth disease, unlike anthrax, is terribly contagious and once given foothold is likely to sweep over a whole district, infecting every animal and causing frightful loss. The Department of Agriculture is justified in taking great care that this infection does not have access to this country. Fortunately the foot and mouth germ is easily killed. It readily succumbs to exposure to air, sunlight, temperature and comparatively weak germicides. Foot and mouth disease is ever present in many countries, including the most of Europe and parts of South America. We have been importing hides from these countries for years and yet have never brought the disease here in a way in which hides "were even remotely incriminated," to quote the language used by the Government in a report on the epidemic of foot and mouth disease of 1914. Now it is fair to conclude that, if during the past hundred years the tanners have not imported the disease and during this time have continuously imported millions of hides, the methods of curing the hides—exposure to light and air in the case of dry hides, to salt or brine in the case of green or dry salt hides—must destroy the infection.

This is a matter of easy determination by bacteriological study; but impossible in this country for there is not one individual foot and mouth germ known to inhabit this broad land and the Government does not propose to admit one. It would be much easier in this time of war to pass into the port of New York a six foot German than a microscopic germ. The work must be done abroad. There are splendid facilities for the investigation at Buenos Aires where foot and mouth disease germs are available and where well equipped laboratories and trained scientists are competent to undertake the work. This is a matter of great importance and, it seems to me, would justify the active co-operation of the American Leather Chemists' Association.

Rinderpest we know little about. It has never visited this country. It is, in fact, such a rare disease that it seems hardly worth consideration and certainly does not warrant the formation of a special set of rules for its control. In our history of over 200 years we have been free from rinderpest. It is safe to say, therefore, that the mere commercial treatment of hides and skins for their safe preservation is precaution enough for this disease.

Since writing the above, the Department of Agriculture through the Bureau of Animal Industry has issued another circular stating that the rules governing the importation of hides into this country are to be again re-written. It is the earnest hope of the leather men that before another change is made, a full conference on the subject will be accorded to the National Association of Tanners and that these changes will not involve unnecessary and prohibitive expense. At the present writing, however, we are much in the situation of the hopeless optimist who says "Cheer up! the worst is yet to come."

THE FUTURE OF HIDE SUPPLY.*

By Alfred Seymour-Jones.

MR. PRESIDENT AND COLLEAGUES: The great war is the one predominating and all-absorbing topic of conversation, theme of thought, and cause of anxiety throughout the entire world. Its effects have been felt in every corner of the globe. Twenty-seven out of twenty-eight human beings are directly concerned as belligerents, representing seven out of every eight acres of the land surface of the world. With a battle front of over 2,000 miles in length; with millions of acres of the fairest lands out of cultivation; with millions of cattle slaughtered and whole areas decimated of animal life; with approximately 300,000,000 of men, women and boys withdrawn from avocations of peace and today engaged in producing munitions of destruction; with millions of men and women in the Allied Armies clothed, shod and fed as has never been so handsomely and generously performed before; with the arts and crafts products of peace times lying dormant; with millions of men, from the battle zones, broken and mutilated for life; and the millions of brave friends and foes,

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* Read at the Atlantic City Meeting A. L. C. A., June 8, 1917.

whose only war decoration is the little wood cross which marks their last home, many of them our colleagues, the situation, present and future, embraces problems sufficient to stagger humanity.

What the future may have in her "cold store" for us must be left in the lap of the gods. Sufficient unto the day is the evil thereof. If we are wise men, we will amidst this world cataclysm endeavor to take a calm survey of the probable aftermath of the war, so far as we can judge of it. In my opinion we scientists should endeavor to keep a level head, taking time by the forelock, seeing where we can be of service to-day and preparing to attack the problems which will arise when the war is over, which will require the best that we can do to elucidate. Not the least among these will be "the future of hide supply." It is my earnest desire that the leather trades scientists shall play their part to the best of their ability in the commercial regeneration of our industry. Just where, when, what and how, it is my present hope to show.

The great war has created and will yet create a very serious shortage of hides, over and beyond that to which I shall refer later. This shortage is due to several causes, most of which common sense gauges from what I have already stated. The equipment of the armies with leather accoutrements, boots, etc., has been liberally and, generally speaking, well done, nevertheless, the destruction is prodigious, and the wastage has to be kept replaced from day to day. Add to this the heavy reduction in numbers of cattle due to the war in various parts of the war zones (the Central Powers are said to have lost 60 per cent. of their cattle), we have to face, in Europe (and Europe's difficulty is the world's own), a most grave situation, while the after-war demands for hides alone will provoke an unprecedented rise in hide values.

Further, China, India and Japan, formerly large exporters of hides and scorners of leather foot wear, have erected large tanneries, boot factories, etc., and are beginning to appreciate the occidental luxuries. What the future will bring forth in those countries must for some time remain a mystery, but as those three lands represent more than half the population of the world, they and their wants must ever be present in our calculations and forecasts of the future.

It is not without interest to-day to recall some of my earlier articles on the hide situation, especially in regard to the ever changing ratio between cattle and population. In 1910 I wrote: "There seems every probability that the population of the world will increase faster than the live stock, and the next generation will have to pay dear for its meat and hides unless some radical change is made either in the method of producing meat or in the diet of the white races." That judgment was based on the following evidence: Taking the total cattle in the lands occupied by the white race, excluding China, Japan, India, and the like, the returns showed that betwen the years 1880 and 1908 cattle increased 77,000,000 as against an increase in population of 162,000,000. That statement has been altered during the war because the loss in cattle during the Great War is far larger than the loss of population.

Up to 1894 hide values showed little or no marked tendency to advance, due to economic forces then operative, but from 1894 the advance has been steady annually until prior to the outbreak of hostilities, when hide values reached unprecedented heights. But even these high figures were soon passed after the outbreak of war until it became imperative that prices should be fixed by the Allied Governments for the duration of war. To-day's war condition prices for raw hides are in no sense the economic value such as would be presented in "open market." When the war ends and the embargo as to prices of hides is removed, the present figures will soar to heights never dreamed of, and it will be very many years (probably most of us will not live to see it) before the world will or can recuperate, economically, from the exhausttion which must be the final outcome of this great world war.

Having stated as briefly, and within the limits, as I am able the present situation and outlined the future prospects, let us inquire in what manner we, as scientists, can assist in making the after war conditions meet the then prevailing circumstances.

It is perfectly true the great economic law of supply and demand will continue to operate, so that the highest bidder will get the goods, and that buyer will be he who realized the power of the scientist to aid him in making not only superior leather but by cheaper means. But what of the hide supply? Will they be all that human brains can make them? Will their cure be so perfect that not a gram of the precious hide substance will be wasted? Will the large supplies of dry hides be free from sun blisters, or the flesh cleaned of excessive flesh, or free from the results of the crafty native's ingenuity in stealing his neighbor's real estate and passing it off as sound hide substance at almost the price of gold?

It seems to me we can devote some of our thoughts and actions to planning an educational crusade in regard to the correct methods of hide cure suitable to the local conditions. These methods are well known and practised in large abbatoirs, but good as they may be there is still too large a loss in valuable hide substance in the best of the cures. Then in regard to dry hides, much ignorance and carelessness is displayed.

It would be folly to combat the system of drying hides, but much good may be accomplished by a sound educational propaganda. Against the principle of drying hides when it is correctly performed, there can be no reasonable opinion or objection. The principle of drying is not an ideal one from the leather making standpoint, yet it is the only method which is readily available or practicable to-day in many lands, meeting the difficulties of cure and transport. In the realms of the dry hide much useful work can be carried through, provided the governments, the tanners' federations, and hide merchants will provide the requisite funds, while the scientists provide the brains. The A. L. C. A. is the proper body to lay down the correct regulations for cure or drying which may be applicable to the various local conditions, and so stated that they may be comprehended by the average native. Such a crusade is not one which will show immediate returns, and if it is to be successful the old adage must be strictly followed: "It's dogged as does it." If such a plan is fairly launched and the native also receives his share of the increased value, the final result will in a large measure assist in meeting the after-war hide famine. The scheme will fail unless strong measures are taken to secure the interest of the hide dryer himself, and this may be done by increased pay. It may be as well to quote Adam Smith's "Wealth of Nations": "A nation that would enrich itself by trade is certainly most likely to do so when its neighbors are rich, industrious and commercial nations."

There is another and ever present problem which confronts all civilized nations, and there are people, careless in their talking and thinking, who persistently reiterate the statement that hides are a cause of certain diseases being imported into our midst. It is the old story: Give a dog a bad name, etc. To this question I have given years of thought, attention and research, and so far as my investigations have led me, the only disease that can be truly traced to hides is anthrax, and then only to certain dry hides from given ports. Diseases like symptomatic anthrax, though infectious among animals and usually fatal to them, are due to organisms distinct from *B. anthracis.* Among the diseases so classified are grouped quarter evil, quarter ill, black leg, black quarter, black spaul, bloody murrain and bauschbrand. Their micro-organisms are so delicate as to be destroyed by all systems of hide cure. This remark applies to foot-and-mouth disease. Nevertheless, the authorities often become, in my judgment, unnecessarily alarmed when a specific disease breaks out among cattle, and again in my opinion, they act hastily, unwisely and injudiciously, by placing regulations on hides. It is surely the time-honored basis of all laws, that a defendant is considered innocent until he has been convicted by a jury of twelve of his fellow men. Why in the name of honesty and common sense should the law be violated even by authorities? I have always deplored and viewed with alarm and surprise the action of the U. S. A. authorities in regard to hide sterilization regulations. To those who have given the best years of our lives to the study of industrial sterilization of goods which may act as carriers of diseases, the order appeared as panic regulations, resulting in inefficient sterilization and irreparable damage to an increasingly valuable commodity and grave irritation to the members of the sixth greatest industry in the world.

Common sense dictates the course which could be pursued with all-round advantage. To-day the scientists of the leather industry are well organized throughout the world, and they have within their bodies men who at least understand the situation and its possibilities better than the authorities; therefore, the authorities of all countries should at once acknowledge our associations and not ignore us.

Anthrax is imported by certain dry hides only! Some years ago I pointed out that provided no sporulation took place in an anthraxed hide, and it was dried in the tropical manner, all the bacilli, on drying, would be killed. That statement has been confirmed in many quarters. Dr. Georges Abt, Pasteur Institute, Paris, a scientist thoroughly trained in the arts of leather production, was employed by the French Syndicate of Tanners to investigate the question of "The sterilization of anthrax infected hides and skins" in 1913. Abt's work carried our knowledge a stage further. He confirms von Esmarch's observation that *anthrax spores form only in the dark and at temperatures not exceeding blood heat.* Abt succeeded in obtaining spores in all cases in the dark but when he exposed the bacilli to sunlight but shaded under a wire gauze he failed in all cases to obtain spores. His conclusions are important: "If the skins could have been sun dried immediately after flaying, it seems they would not contain any spores." Abt's work confirmed some old notes of mine that throughout I had observed that sun- or flint-dried hides were free from anthrax contagion.

The experiment of Sevcik, wherein he claims to have produced anthrax growth from the center layer of a hide reputed to have been flayed off a beast dead of anthrax, and which he dried, has been frequently cited, and would appear to conflict with the foregoing statements. When Prof. Schnuerrer wrote me in regard to Sevcik's alleged discovery, I asked for complete details of Sevcik's methods, especially in regard to drying. Schnuerrer reported and Sevcik confirmed that the piece was dried in an oven, and was *in Sevcik's opinion* comparable with hide dried by the tropical methods. While the letters were in transit Sevcik transmitted his findings to his University Journal. I at once tried to repeat Sevcik's method of drying and in every case failed to dry equal to tropical conditions, the center layer always remained slightly moist as the temperatures employed did not admit of hasty drying, otherwise if higher temperatures had been employed dissolution would ensue. Again drying in an oven implies drying in the dark but sporulation would only occur on the surface, and as Sevcik cut the surface layers away, using only the inner, it is perfectly evident that although he endeavored to sterilize the whole hide substance, the growth ensued from bacilli, and was due to imperfect sterilization and reduction of time allowance. Had the hide been dried in the sun as it occurs in Africa, it is obvious no sporulation would have ensued. I laid the question before Prof. Eitner and he agreed with my conclusions. Dr. Eurich, Bradford, England, has for many years devoted himself to the study of woolsorters' disease (pulmonary anthrax), and he holds a definite opinion that provided the "bloody fleeces" are eliminated from the bulks at the base, and incidence of woolsorters' disease would become a minus quantity. Eurich's discovery bears upon the blood clots which may be found adhering to certain dry hides, especially on the hair side. It has been found that sporulation can only ensue under suitable conditions in blood clots. These blood clots are removed by the formic-mercury process of soaking the hide back. This being the case, it is not without importance to the solution of the anthrax infected hide problem that all such adhering filth should be left in the country of origin, and the adoption of the formic-mercury process would accomplish this.

It would therefore appear that provided hides are well opened out on poles, or pegged out, and with sufficient air and light striking on to the hide surface, until flint dry, no sporulation does take place, but when the drying is performed in darkened chambers or the hide is carelessly opened then sporulation may follow.

In the formic-mercury process the proportion of acid and bichloride of mercury is very low. This has been adopted advisedly. Disinfectants as a rule do not depend on their volume for effectiveness; in most cases the weaker the disinfectant the more potent; but they do depend on the time factor. The formic-mercury process does two things which are important in the case of dry hides, the special case for which the process was devised: first, to soften the hide back to the wet condition without any loss of hide substance, and secondly, to hold up the proteids, thus preventing the immediate precipitation of the mercury salts. The addition of the salt bath is for the purpose of cure only.

It is the common practice to employ sodium sulphide as a test of efficiency as to sterilization. As a test of any process being efficient from the leather trade standpoint it is negative. Sodium sulphide is a perfect sterilizer of anthrax spore under conditions prevailing in the tannery lime yard employing sulphide limes. If anthrax spores are immersed in a solution of sodium sulphide of tannery strength and for the same period, they will dissolve, probably due to the supposed character of the cell wall being keratinous. This fact appears to have escaped the attention it deserves.

In conclusion, the verdict is that certain dry hides imported from given ports are carriers of anthrax, and that the dust therefrom is liable to infect foodstuffs and the like during transit if these are carried aboard the same ship or landed at the same dock or in the same warehouse. During this process men may fall victims to the disease. What then is a possible and probable remedy?

It has long appeared to me that provided a simple method could be devised for restoring dry hides to the wet salted condition at the port of export, which would be acceptable to the leather industry, then that act alone would cause the incidence of anthrax to gradually diminish. In pursuit of this idea throughout many years I travelled the countries from which such hides come, studied both them and the men who would probably be called upon to administer any method which could or would be devised. The formic-mercury process was the final result. With the knowledge of a lifetime behind me, with years of work devoted to the solution, without hope, expectation or desire of reward, except to save life, and the kind memory of a host of friends; with a lifetime devoted to the production of leather in many lands, and the knowledge of my limitations, it would be folly for me to say that the formic-mercury process is the final word, yet it is in my mature judgment the only scheme to-day which offers an acceptable chance of succeeding. In future years when our knowledge of sterilization has increased beyond that permitted to us to-day, a new process may arise which will mark a new advance in our science of industrial sterilization, but until then it is the bounden duty of civilized nations to adopt that process which offers the best solution and one that is acceptable to the industry concerned.

Any such action should be prompted by the industry concerned and not introduced by the authority under whose control it may happen to come. It is our duty to lead as traders and not wait until compulsion is forced upon us. In this movement the leather industries' scientists should take a leading part. It is for them to approve of the scheme in the first instance and having approved to approach the tanners' federations to adopt their scheme or schemes for the betterment of hide conditions and especially the hygienic conditions attendant thereon. I appeal in the strongest words at my command for all leather trades' scientists to start this great work, to lay low the scourge within our midst.

That this is possible at the present time is due to the great war which has produced a revolution in the thoughts and ideals of all right thinking men and women. Schemes of social improvement which would in the past have taken years of bitter political struggle to carry into effect have been carried out. The outlook on life and affairs has undergone a wonderful change. All political rancour has been promptly buried. The deaths of our gallant sons has awakened within us a nobler and higher ideal. Death has been ever present in our midst. The old order changeth. Twenty years ago the first assembly of leather trades' scientists met in London and founded the International Association of Leather Trades' Chemists, of which I had the honor of being the first president. That body has to-day ceased to exist, to the sorrow of most of us. Nevertheless, from its ruins will arise an "Alliance" of leather trades' chemists which will have a broader view of life and its affairs. I ask my colleagues of the A. L. C. A. to rise and silently salute the memory of our fallen hero comrades of the I. A. L. T. C., both friend and foe.

DISCUSSION ON ANTHRAX.*

By Dr. R. W. Hickman, and others.

Mr. President and Gentlemen: My name is on the program, as you will notice, under "Discussion." I don't know why it was put there except as a compliment to me as the senior representative of the Bureau of Animal Industry from Washington. The addresses of the morning as applying to anthrax and disinfection were so ably presented and have so fully covered those subjects, as related to one another, that further discussion would seem most naturally and appropriately to lead to the consideration of ways and means, measures, and methods for the practical and satisfactory sterilization of the anthrax spore as present in hides and skins.

* Atlantic City Meeting A. L. C. A., June 8, 1917.

Anthrax disinfection, as it concerns the great tanning industry and the importance of efficient disinfection as related to imported hides and skins, seems to have been emphasized by the number of cases of anthrax infection which have come to our attention within recent months, principally through newspaper articles, the authenticity of many of which reports have been the subject of investigation by the Bureau of Animal Industry.

Then, also, in connection with the efficiency of the method, we must give equal consideration to practicability or the use of methods of disinfection that are dependable in accomplishing their purpose and that will not burden the industry with unnecessary expense, either in the process of their application or by loss through injury to the product.

Hides may be subjected to methods of disinfection not applicable in the case of skins. It therefore seems desirable and necessary that regulations shall be formulated as to permit of a choice of methods until, if possible, a single method is evolved that has proved to be efficient, practicable, and inexpensive; and it is just such meetings and discussions as this that will eventually, we hope, bring to our aid just such an agent.

Suggestions as to several methods were submitted recently by the Bureau of Animal Industry to the National Association of Tanners and the Morocco Manufacturers' National Association. A number of the members of these associations are present.

Now, with regard to anthrax in hides. We won't go back into the past at all, but we will endeavor to deal with the present and show what the conditions actually are as they have been coming to our attention recently. While we only have to do with the animal phase of the subject, the regulations, as you are aware, are joint regulations. They are issued jointly by the Department of Agriculture and the Treasury Department. The Public Health Service is under the Treasury Department, and the Public Health Service has been active in the matter of looking up anthrax infections among human beings.

Eleven cases of human anthrax in Massachusetts were reported between April 15 and May 24 of the present year, nine of which occurred at the Woburn Tanneries, one at the Armstrong Leather Co., Peabody, Massachusetts, and one at Chelsea, Massachusetts, docks. The Chelsea subject died. He became infected in unloading hides at the Chelsea docks at Boston and the case was reported by Dr. Kelly, Director of the Division of Communicable Disease of the State of Massachusetts to the United States Surgeon-General, and was forwarded with a letter of transmittal to our Bureau from the Surgeon-General's office. Of the ten other cases, seven have recovered and three are still under treatment with considerable hope of recovery.

An employee in the Strauss Tannery, Newark, New Jersey, was taken ill on February 2 and died on February 25. He was taken to the Beth Israel Hospital, Newark, New Jersey. The diagnosis of anthrax was confirmed by microscopic examination, and the poor fellow was taken to the hospital probably too late to save his life.

A workman handling wet salted hides at Pier 18, Brooklyn, about February 11, was infected in the neck. He was taken to the Melba Sanitarium, Brooklyn, on February 20. The diagnosis was confirmed by a microscopic examination. He was discharged on March 13.

A man engaged in handling hides at the pier at the foot of 33rd Street, Brooklyn, was admitted to the Harlem Hospital on January 17 with the infection in the right side of the neck. An operation was included in the treatment and he was discharged on January 30.

An employee of the Elk Tanning Co. at Port Alleghany, Pennsylvania, was infected in the chin and neck while handling Calcutta buffalo hides. These are dry hides. The date of infection was March 14. He died on March 17. This case came to our attention through one of our employees (W. Collins) who supervises the disinfection of hides at tanneries in the State of New York. The surgeon who reported this case operated on Collins for appendicitis some time ago, and on that occasion told him of the case.

The New York *Evening Telegram* of May 30 reports two cases of anthrax infection. One died at Bellevue Hospital, and the other was reported as recovering by Dr. Schwartz. Dr. Schwartz also reported that Dr. Dudley, medical director of the Endicott-Johnson Company, had successfully treated ten cases of anthrax infection in human beings during the past ten months.

Anthrax has been exceedingly prevalent during the past year in Argentina. The fact that we have not had more cases of the disease, I think, is not because anthrax hides have not been shipped to this country, but rather to the absence of skin abrasions in the handlers. An article in the Buenos Aires *Herald* of January 21, 1917, dated at Rio Cuarto, Cordova, states that the spread of carbuncle among cattle was becoming alarming, and that during one month 30 persons contracted the disease, of whom several died. *La Prensa,* the leading daily paper published at Buenos Aires, on March 29 and 30 reported that 15 deaths from anthrax had occurred among hide workers at two frigorificos just across the river from Buenos Aires at Avellaneda—just the same as Camden is across the river from Philadelphia. There were 15 deaths at that town. The Buenor Aires *Herald* of March 25 says that employees are threatened with discharge if they reveal the facts with regard to the conditions as applying to anthrax infection among cattle at that place.

We received a report on June 2 regarding the beam-house foreman of the Ohio Leather Co. at Girard, Ohio. He was infected in the face. The diagnosis was made by a Dr. Smith, who operated on April 16. He was improving but was still unable to work. At the time of infection he was working on uncertified buffalo hides from India and also on certified hides from China.

Under date of June 4, 1917, we received a report from Dr. A. E. Rishel, Bureau Inspector in charge of the importation of hides at New York City, to the effect that Dr. H. J. Blumensohn, of the United States Public Health Service, on behalf of the New York Health Department, had for several months been engaged in an investigation of the handling of import animal products and their relation to certain occupational diseases. Dr. Rishel states that so far as the handling of hides and other products on the importing vessels are concerned, the general practice is to keep them segregated from food products by stowing them in separate holds. On the landing piers, however, hides, wool, hair, glue stock, etc., are of necessity, on account of the congested condition of the piers, placed in close proximity to edible and other merchandise.

It has been the practice of several large importers to break the bales, examine, and rebale approximately 20 per cent. of the hides in shipments. There should be some way, it appears to me, to avoid that. All hides, wool, hair, and so on are weighed on the piers, the result of which in the case of dry hides, whether certified or not, is the spreading of dust from such hides. This appears to have received considerable attention from Dr. Blumensohn. The dust from these hides causes a catarrhal affection and considerable irritation of the respiratory tract, and he has given considerable thought to a means for its control or suppression. Dr. Blumensohn has also given some thought to the feasibility of using some form of respirator as a means of protecting those engaged in handling dry hides. He also expresses the opinion that whitewashing affords no protection whatever.

Dr. Rishel states that the various cases of anthrax reported in New York during the past few months have apparently been transmitted from certified South American hides, and he thinks it a noteworthy fact that not a shipment of South American hides has been received at that port without certification. He mentions the fact also that the prevalence of anthrax among men engaged in the handling of import hides appears to be attracting the attention of both the state and local health authorities.

It would seem to be unwise to underestimate the danger of anthrax infection from hides and skins. We face an actual condition, and it appears to me that what we want to do is to find some means for effectually preventing the introduction of anthrax to our live stock in this country through imported hides and allied products, and at the same time to prevent human infection.

While the Public Health Service is particularly interested in the human side of the subject, the Bureau of Animal Industry administers the regulations, and they hold us responsible. I hope the time will soon come when we can handle the matter satisfactorily. I thank you.

DR. M. DORSET, Bureau of Animal Industry: I am rather at a loss to know whether there is anything I can add to the discussion that you have already heard. It has seemed to me that the problem of the control of anthrax, particularly with relation to the spread of the disease through tanneries and tannery products, can perhaps be best understood by considering the infection of men, on the one hand and of animals on the other.

There really are two phases. I think it is generally admitted that most cases of human anthrax arise through the handling of skins and hair among workers about tanneries, whereas animals are seldom infected through such a source. The animal, as a rule, contracts anthrax from an infected field, and is not infected, directly at least, from the tannery products.

With regard to human anthrax and the relation of tanneries to the spread of human anthrax, it seems to me that just so long as the skins and hides from animals that have been infected with anthrax can enter the channels of commerce, we must have cases of human anthrax, and that the chain of cases will follow right through all the handlers of those products until they finally reach the tannery.

Whatever steps the tanner may take will not, of course, protect the longshoreman who has helped to unload the boat before the hides get to the tannery, so that whatever the tanner does, he can only protect his own particular force and the people who may thereafter come in contact with the products.

I shall not attempt to discuss the various ways of preventing human anthrax. It is perfectly clear that in the tannery the workman who handles the hides before they are subjected to tanning is exposed, the degree of exposure depending perhaps upon the susceptibility of the individual and the degree of infection on the hides. It would seem to me, in the few tanneries I have had the privilege of going through, that the warehouse and the warehouse dust, particularly places where hides are cut or trimmed when they are dry, are sources of danger that could easily be reduced by the use of a suitable exhaust to prevent the flying of dust about everywhere as the hides are sorted, thus drawing that dust down to some suitable place where it could be collected and later incinerated. I think it is only by such general sanitary measures that you can protect your workmen up to the time that the hide gets ready for the soaking bath or is ready to be placed in soak. Of course, the use of anthrax serum and the medical supervision of employees will be indispensable.

But with regard to the treatment of the hide; nothing, practically, can be done to treat the hide to render that safe until you get to the soaking bath. The question arises at once, can the hide, while it is in soak, be disinfected, so as to make it safe in so far as food-and-mouth disease and anthrax are concerned? Personally, I believe that we know only two methods by which such a disinfection can be done, that is, a disinfection that will render the hide and the hair as well as the effluent from the plant, safe. Those two methods are what are known as the Seymour-Jones method and the Schattenfroh method.

The Seymour-Jones method, in the work of Dr. Tilley of our laboratories, we have found satisfactory, but we had to change the proportions of the mercury. We didn't think Seymour-Jones used enough mercury. We had to have more—1 to 2,500 instead of 1 to 5,000. Then it required, according to Dr. Tilley's experiments, that the hides be held for about two weeks after disinfection before they could be safely neutralized in sulphides or otherwise. This makes the process seem too complicated. Those of you here will know better whether that is so or not. It has also been reported to us in one experimental case that the hides were stained somewhat by the use of the mercury in this process.

With regard to the Schattenfroh method, that requires 48 hours' soaking in 2 per cent. hydrochloric acid and 10 per cent. salt. It is effective as far as anthrax is concerned. We have had little experience with it in practice. It was tried once at two tanneries, at Coudersport and Ralston, Pennsylvania. I think perhaps Dr. Balderston, who is a member of this Association and who may be here, may know something of that. The hides, at any rate, when they went through the disinfectant were reported as being injured, due to excessive plumping caused by the acid treatment.

We have been doing experimental work with this Schattenfroh method. We have nothing very definite to announce, but Mr. Chapin, who is working particularly on the chemical side of the disinfecting problems, tells me that the swelling of the hide, as you may know—those of you who have tried it—does not take place in the acid bath. It takes place when the hide is washed, placed in water after being subjected to the acid. He says that this swelling does not take place if instead of water, a salt solution is substituted. Three per cent. solution of sodium chloride will prevent the plumping and the swelling of hides treated by the Schattenfroh method. He furthermore thinks that perhaps a satisfactory method of neutralization of the acid that is used could be worked out by adding calcium acetate with the sodium chloride and thus displace the hydrochloric acid and substitute acetic acid and follow that by washing and neutralization, there being less swelling.

There are a great many problems along this line that we are very much interested in and that we cannot solve ourselves, but we would like very much to have the assistance and co-operation of any tanners who are interested in this particular subject. So far as we know, these two processes, the Seymour-Jones and the Schattenfroh methods, are the only processes that will disinfect hide, hair and effluent if properly applied. If neither of those methods is acceptable, if you cannot apply a disinfectant, which will be effective, to the hide or the skin itself, then you are forced to try to prevent the spread of anthrax infection through the effluent of the plant, through the hair or any other by-product.

Mr. Buswell has already discussed the use of chlorine on the effluent from tanneries. We have done some work ourselves with chlorine and with other methods. In our work, which has been limited and not anything like as extensive as Mr. Buswell's, we were not able to find that 50 parts of chlorine per 1,000,000 was sufficient to secure disinfection against anthrax and we do not feel sure as to that. We do believe, however, that the disinfection might be accomplished. We believe that enough chlorine might be added to the effluent to secure satisfactory disinfection and perhaps the amount required would not be beyond the price that the tanner could afford to pay, particularly if this chlorine was added only to the soak waters and the milldrum washings, which we would regard as the most dangerous part of the effluent, and perhaps also to the washings from the hair.

We have done some recent work with respect to the effect of heat on the anthrax spore. I shall not announce a definite conclusion. I don't feel that we have reached that at all, but I think you should know what we have done thus far. We have found that anthrax spores from 13 different strains of the organism, quite active and virulent spores, when subjected to heating and brought up to 100° C., were killed, that practically a momentary heating at 100° C. sufficed.

Now, a statement of that sort is entirely contrary to most of those found in the literature. We know that perfectly well. We constantly find statements that two hours' or three hours' boiling is necessary, and I have no doubt that in the other experimental work that has been done they did not get live anthrax spores from certain material or from certain experiments after heating two or three hours. It may be that we have gotten 13 especially weak anthrax organisms. I hardly believe that that is true. I believe that the organisms we have experimented with have been killed and that they are fully virulent and fully resistant.

I think perhaps the explanation may lie in the fact that in our heating tests we have used comparatively small numbers of anthrax spores. This work that I am speaking of has been actually done by Dr. Tilley, who could not be here to-day. We have added anthrax spores in the proportion say, of 500 to 1,000 per cc. That is very small so far as a culture of anthrax is concerned. Cultures, of course, will perhaps contains millions per cc., and yet I think it is pretty high if it is intended to show the condition that would exist in a tannery effluent. It is very rarely, if ever, I suspect, that a tannery effluent contains 500 or 1,000 spores per cc.; therefore, we thought we were safe in that respect.

Perhaps it was because we used small numbers of spores that we had such success in heating. Perhaps, also, it was the particular technique that was used. I don't know how that is. At any rate, the anthrax spores were all killed, and we have repeated it over and over again and we get the same results over and over again.

I believe that the length of heating required will depend somewhat on the condition of the effluent. If there are very large particles of material in it, some of the anthrax spores imbedded in the center of the large particles will probably escape, and the larger particles, the greater the likelihood that the spores will escape, given a fixed time and heat.

Mr. President, it has been a very great pleasure to me to come and take part in this discussion, and I thank you very much.

DR. KLABER asked whether it had been definitely established that the anthrax spore exists only on the surface of the hide, as stated by Mr. Seymour-Jones. Mr. Oberfell replied that investigators state that the spores only occur on the surface, especially in blood-clots, and not in the interior. Dr. Dorset said that the work in the Bureau of Animal Industry had not touched on this point.

Mr. Buswell described an experiment by Sobernheim in which a drop of blood was placed on a hanging drop slide and sealed in, and placed in an incubator. Spores developed only on the surface of the drop.

S. S. **Sadtler**, Philadelphia: Mr. President, I am glad you said I could give you some data, because I have made no special preparation for you, but I should be glad to look over some results of analytical work and make comments merely designed to touch upon points that I think may be of interest or may not have been brought up already. I do not expect therefore to go into any discussion of the general subject or to say why I have confined these results to a certain attack on the subject.

These analytical results here were mainly designed to compare two methods of disinfection of the waste effluents. I might say that they are made upon mixed soak and milldrum effluents taken in establishments making glazed kid. These tests are made upon the effluents of eleven or twelve different plants belonging to the association.

We took waste soaks, in the proportion of one-fourth of the total effluent, and milldrum effluent to the extent of three-quarters, because that seemed to be a reasonable proportion of the waste liquids. I might say, however, that in some establishments there is a very much smaller proportion of the milldrum effluent, and there is no great uniformity. It looks, however, as if it would make comparatively little difference, as where a great amount of waste is used, there would be no corresponding increase in chlorine. It would, however, entail more expense of boiling waste water.

I do not want to make any general statement about the prevalence of anthrax, but in all these cases we found it in the raw effluent. Our tests were presumptive tests for anthrax and might be attacked by a bacteriologist as not conclusive. We were under a great strain to carry out a series of tests in the shortest time possible, as when we were first retained in the matter we were told it was only about two weeks before the regulations would go into effect, and we then undertook no laboratory work. Later on, we did go into a series of analytical tests.

The sheets that I have here represents tests with chlorine, both in the neutral or alkaline condition as received, and after acidification to render the effluents neutral. The chlorine consumption was checked up by what we might call total chlorine figures. We added 1,000 parts per 1,000,000 of chlorine to some of the effluent and noted the amount of chlorine that remained after an hour's standing in the dark. These figures varied quite considerably. The lowest we got was 151 parts per 1,000,000 and the highest was nearly a thousand, 984. I might say right here, however, that it didn't take noticeably more chlorine for disinfection where a great deal was absorbed as compared to where only a small amount was. There were some differences and we hope later on to prepare curves or in some way codify these results.

We made some chlorine tests on the liquids as received and after neutralization with acid. The differences do not seem to be very great in most cases. We have a list of figures of the total solids, and in many cases the organic solids. They varied quite considerably. The highest we obtained was four parts in 100, or 4 per cent. The lowest was about two-tenths of 1 per cent. The amount of organic solids generally ran around half of the total solids, although in this very high case the organic solids were only $^7/_{10}$ of 1 per cent., or even less than that, so there was a great deal of mineral matter in that one case.

We thought it well to determine the ether-soluble in these liquids to see what influence grease might have on absorption of chlorine. The amount of ether-soluble varied from sixteen thousandths of 1 per cent. to twenty-four hundredths, with no very corresponding difference in the amount of chlorine absorbed or necessary for disinfection.

We made records of the temperatures of the soaking and have not yet found that any great influence comes from that factor, as in most cases the temperatures are controlled by heating in winter, so as not to vary so greatly.

With regard to the chlorine tests, we separated the soaks and the milldrum effluents, having no limes or sodium sulphides or anything of that kind to contend with. However, there was generally a considerable amount of alkalinity, and we therefore made the chlorine tests both with and without neutralization. The alkalinity varied quite considerably. The greatest amount required was one and six-tenths grams per 1,000 cc. The smallest amount of acid required to neutralize was nine-hundredths of a gram per 1,000 cc. In many cases the liquids were practically neutral.

We found in all cases that 50 parts per 1,000,000 of chlorine was ineffective. The series that we started out with was 50, 125 and 250 parts per 1,000,000, both in the condition as received and after neutralization. In about two cases out of eleven, we found positive results with 250 parts per 1,000,000, but in both of these cases when neutralization was effected, there were negative plates for anthrax. That is to be expected, as the alkalinity would tend to absorb chlorine. The alkalinity is probably due to ammonia and it would react with chlorine.

I approach the matter of the boiling test just referred to by Dr. Dorset with a great deal of reserve, because it is so particularly a bacteriological matter, but I would say that in two very recent tests, we found what seemed to be negative presumptive tests for anthrax after momentary boiling. We took our plates to the Bureau of Animal Industry and asked them to check up in one case. I have not had time to get any other corroborative opinion. The tests were carried out very carefully to avoid any splattering on tubes so as to prevent insufficient heat, but I think the most important point that I could call attention to in the heating tests was what seemed to be the fact that we had very dilute solutions with regard to anthrax, and that was one reason why I wanted to carry out these tests on actual effluents, because in the laboratory, thousands or even millions of spores are made use of in a test, and here we took just what we found in the effluent.

From the plate cultures there seem to be only a very few to a cubic centimeter, maybe 10 or 20, and so it might be that in 1,000 or 1,000,000 some would survive. We do not believe it is going to be possible to remove all danger from anthrax, and anything approaching the limit should be reasonably satisfactory. In several instances where we did not keep the sides of the tube free of solution, even four minutes at 99° C. did not give plates free from anthrax colonies. In one case the effluent (No. 11) frothed so much that we could not get a satisfactory test.

Another point of possible interest is that we have mixed waste chrome liquors with this mixed effluent and obtained a disinfection according to these presumptive tests, with 25 per cent. of waste chrome liquors and enough sulphuric acid to change all the bichromate to chromic acid. That required a very small

TABLE I.

Sample	Character	Alkaline or as received Parts per mil.			Neutralized Parts per mil.			Raw	Chlorine absorbed		Solids		Ether soluble Grams per 100 cc.	Sulphuric acid required to neutralize 1,000 cc. Mixed soak Grms.	Temperature	
		50	125	250	50	125	250		Alkaline Parts per mil.	Neutral	Organic Grms. per 100 cc.	Total			Mill water	Soak
1	Very muddy	Pos.	Doubt	Neg.	—	—	—	Pos.	755.1	—	—	2.356	—	—	60	—
2	Cloudy	Pos.	Neg.	Neg.	—	—	—	Pos.	151.5	—	—	0.304	—	—	54	—
3	Alkaline Very cloudy	Pos.	Neg.	Neg.	Doubt	Neg.	Neg.	Pos.	879	—	—	0.214	0.03	0.426	70-75	—
4	Alkaline Very muddy	Pos.	Pos.	Pos.	Pos.	Pos.	Neg.	Pos.	713.7	--	—	1.463	0.0695	0.419	64	70
5	Neutral Very cloudy	Pos.	Neg.	Neg.	-	—	—	Pos.	646.0	—	—	0.262	—	—	85	—
Proportions of chlorine in samples 6 to 3B increased.																
		100	200	300	100	200	300									
6	Alkaline Very cloudy	Over-grown	Over-grown	Neg.	Over-grown	Over-grown	Neg.	Pos.	812.5	810.5	—	2.516	0.0166	0.092	—	—
7	Alkaline Muddy	Pos.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	737.3	585.8	—	1.290	0.021	0.833	65.5	67
8	Cloudy Neutral	Pos.	Neg.	Neg.	—	—	—	Pos.	406.9	—	0.135	0.212	—	—	63	—
9	Alkaline Cloudy	Pos.	Doubt	Neg.	Pos.	Pos.	Neg.	Pos.	641	640.1	0.144	0.303	0.0024	1.659	70	—
10	Alkaline Muddy	Pos.	Pos.	Neg.	Pos.	Pos.	Neg.	Pos.	755.5	731.5	0.556	1.042	0.246	0.229	—	—
11	Alkaline Muddy	—	—	—	—	—	—	Pos.	983.6	966.1	0.672	4.016	—	—	—	—
3B	Alkaline Muddy	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	863.6	860.0	0.242	0.368	—	0.217	75-78	75-78

amount of sulphuric acid, although it is, of course, a matter of importance when it comes to disinfecting 100,000 gallons, or anything like the effluent of a works.

(Mr. Sadtler submitted Table I for publication in connection with his remarks.)

The following tabulation shows a boiling test made following instructions from Dr. Dorset, and a test with a chrome effluent from works No. 11 upon their mixed soak and milldrum effluent:

TABLE II.

Raw........................	Positive	1% Chromic acid	Positive
Heated to 100° C. momentarily	Negative	5% Chromic acid	Positive
Heated to 100° C. 1 minute	Negative	10% Chromic acid	Positive
Heated to 100° C. 2 minutes	Negative	15% Chromic acid	Positive
Heated to 100° C. 3 minutes	Negative	18–20% Chromic acid	Positive
Heated to 100° C. 4 minutes	Negative	19–25% Chromic acid	Negative
Heated to 100° C. 5 minutes	Negative		

We have carried out some tests with the Schattenfroh method and, so far as can be determined at the present writing, the skins are uninjured.

We made various tests in which we neutralized the acid by lime, lime in the presence of salt, sodium hydroxide in the presence of salt, sodium hydroxide in the presence of sodium acetate, etc., but apparently the simplest neutralization with milk of lime is entirely satisfactory.

The tests were carried out in 24- and 48-hour periods. In both cases all anthrax spores were found to be absent. In a blank test made on the soaks which were made in the ordinary way, anthrax was found to be abundantly present.

TREATMENT OF TANNERY SEWAGE.*

By C. Lee Peck.

I want to make just a remark or two about the work that has been done by the Proctor-Ellison Co., of Elkland, Pennsylvania, during the last year and a half, but as introductory I want to say that I find that very few tanners have much of an idea of the volume of their sewage. I have tested a few places, carefully tested, but in this one particular plant I have been running tests now for six months. They told me that they had 300,000 gallons of sewage to be treated. By weir measurements, under a system of recording so that I have a complete record for every moment of time for the last two months, as well as for a period last winter of about the same time, I find that their solutions amounted to over a million and a half gallons per day; that is, treating 4,000 sides of sole leather per day—a million and a half gallons.

At another tannery in the western part of the state, I was told that their effluent amounted to between 80,000 and 100,000 gallons, and by the most cursory calculations, it was found that it amounted to at least 200,000 and probably nearer 300,000.

The Proctor-Ellison Co., in February of 1916, retained the Dorr Company, of 17 Battery Place, New York, to investigate the treatment of their waste waters. We were asked to approach this problem not from the standpoint of the chemist, to see what could be done in the way of purification, but were told that they had a certain amount of money which they were willing to spend for this purpose and asked to go as far as we liked but to keep within that sum, so that our work has been done on a basis not of attempting to secure the best results possible, but of attempting to secure results which would be satisfactory to the State at a sum which the tanner could afford to pay.

We have now in operation the first unit of what we deem to be a successful plant. We are completely disposing of 50,000 gallons per day of this sewage, burning the thickened sludge and sending the clarified solution into the ground by absorption, so that no drop of it leaves the premises of the tannery except by channels underground. This, of course, could not be done at many tanneries, but this particular place is so located that the

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* Address at the Atlantic City Meeting A. L. C. A., June 8, 1917.

drainage toward the river offers no objection, there being no wells or no other methods whereby this solution could be reached after it once enters the earth.

The results which we have obtained have been effected by withdrawing the sludge from our primary sedimentation basin before it has had an opportunity to decompose. By this means we have been able to sediment upwards of 90 per cent. of the suspended material in the sewage in one operation. We find certain things are necessary in sedimentation of tannery sewages, and these are no new discoveries; we are traveling the well beaten path.

The first thing is that your sedimentation tank must have sufficient volume to contain a complete cycle of your sewage, so that the acid solutions and the alkaline solutions may react one with the other, for the purpose of securing effective precipitation and for the further purpose of affording an effluent of a reasonably uniform character as to its reaction for further treatment if it may be deemed necessary.

Through the courtesy of the Proctor-Ellison Co., I am enabled to extend to you a cordial invitation to visit their plant and see this unit in operation at any time during the next 30 days. At the expiration of that period we expect to tear down that unit and put in a larger one to treat 500,000 gallons, and from that, step up to the total sewage. They ask only that you come to the office and there a guide will be provided, because, under the present condition of war, they are compelled to guard their plant very carefully.

The cost of the installation, handling 50,000 gallons per day is about $1,400. We don't know that we are going to satisfy the State, because they may require something further in the way of treatment for disinfection; but so far as the sedimentation part of the plant is concerned, we feel that it is absolutely effective.

The Proctor-Ellison Co. has given me the exclusive service of their chemist during the period of these tests, and we have records month by month of the work which has been done. These records cover the total of gallons of sewage which the plant sends forth, the total solids, the soluble solids, the suspended solids, the settleable solids,—all of these in parts per million—the alkalinity, as bicarbonate, carbonate, hydrate, the odor, the color and the oxygen consumed; and these results are carried through the two steps, in the treatment of the effluent.

The following is a summary of these results:

SUMMARY OF RESULTS OBTAINED FOR MONTH OF MAY, 1917, BY DORR METHOD OF SEDIMENTATION.

Material Treated—Effluent from sole leather tannery in Pennsylvania.
Quantity—45,000 gallons per day.
Total Solids in Effluent—Averaged 4,765 parts per 1,000,000.
Removed by Treatment—55 per cent.
Suspended Solids in Effluent—Averaged 1,650 parts per 1,000,000.
Removed by Treatment—93.15 per cent.
Organic Materials Subject to Oxidation—51 per cent. removed or oxidized during treatment.
Degree of Stability—Raised from 0 to 99.
Odor—87 per cent. removed, based on the following table:

5 = Putrid to nauseation
4 = Strong animal
3 = Animal
2 = Strong tan
1 = Tan
0 = No odor

Turbidity of Treated Effluent—Equivalent to 174 parts of kaolin per 1,000,000 in water.
The results obtained above were made possible by the Dorr method of removing the sedimented material before either putrefaction or fermentation took place.

Now, I should be glad to give to each of you who cares for it, detailed printed or written matter in regard to this as fast as it is available. I have cards here for that, and if you will give me your names and addresses and the companies which you represent, I will see that this matter is sent to you. At the present time I have available no copies of the blue print for distribution, or descriptions of the plant. I have, however, photographs of the plant with me and rather complete data, which I will be pleased to go over with any of you after the meeting or at any time before to-morrow morning. I expect to be here until then.

BOOK REVIEW.

ANTHRAX AS AN OCCUPATIONAL DISEASE. John B. Andrews, Ph. D. Bulletin of the United States Bureau of Labor Statistics. Government Printing Office, January, 1917. 155 pages. Price, 25 cents. This pamphlet may be obtained from the Superintendent of Documents, Government Printing Office, Washington.

The subjects of the chapters are as follows: 1, general description and history of anthrax; 2, medical aspects of human anthrax; 3, industries affected; 4, anthrax in the U. S.; 5, anthrax in Europe; 6, present status of the problem of disinfection; 7, recommendations for the control and prevention of anthrax; Appendix A, rules and regulations in the U. S.; Appendix B, text of European regulations.

Chapter 1 contains nothing not covered by the papers published in this number of the JOURNAL. In connection with Chapter 2 are given colored plates of the anthrax pustule in various stages and of the bacillus and spores. The difficulty of diagnosing intestinal anthrax is emphasized, and it is suggested that many cases of this and the pulmonary variety (woolsorter's disease) escape detection. In the chapter on industries affected, beside the leather industry are mentioned the hair and bristle industry, the wool industry, the horn and bone industry and transportation. A number of cases are reported in which no connection can be traced between the disease and the occupation of the patient. Of 132 deaths from anthrax reported in the six years from 1910 to 1915 inclusive, the occupation of 18 persons is not reported (eight of these were children under 10 years old). Thirteen were reported as housewives, domestics and other home occupations. One was a teacher and three school children. Sixteen were farmers or farm laborers. Twenty-two are reported as tannery workmen, and seven were stevedores or freight handlers. Seven were workers in hair or wool. One was a veterinary surgeon and one a medical student. A number are reported as laborers without further specification, and many occupations are specified which have no evident connection with the disease, such as lawyer and post-office clerk.

Tables are given showing data on cases of anthrax in two hospitals, one in Massachusetts and one in Philadelphia. The total number of cases in seven years in the Philadelphia institution was 32, and in the Massachusetts hospital in thirty-five years 35. Of these 67 cases, 12 died. Twenty-six of the cases were of workers in hides and skins, with 4 fatalities. Twenty-two cases were wool and hair workers, with 4 fatalities. Eleven were transportation workers, of whom 2 died. Twenty-three cases were reported to the New York State Department of Labor in five years. Of these 10 were hide and leather workers, with 4 deaths, and 3 transportation workers with 2 deaths. The New Jersey State authorities received reports on 13 cases in four years, of which one died. Eight were leather workers. In Pennsylvania 49 cases were reported in three years, of whom 20 were hide and leather workers and 9 hair and wool workers. The 132 fatal cases for the whole United States during the six years, 1910-15 inclusive, are described in some detail. As late as 1911 only seven states required anthrax cases to be reported, so that no extended statistics are available.

Legislation in various states in relation to the prevention of anthrax is described. This legislation aims at the protection of industrial workers and the prevention of the spread of the disease among cattle and other animals.

More extensive work has been done on the subject of the prevention of anthrax in Europe than in this country. A number of associations exist in England, Germany, France and Italy for investigating and combating the disease, and there has been a good deal of legislation in several countries on the subject.

The total number of cases reported in England during fourteen years was 729, of whom 150 died. Of these, 209 were of workers in hides and skins, with 38 deaths, 323 wool workers, with 66 deaths, and 128 hair workers with 26 deaths. Of 144 cases in the wool industry in the Bradford district in eight years, 129 were external and 15 internal. The total number of deaths reported was 32.

In Germany complete returns are available only from 1910 to 1912 inclusive. In these years the total number of cases reported was 842, of which 116 were fatal. The number traceable to the occupation of the patient was 770, of which 377 were agricultural workers, 256 leather workers, 47 cattle dealers, veterinarians or flayers and 55 hair and bristle workers. For the same years the total number of cases reported in France was 134, including 81 leather and hide workers, 23 wool workers and 12 hair workers.

In Italy the number of cases is much greater. For the fifteen years 1890 to 1904 inclusive the total number of cases reported was 36,426 with 7,308 deaths. Most of these occurred outside of the manufacturing districts. In Russia the disease is even more prevalent. It is there called "Siberian pest." Popov in the Russian medical journal *Russki Vratch* for June 14, 1914, asserts that the total number of cases in the whole country for the five years 1904 to 1908 inclusive was 80,498. Here again the cases were mostly outside of the manufacturing districts.

Protective regulations for workers in wool, hair and bristles have been adopted in England at various dates since 1884. These include the soaking of baled material in water before opening the bales, and handling the material only in a damp state. Rigid precautions in regard to the care of cuts and other wounds are enforced, and regulations in regard to washing and disinfecting hands and clothing seem fairly complete.

Similar regulations are in force in Germany, and here employers are permitted to discharge summarily any worker who disregards the regulations. France has similar regulations, but not so minute, and no provision is made for penalizing carelessness on the part of the workers.

The disinfection of bristles and hair may be effected by any one of the three methods following: 1, exposure to steam at a temperature high enough to kill the spore; 2, boiling for 2 hours; 3, boiling 15 minutes in a 2 per cent. solution of potassium permanganate and then bleaching with 3 per cent. sulphuric acid. Wool is less easily managed. Saturation of the wool for 7 hours with 1 per cent. formaldehyde solution is efficient, but it injures the spinning quality of the wool. Steam disinfection of wool injures the wool both in color and quality.

Disinfection of hides and skins is discussed, and the difficulties to be overcome are pointed out. All the matter on this topic contained in Chapter 6 has already appeared in this JOURNAL at various times.

ABSTRACTS.

Manufacture of Artificial Leather. *Textile World Journal,* through *Leather Manufacturer.* Artificial leather goods are produced by processes based on the employment of drying oils, rubber, celluloid, etc. Those made by the use of drying oils are really oil cloths, to which the leathery appearance desired is given by passing through embossing rolls. In some cases an ordinary boiled linseed oil is applied to a cotton or hemp fabric, along with a suitable pigment. This is dried in the air or in a special oven. Better results are obtained by applying linseed oil (which has been thickened by boiling) to the cloth while warm. The necessary amount of drying is then much less. The smell of these substitutes is characteristic, and quite different from that of leather. The use of rubber as a coating fabric is accomplished either by mixing it with hot linseed oil or by bringing on to the cloth in solution in benzine or other solvent.

Japanese Leather Industry. *Shoe Trades Journal,* through *Leather* increased sixfold in the last six years. Much of this increase is in increased sixfold in the last six years. Much of this increase is in Chosen (Korea), where a number of modern tanneries, equipped with the newest machinery, have been erected. The center of this industry is Seoul. Because of the size and urgency of Russian Government orders, the Japanese manufacturers seem to have begun to attach more importance to rapid output than to the quality of their products, with the result that the reputation of these leathers in Russia is suffering. It is alleged that some goods for Russia have lately been marked "Made in America," although really made in Japan.

Trimming Sole Leather Sides in Switzerland. *Journal Suisse des Cordonniers,* through *Leather Manufacturer,* July, 1917. In tanneries when heavy leather intended for use in shoes is divided up into classes, as butts, flanks, etc., the work is generally done in a certain way, and almost always by the same workmen, who acquire considerable skill in the operations. It is understood in the tanneries that more than 50 per cent. of the weight or of the area of the side should go into the butts or "croupons." In a shoe factory they generally calculate the butts as 50 per cent. of the total weight, and then to fix the price of the butt they add 50 per cent. to the value of the part trimmed off. In this way the flanks, etc., are valued at 50 per cent. less than the purchase price of the whole side. In the leather trade supply and demand exercise a certain influence on the price of butts, flanks, etc., and for that reason the proportion of the figures is often subject to considerable variation. It is the same way in the tanneries—in most cases the hides are trimmed as soon as they come from the beam-house and the tanning is done separately, the butts being given the usual treatment for sole leather, while the trimmings are given that for cow-hide or kip. On the other hand, when the trimming is done by the leather dealer or by the shoe manufacturer, it is almost invariably the case that the flanks undergo the regular tannage. The extraordinary dividends made by some leather manufacturers are due in large measure to the fact that in trimming the hide they realize an exorbitant profit. In this case the profit of the tanner is the loss of the consumer; that is, the people who work up the leather pay too much for it. In general way now-a-days it is the rule to give the butt a great deal more than 50 per cent. of the side. Besides this special efforts are made to increase its weight. It may be stated without hesitation that in trimming the butts an extra profit of from 5 to 10 per cent. is made by including portions of the neck and flanks that should be classed as offal. As is proved by the market quotations, the difference between the price of butts and that of the offal is not nearly as large as is allowed by the shoemaker, and the leather dealer who trims the sides has to figure closely if he wishes to come out right. For first quality sole leather, for instance, the difference varies about one-third the value of the hide, and a balance can only be made by adding more than 50 per cent. to the output of the butt. It is natural that the butts that are specially tanned are heavier almost regularly than those prepared from the finished leather. Shoe manufacturers are always large buyers of necks, heads and flanks and these materials are always scarce, hence the high prices they demand. Any one who gets the offal at 50 per cent. off would do an excellent business selling it at the highest market rates. For some time, complaints have been made regarding the poor condition of butts sent out by certain tanners who are disposed to enlarge the butts unwarrantably to the disadvantage of the consumer. In this way the leather suffers a further increase in cost, in addition to the immense advance due to the war. In order that this injustice shall not become a fixture, it is necessary to protest vigourously against such practices, and to return to our healthy traditions in trimming side leather.

South China Hide Trade. CONSUL GENERAL GEORGE E. ANDERSON, Hongkong, British China. *Commerce Reports,* May 16. The shipment of cowhides from the South China field to the United States has not been undertaken in large volume until comparatively recently. For a number of reasons direct shipment has been found difficult. However, considerable quantities of these hides have reached the United States by way of Great Britain. There are now on hand in Hongkong in preparation for shipment about 250,000 hides roughly valued at $725,000, 50,000 of which are for direct exportation to the United States and the rest, apparently at least, for England, though it is understood that a part of them will eventually go to the United States. It is generally stated in the trade here that hides to a value considerably in excess of $6,000,000 will be shipped out of this field to the United States this year. In normal years cow and buffalo hides are exported from all China to the value of $10,000,000 to $12,000,000 gold, but of this total not more than $2,000,000 usually comes from the South China field. With the advent of war and the increased demand for hides generally, and with the change in freight and transportation conditions, it has been found to be advisable for a good many reasons to develop the trade in this part of China. For a time the trade has been hindered somewhat by quarantine restrictions respecting anthrax, rinderpest, and foot-and-mouth disease, but as a result of the investigations of the colonial veterinarian of Hongkong, and also as a result of reports made at the recent convention of medical men at Canton, the situation is somewhat clearer, and the trade is proceeding with little difficulty. Most of the hides in the Hongkong market come from South China, the island of Hainan, parts of Indo-China, and from Kwangtung and Kwangsi Provinces. The hides, as a rule, are small but are of fair grade otherwise. They usually come sun dried, although by reason of the shape in which they are dried it usually pays to soak and disinfect and redry them. They are usually shipped in bales of 100 hides each and average about 10¾ pounds to the hide for the first grade and a little less than 10 pounds to the hide for the second grade. Practically no salted or wet hides are shipped from the South China field. The disinfection commonly used in this field is immersion for half an hour in a 1 to 1,000 solution of bichloride of mercury. No goat, kid, sheep, or lamb skins are exported from the South China field. A few such skins are collected but most of them go to northern ports through Chinese channels.

Modern Tannery at Hongkong. CONSUL GENERAL GEORGE E. ANDERSON, Hongkong, British China. *Commerce Reports,* June 21. There is now being erected at Mongkoksui, in the mainland portion of Hongkong, a modern tannery which promises to be an important factor in the leather situation of the Far East, particularly in South Asia. The concern has been organized under Hongkong laws with a capital of $5,000,000 Hongkong currency. The plant now being erected is to be of the latest modern pattern in every respect. It is being constructed under the supervision of a Chinese tannery expert who has served an apprenticeship in the business in various portions of Europe and the United States. The machinery for the establishment has been ordered from France, Great Britain, and the United States in about equal proportions, selections being made of machines manufactured in the various countries to meet the particular needs of the concern here. The plant will have a capacity of 3,000 cowhides and 100,000 sheep and goat skins per week. The concern proposes to tan all grades and varieties of leather. The importance of this undertaking is unusual. While there has been some effort to tan the hides and skins available in South China in a Government plant at Canton, the present Hongkong concern is the first properly commercial undertaking of the sort planned upon a comprehensive basis and with practical supervision in southeastern Asia. The imports of leather into Hongkong for local use and for distribution all over this portion of the Far East are large, and shipments of hides and skins abroad are large and are increasing. The Hongkong concern proposes to use China tan bark and other materials so far as possible, indicating that while the Chinese oak's bark is not as rich in tannin as similar barks in Europe and the United States. it can be had at a much lower price. The concern expects to have its plant completed by November.

(The name of the company can be obtained at the Bureau of Foreign and Domestic Commerce or its district or co-operative offices. Refer to file No. 89657.)

Industrial By-products of Sewage at Bradford. CONSUL AUGUSTUS E. INGRAM, Bradford, England. *Commerce Reports*, June 15. The sewage works of the city of Bradford recover the grease turned into the sewers by many of the wool washing and scouring establishments and thereby convert into a highly profitable by-product a waste effluent formerly difficult and costly of disposal.

The sales of this recovered grease amounted in 1916 to £80,000 ($389,320), an increase of £19,000 ($92,463) over 1915, owing to the high price now obtainable, which is about £25 ($122) per ton; and it is estimated that in 1917 £70,000 ($340,655) will be derived from that source, in addition to £5,000 ($24,332) from the sale of manure or fertilizer made from the precipitated sludge after the grease has been extracted. The municipal expense of maintaining the sewerage department has steadily declined in recent years, and it is believed that the enterprise will be self-supporting in 1917.

Samples of the grease and manure were analyzed by Government experts, who report that the grease is of great value to the leather-dressing trade and to certain branches of the textile industries. The whole of the waste effluent is not treated for grease recovery because the plant is not adequate; the Government urges an increased output. The Food Production Department has inquired about the quantities of manure available at Esholt, which is said by experts to have a high fertilizing value.

Sumac Cultivation in Sicily. ANONYMOUS in *Journal of the Royal Society of Arts*, June 8, 1917, p. 526. Two species of sumac grow in Sicily, the wild and the cultivated. The wild variety has a short stalk, small leaves attached two by two to a short stem, the leaves sparsely covered with white fuzz on both sides, the stem with no small leaves near its base. The cultivated plant (*Rhus coriaria*) has a longer stem than the wild, its leaves are larger, and are covered with fuzz only on the lower side, and the stem of the leaf has small leaves along its entire length. Sumac requires a dry, loose soil. The best is a clay soil with lime and silica mixed. It does not grow well in damp, compact ground. The soil may be rich or poor, so long as it is dry. However, the best sumac is grown on soil of volcanic origin. This soil, together with high temperature, produces the greatest amount of tannin. In Sicily, sumac is grown at all elevations up to 2000 feet. It appears from a report by the United States Consul at Palermo that sumac is planted in furrows 8 inches wide, 6 inches deep and 27 inches apart, the plants being placed 27 inches apart in the furrow. The sprouts should be taken from a full-grown plant and care exercised to have the roots entire. They must be a year old. The planting is usually done in December or January. The ground should be plowed twice about four or six months previous to the planting. The plants should be cut down within six inches of the ground. During the year the ground should be spaded six times, as follows: immediately after planting, then in February, April, May, June and September. The first three spadings should be deep, the others only light. During the second year there should be three spadings, in January, March and May. In December the little shoots which have appeared at the root of the plant should be cut off. Sumac should be cultivated alone. The shade of trees retards development and reduces the amount of tannin. The gathering of the leaves takes place when they commence to turn yellow, usually in July and August. Some growers cut the twigs off near the stem and send them in this form to the thrashing floor, where the leaves are separated from the stems by beating or by thrashing with horses. However, it is not a desirable method, as it does not produce a good quality. The best method is to gather the crop in three periods. First, the leaves near the stalk, up to about the middle of the limb are gathered. Twenty or twenty-five days later half of the remaining leaves are gathered. A few days after this the ends of the twigs are cut off. This method gives two or three qualities of sumac, but as it requires a great deal of time and labor the usual method is to cut off the whole plant near the ground. The twigs are piled on a floor and are turned three or four times a day with a fork. After the leaves have been separated from the wood they are taken to the mill, where they are packed in bales or ground for shipment. There is no treatment at the mill which affects the amount of tannin contained in the sumac.

Leather. L. BALDERSTON. *Proceedings* of the Engineers' Club of Philadelphia, June, 1917; *Hide and Leather,* June 23, 30 July 7, 21, 1917. Lecture before the Philadelphia Section of the American Chemical Society. Review of materials and methods of manufacture.

Distribution of Leather in the Netherlands. PAUL L. EDWARDS, clerk to commercial attaché, The Hague. *Commerce Reports,* May 24. The Dutch Ministry of Agriculture, Industry and Commerce has established a Royal Distribution Bureau of Hides and Leather to oversee the Dutch leather industry in all its phases, from the slaughterer to the shoemaker. Stock will be taken of all hides and leather in the country, and statistics as to the requirements in each commune of shoe-repairing leather will be gathered. After this information is obtained a strict governmental regulation of the hide and leather industry will go into effect along the following lines: All slaughterers, dealers in leather, groups of dealers (so-called hide clubs), and tanners must be registered with the Distribution Bureau. The Minister of Agriculture, Industry, and Commerce will fix a maximum price which the slaughterers may charge for their hides. In turn, the maximum price which the tanners can charge the dealers and consuming factories, shoemakers, and cobblers will be regulated by ministerial decree. Anyone wishing to have his shoes repaired will have to obtain a coupon from his communal authorities. This will state the maximum price which he will have to pay for the repairing and will indicate the name of the shoemaker or cobbler who is to do the work. Leather for repair work will be delivered to shoemakers only upon the surrender of these coupons.

An Odd Turn of Affairs. ELWOOD HENDRICK, Public Committee, A. C. S. The United States Bureau of Mines has lately issued a statement in regard to a Portland cement plant at Riverside, Cal., which shows how an apparatus, installed to avoid nuisance and save the health of the workers, has become the central feature of the whole establishment. One of the great troubles of a Portland cement mill is the dust. It is likely to disturb vegetation by settling down on growing things and it is unwholesome for the men employed in the mill. The factory in question was in trouble on this account and it availed itself of Prof. Cottrell's invention to precipitate the particles on their way to the stack by means of electric currents. Now this dust contains potash, and so efficient is the installation that 90 per cent. of the content of this precious product is recovered in the form of potash salts. The present demand for potash in this country is something like Coal Oil Johnny's thirst, which according to the legend, was unquenchable. As is well known, we formerly obtained our entire supply from Germany, and these salts which they produce in California bring as high as $400 and $450 a ton, and even then are hard to find. The Riverside concern finds that its potash salt output pays its entire operating costs plus a reasonable profit, leaving the cement, which it will soon be producing at a rate of 5,000 barrels per day, as clear profit—"velvet" in the vernacular. It has no immediate market for much cement, but what is not sold is kept as clinker in dry storage. The covering costs are slight—and there are worse things to own as an investment than large quantities of Portland cement; especially if it does not cost anything.

PATENTS.

Treating Sewage. British Patent 105,654. T. Caink, Worcester. A device for the more efficient aeration of sewage being treated with activated sludge.

Work-Controlling Attachment for Leather Rolling and Embossing Machines. British Patent 105,859. P. R. Barker, Otley, near Leeds.

Leather Staking Machine. British Patent 105,737. Alfred Seymour-Jones, Pendower, Wrexham, Wales. The grain side is worked by two blades, both of which may be dull, or one of them a rough stone ; or a revolving cylinder may be substituted for one blade. The flesh side is worked by a roll of felt or loose fiber spaced between the blades and by a revolving roll having a roughened surface, placed in front of the first blade.

Tanning. British Patent 105,925. F. Gilardini, Turin, Italy. Hides or skins are tanned by applying a strong extract under pressure to one surface while the other is under atmospheric or a reduced pressure. The hide may be stretched in a suitable receptacle and arranged to form a partition, the tan liquor being supplied under pressure to one compartment, the other being exhausted. Or the hide may be wound on a drum permeable to the tan liquor.

Tanning. U. S. Patent 1,232,620. Edmund Stiasny, Headingley, Leeds, England, assignor to the Badische Company. This is apparently the original patent on the neradol process of tanning. The application was filed Dec. 13, 1912. Dr. Stiasny has not been in England since July, 1914. 1. The process of tanning which consists in treating hides with a soluble aromatic compound obtainable from formaldehyde or a body giving rise to formaldehyde and a phenolic body, and which compound contains at least one hydroxyl group in the molecule, but not more than one hydroxyl or skins are tanned by applying a strong extract under pressure to one acid salt-forming group. 2. The process of tanning which consists in treating hides with a soluble aromatic compound obtainable by treating cresol-sulphonic acid with formaldehyde.

Boarding Machine. U. S. Patent 1,232,975. Carl A. Rausch, Assignor to the Fortuna Company, Stuttgart, Germany.

Leather Rolling Machine. U. S. Patent 1,232,833. James R. Nichols and Gustave R. Johnson, Corry, Pa. A table-lifting device for the type of machine using a reciprocating roller and bringing the work into contact with it by lifting the table.

Apparatus for Tanning. U. S. Patent 1,233,730. Adiel Vandenweghe, New York, and August d'Huyvetters, Ridgfield Park, N. J., assignors to Ideal Cooney Dressing & Dyeing Co., Inc., Paterson, N. J. The apparatus comprises vats at different levels and means of heating the liquors.

Machine for Scrubbing or Brushing Leather. U. S. Patent 1,233,709. Carleton Ruhe, Olean, N. Y.

Artificial Leather. British Patent 106,336. A. E. Alexander, High Holborn, London (Duratex Co., Newark, N. J.). The process consists in coating a fabric with a solution containing nitrated cotton and vegetable oil, calendering it, and then applying a baked coating of leather japanning composition. Rape-seed oil is preferred in the first solution, and three coatings of this are applied. The japanning composition may be made up of linseed oil, naphtha and an opaque pigment.

CORRECTION.

Mr. J. A. Wilson calls attention to an error in the abstract of discussion on the report of the Committee on Determination of Free Sulphuric Acid in Leather, page 347. The last sentence speaks of positive tests for free sulphuric acid. The method used was the Procter-Searle, which indicates free mineral acid, without determining what acid, so that the use of tin crystals in bleaching, by introducing free hydrochloric acid would account for Mr. Oberfell's results on the splits.

THIRD NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

This exposition is planned for the week of September 24, in the Grand Central Palace, New York. On Monday the opening address will be made by Dr. Charles H. Herty, Chairman of the Advisory Committee of the Exposition, and editor of the *Journal Industrial Engineering Chemistry*. On this day the following gentlemen will also speak: Dr. Julius Stieglitz, President of the American Chemical Society; Dr. Colin G. Fink, President of the American Electrochemical Society, and Dr. G. W. Thompson, President of the American Institute of Chemical Engineers. M. T. Bogert and L. H. Baekeland will also speak during the week. Moving pictures of manufacturing processes will be a feature of the Exposition.

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ELECTIONS.

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George H. Raymond, 39 Frankfort St., New York City (% Haas Rees' Sons).
G. Walter Currigan, Stanbridge East, Quebec, Canada.
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Samuel French, to % McElwain Tannery, Manchester, N. H.
K. G. Mackenzie, to % The Texas Co., 17 Battery Place, New York, N. Y.
C. F. Landsheft, to 836 Niagara St., Buffalo, N. Y.

RESEARCH LABORATORY.

The subject of research laboratories was brought forcibly to the attention of tanners and leather chemists in 1913, when the project to establish an international leather research laboratory at Leeds University as a memorial to Henry R. Procter was launched. There had been some correspondence between the President of our Association and Dr. J. G. Parker, in which the plans for the proposed laboratory were outlined, and a subscription list was started under the care of a committee. This committee gave a report on the aims and management of the proposed institution which appears in the JOURNAL for July, 1913. Subscriptions to a considerable amount were forwarded from America, and also from France and Germany. The building was completed late in 1914, and work begun.

The successful carrying out of this project may be said to have been responsible for setting on foot a plan for the establishment of a laboratory on similar lines in this country. The first published suggestion on the subject, so far as we are aware, was an editorial in *Hide and Leather* in January, 1915. An abstract of this appears in this JOURNAL for February, 1915. A joint committee of the National Association of Tanners and our Association was deputed to formulate a plan, and they reported in October, 1915, at the annual meeting of the National Association of Tanners. The necessary funds for the purpose were secured by November, 1916, and early in 1917 the N. A. T. appointed an enlarged committee to carry the plan into effect. We are now informed that Mr. Churchill has been appointed director to begin his duties in the Fall, and that the research laboratory will be established in connection with Pratt Institute and the Tanning School. Particulars are promised for the October JOURNAL.

NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

The Third Exposition of Chemical Industries will be held in the Grand Central Palace, New York City, during the week of Sept. 24. There will be many exhibits of great interest to all chemists, as well as moving picture illustrations of chemical manufacturing processes. A number of addresses by well-known chemists are scheduled for the opening day, and several others for later in the week.

COUNCIL MEETING.

A meeting of the Council of the American Leather Chemists Association was held at the Chemists' Club, East 41st St., New York, on Saturday, August 11. Present: Charles R. Oberfell, H. C. Reed, W. K. Alsop, F. P. Veitch, F. H. Small, John H. Yocum.

The matter of the proposed provisional method for the determination of Epsom salts in leather, published in the July JOURNAL, was brought up. The Secretary announced that the method would be submitted to a mail vote of the active members within one week from that time. Mr. Yocum drew attention to the fact that in the analysis of leathers containing Epsom salts a portion of the water of crystallization of the salts was driven off in the drying for moisture determination, and was thus estimated as moisture, while after the magnesium was determined the MgO is figured to $MgSO_4.7H_2O$, and thus the same water is included twice in the analysis.

The Secretary reported that he had communicated with President Wilson, offering the services of the Association as he was directed to do by the Council at the meeting of June 9. The following reply was received:

> The President is very grateful for your generous pledge of co-operation and support, and he hopes that you will accept this informal acknowledgment of your message as an expression of the deepest appreciation of your patriotic offer.

A further reply was also received, as follows:

> Subject, Offer of Services—Analysis of Leather.
>
> 1. This office is in receipt of your communication of the 29th inst. having reference to resolution passed subject to the approval of the Council of the Association, with reference to aiding the Government in the leather industry.
>
> 2. In reply your attention is invited to letter of this office of June 2nd, directed to the American Leather Chemists Association, Boston, Mass., which was returned by the Post Office Department owing to lack of address. This letter read as follows:
>
> "This office is in receipt of your letter of May 21st, addressed to Captain Mulford, wherein you offer the services of the members of your Association in connection with the analysis of samples of sole leather. Your courtesy in this matter is greatly appreciated by the Department. However, the Government laboratory is at present

making tests for the Department; but if in the future the Department finds it necessary to avail itself of your generous offer, it will gladly do so."

3. Should the Government find it necessary or desirable to utilize the services of your Association, you will be duly advised.

(Signed) HENRY G. SHARPE,
Quartermaster General.
By L. HARDEMAN,
Major, U. S. Army.

The Secretary further reported that he had purchased a $1,000 Liberty Bond, as authorized by the Association at its Annual Meeting at Atlantic City, and had also paid over $200 to the American Red Cross.

The Council then took up the matter of committee work, and made the following decisions:

Committee on Comparative Analysis. Mr. R. W. Griffith was appointed Chairman, with power to select his own committee. It was agreed that the work of the committee be directed to the analysis of the following materials: Ordinary quebracho extract, liquid chestnut extract, mangrove bark and divi-divi, and that no instructions be given as to whether the rapid or slow cooling method shall be employed.

Solubility of hide in salt solution and the effect of alkali on the soaking of dry hides. It was voted that Dr. Balderston be continued in the chairmanship of this committee, to select his own committee and proceed in any manner that seems best to him.

Specifications for Kaolin. Mr. Frey is continued as chairman of this committee, and it is suggested that the Standard Manufacturing Co. take the matter up with the view of centralizing the production of kaolin and standardizing it in a manner similar to that of hide powder, so that the kaolin might be obtained from a central source; Mr. Frey to select his own committee.

Committee on Dye-testing. Mr. Guy T. Creese was appointed chairman of a committee to work on natural dyes, and Mr. H. P. Davies chairman of another committee on testing of synthetic dyes. To the latter committee was assigned the subject of the investigation of the possible use of sulphur dyes for leather.

Committee on Sulphonated Oils. Mr. Alsop accepted the chairmanship of this committee with the provision that the work of the committee was not to include any new problems. It was suggested that the committee should frame provisional methods for sulphonated oils, and Mr. Veitch thought it would be well to have the proposed provisional methods submitted to the Council before publication.

Analysis of Tannery Effluent. No committee was appointed on this subject. Members are encouraged to do individual work as opportunity offers.

Effect of Hard Water on Tannin. Mr. Faust was made chairman of this committee, to select his own committee and line of work.

Uniform Analysis Blanks. A mail vote of the members is to be taken on this subject.

Disinfection of Hides. On motion of Mr. Reed, Messrs. Alsop and Levi were appointed to represent the Association on a committee which the National Association of Tanners is to create to take up this problem with the Bureau of Animal Industry.

On motion of Mr. Small, it was decided to publish in the JOURNAL a notice asking for suggestions in regard to a method for the determination of free sulphuric acid in leather.

A letter from Mr. V. A. Wallin was read, suggesting that the next meeting of the Association be held in Washington instead of Atlantic City.

Mr. Alsop made a report in regard to the proposed ten-year index of the JOURNAL, stating that an edition of 400 copies would not cost more than $500. He was authorized to proceed with the compilation and publication of the index. (Up to Aug. 23, in reply to the question mailed to members and subscribers, 100 orders had been received.)

Six associate members were elected.

THE ANALYSIS OF ONE-BATH CHROME LIQUORS.

By Douglas McCandlish.

The interest shown in the proper analytical control of single-bath chrome liquors may be judged by the number of contributions to the subject which have appeared in recent years. For a convenient summary of the various methods, reference should be made to a paper by Harrap and Hayes,[1] which ably points out advantages and disadvantages of all of them. The provisional method of the A. L. C. A. for the analysis of chrome liquors is probably in most general use for tannery control, and in the majority of cases appears to give results which are sufficiently accurate for practical purposes. By this method, the chromium is estimated by oxidizing with sodium peroxide, boiling to decompose the excess of it, acidifying with concentrated hydrochloric acid and titrating the iodine liberated from an excess of potassium iodide with standard sodium thiosulphate solution. The acid in the liquor is determined by titrating the boiling diluted chrome liquor with standard sodium hydroxide, using phenolphthalein as indicator.

In practice used chrome liquors have been found which behave abnormally when the estimation of chromium is carried out in the manner described. Such liquors have well defined characteristics. They froth very considerably during the boiling which follows the addition of sodium peroxide and careful manipulation is necessary to avoid loss from this source. When the cooled oxidized solution is acidified with conc. hydrochloric acid, it assumes an olive-brown color instead of the characteristic orange-red of chromic acid solution. Further, if some of the filtered chrome liquor be evaporated to dryness and ignited, the odor of burning hide substance is easily detected. Invariably the amount of chromium found by the A. L. C. A. method in such a case is lower than is found by the ordinary gravimetric determination.

Attention has been drawn[2] to the possible interference of organic matter with this method of chromium estimation, although it was shown that the addition of limited quantities of gelatine peptones had no appreciable effect on its accuracy. The subject

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[1] *Collegium* (London), 1915, p. 305; this JOURNAL, 1916, p. 66.

[2] Procter and McCandlish, *J. S. C. I.*, 1907, 26, p. 458.

has been further investigated by the author with interesting results. A solution of gelatine peptones was prepared by heating 5 grams of gelatine dissolved in 50 cc. of water with 10 cc. normal sodium hydroxide for 20 minutes at 100° C., neutralizing with 10 cc. of normal hydrochloric acid and making up the cooled solution to 100 cc. This solution was added in increasing amounts to a chrome alum solution of known strength and its effect on the chromium determination noted. When a chromium solution contains less than 1.25 per cent. peptones—the maximum used in the earlier experiments—the chromium estimation was found to be accurate. As the proportion of peptone in the solution is increased, difficulties arise and the presence of 2 per cent. produces a notable lowering of the chromium figure. When 3 per cent. of peptones are present in the chrome alum solution, it behaves very much like the abnormal used chrome liquors already described and analysis by the volumetric method shows only one-half of the correct amount of chromium. The behavior of such liquors during analysis and the low results which they yield, may be satisfactorily explained. The presence of gelatinous matter in the chrome solution will account for the unusual frothing when it is boiled. After oxidation the solution contains sodium chromate and hydrate and if the volume has been reduced to 15 cc., which is the minimum mentioned in the A. L. C. A. method, the concentration of the sodium hydrate will be about 14 grams per 100 cc. The acidification of this solution with concentrated hydrochloric acid will be accompanied by a considerable rise in temperature and we thus have favorable conditions for the reduction of the chromium compound, namely, a hot solution of chromic acid containing organic matter. Consequently, some of the chromic acid is reduced to chromium chloride and the green color of this salt combined with the orange color of the unreduced portion of the chrome, gives the solution the olive-brown color already noted.

The proportion of the chromium reduced will vary with the amount of organic matter, the temperature and possibly other conditions, but the chief point to be noted is the fact that the reduced chromium will not be estimated by the thiosulphate titration. It is improbable that a chromium liquor containing 3 per cent. of gelatine peptones will be found in practice. However, some other hydrolysed forms of collagen with greater reducing power very probably do occur in small quantities; although the products obtained by the digestion of gelatine in a slightly alkaline solution of trypsin for 24 hours did not give results appreciably different from those obtained with the peptone solution described.

It is conceivable that decomposed hide substance occurs to some extent in all used chrome liquors. In vat and paddle tanning where successive packs are tanned in a liquor which is strengthened, but not completely renewed for each lot, the accumulated organic matter may have a very pronounced effect in lowering the chrome result below the correct figure, when analysed by the sodium peroxide method. The error may be reduced, but not eliminated in every case, by prolonged boiling of the alkaline solution, an operation which either drives off some of the reducing compounds or renders them inert. After boiling it is essential that the solution should be considerably diluted and neutralized with dilute rather than concentrated acid. Under these conditions the rise in temperature is small and the influence of organic matter is minimized.

For the accurate determination of chromium in used liquors containing dissolved hide substance, the ordinary gravimetric method is quite exact and fairly rapid in the absence of iron and aluminum compounds. A volumetric method which is not affected by organic matter, is based upon a suggestion made by Procter[3] and involves the use of a modified fusion mixture. It is found that when chrome liquor is evaporated to dryness with a mixture of 60 per cent. magnesium oxide and 40 per cent. sodium carbonate and the residue strongly heated, very little fusion takes place and the mass can be almost completely removed from the dish by a jet of water from a wash bottle. The determination of chromium by this method may be carried out as follows:—25 cc. of chrome liquor are measured into a platinum dish containing from 2 to 5 grams of the above fusion mixture and evaporated to dryness on the water bath. The dried residue is at first heated gently over a Bunsen flame and then strongly ignited for about 10 to 15 minutes, stirring occasionally with a platinum wire so as to bring all of the mixture in contact with the hottest portion of the dish. The bulk of the fused cooled mass is washed into a suitable flask with water, any portions adhering to the

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[3] *Leather Ind. Lab. Book,* 1908, p. 265.

dish may be readily dissolved in a small quantity of warm acid and added to the contents of the flask. An excess of hydrochloric or sulphuric acid is then added, the solution cooled, and titrated with thiosulphate after adding potassium iodide and starch. In some cases it may be necessary either to dilute the original chrome liquor or to make the acidified oxidized solution up to a definite volume and titrate an aliquot portion. The addition of 3 per cent. of gelatine peptones to chrome alum solution of known strength, had no effect on the result when chromium was determined by the above method. This might have been anticipated for it is obvious that gelatinous matter will be decomposed by the above treatment.

Apart from the desirability of knowing the correct amount of chromium in a liquor, it is apparent that an incorrect determination of it will lead to an entirely erroneous conception of the basicity of a liquor, when considered in conjunction with the acid determined by titration. As the tanning properties of a liquor are usually judged by its basicity, it is essential that the influence of organic matter on the figure should not be ignored.

The author has found that a rapid and efficient control of the single bath process may be maintained by means of a simple analytical method which probably gives information of greater significance than the chrome and acid determinations in a liquor. The limits within which any chrome liquor will tan are fairly well defined and are dependant not only upon the concentration of chromium but also upon the concentration of acid. When the ratio of acid to chromium exceeds a certain limit, tanning proceeds very slowly, if at all. It is well known that the neutralization of the excess of acid by the addition of a suitable alkali will bring the liquor to a point where tanning will proceed. If the neutralization of the liquor be continued still further, a point is reached where basic chromium salts are precipitated and are either rendered unavailable for tanning or are only capable of slow combination with hide substance. It seems probable that tanning will proceed at the greatest speed when the liquor is almost, but not quite, at the precipitating point. This point may be determined for any given liquor and is suggested as a means of controlling the tanning process.

The chrome liquor is mixed with kaolin, filtered, and 10 cc.

of the perfectly clear filtrate measured into a beaker of about 50 cc. capacity. A N/10 or N/20 solution of alkali such as is ordinarily used for neutralizing the liquor in the process (borax, sodium bicarbonate, sodium carbonate, etc.) is slowly run into the beaker from a burette. The precipitate which at first forms is redissolved as the beaker is agitated, but finally a point is reached where a permanent turbidity is produced in the chrome solution. For the sake of convenience this is called the precipitation point. For any solution it is well defined and duplicate titrations under the same conditions agree fairly closely. From this titration it is easy to calculate the quantity of alkali which must be added, to bring the liquor in the paddle or drum to the precipitation point. Although it is beyond the scope of this paper to deal with the practical application of the method, it may be mentioned that the precipitation point is a danger point which may be easily passed when neutralization of the liquor is not properly controlled.

The stage of the process at which alkali should be added must be determined by the individual operator, as no rule can be laid down to cover all conditions. When pickled stock is being tanned, the chrome liquor may be brought more nearly to the precipitation point, than when unpickled stock is dealt with, as the acid contained in the former will tend to prevent the precipitation of chrome compounds on the surface of the leather. It must also be remembered that during the tanning process, liquors become more acid as tanning progresses, so that a liquor which may have been brought close to the precipitation point at one stage, does not necessarily remain at that point during the remainder of the process. There is reason for believing that the point at which chromium salts are precipitated from solution is influenced by the presence of various salts,[4] but as the sample analysed is drawn directly from the drum or paddle in which the tanning is being carried out, the precipitation point determined by titration, must be correct for the liquor under observation. The method is an empirical one, but in the hands of an intelligent worker may prove

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[4] This view has recently been proved to be correct by Wilson and Kern (this JOURNAL, p. 445), who find that the addition of various salts to a given chrome liquor has a very marked effect upon its precipitation point.

to be a useful addition to the available methods for the control of the single-bath tanning process.

The author takes the opportunity of thanking Mr. Erwin J. Kern for his assistance in carrying out the experimental work connected with this paper.

THE ACTION OF NEUTRAL SALTS UPON CHROME LIQUORS.

By John Arthur Wilson and Erwin J. Kern.

During a discussion[1] at the last annual meeting Dr. Klaber pointed out that the addition of salt makes possible the use of more basic chrome liquors and he wants to know why this is so. Can it be that the chromium compounds are present in the colloid state and that the salt exerts upon them some stabilizing influence? This seems very unlikely since the addition of even small quantities of electrolytes to chromium hydroxide sols results in precipitation. But the effect of the addition of salt is none the less certain, as shown by the following experiment.

Solution A was prepared by diluting 20 cc. of a stock chrome liquor to 100 cc. and solution B by diluting 20 cc. of the stock liquor plus 0.4 gram molecule of sodium chloride to 100 cc. (Analysis showed that the diluted liquors contained 13.7 grams of chromic oxide per liter. The liquor used was a basic chromium sulphate solution.) Ten cc. of each solution were taken and rendered more and more basic by adding tenth-normal sodium hydroxide from a burette. When 3.7 cc. of the standard alkali had been added to each, basic chrome salts began to precipitate in solution A, but solution B remained clear. The point at which precipitation began was determined by the first appearance of turbidity when looking through a thin layer of the solution. No precipitation occurred in solution B until 7.0 cc. of alkali had been added.

In both cases precipitation was due to the reduction of the acidity of the liquors and the difference in results obtained would indicate a difference in acidity, but the addition of sodium chloride could hardly produce an increase in quantity of acid. To make certain on this point, both solutions were tested as follows: 10 cc.

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[1] This issue, page 458.

of solution were diluted to 400 cc. and boiled. Phenolphthalein was added and the boiling solution titrated against tenth-normal NaOH until a faint pink color persisted in the solution after the precipitate had settled. In each case 30.5 cc. of alkali were required, indicating that the total acidity of each was the same.

Although the same quantity of acid per liter of *solution* is present in both cases, this is not true as regards the quantity of acid per liter of *solvent,* for in solution B about 10 per cent. of the volume is occupied by sodium chloride molecules or their ions, and thus the concentration of acid in the *water* of solution B is actually greater than in solution A. This explains the difference in a qualitative way, but how does it work out quantitatively? Solution C was prepared by adding 0.04 gram molecule of sodium chloride to 10 cc. of solution A. If this explanation were sufficient, equal volumes of solutions A and C would require equal volumes of standard alkali to start precipitation, but 6.8 cc. of tenth-normal NaOH were required by solution C. The effect of the volume occupied by the salt is evidently not very great. That there is some much greater cause is shown by the difference between the results of solutions A and C.

The consideration of the portions of the volume of a solution occupied by solvent and solute recalls the large amount of work done recently on the hydrate theory of solution. A clear conception of this theory can be gained by reference to the work of H. C. Jones,[2] who has given convincing evidence in support of the view that all electrolytes in solution are hydrated; *i. e.,* that they have combined with some of the solvent. If this be true, then in solutions B and C the salt has actually lessened the volume of solvent by combining with a portion of it, and on this basis we can explain the difference between the results of solutions A and C. When 3.7 cc. of standard alkali had been added to each, the *quantity* of acid remaining in each was the same; but the *concentration* of acid in solution C was greater, due to its lesser volume of solvent, part of the water having combined with the salt. This greater concentration of acid required more alkali to start precipitation. It should be emphasized that it is necessary to distinguish between quantity of acid per liter of *solution* and quantity of acid per liter of *solvent.* Other factors being equal, it is

[2] "The Nature of Solution" (D. Van Nostrand Co., 1917).

the value of the latter which determines the point at which precipitation of the chrome begins.

According to the theory, those salts are hydrated in solution to the greatest extent which crystallize with the largest number of molecules of water, but all electrolytes are hydrated to some extent. The determinations listed in Table I were made in order to ascertain the relation between the degree of hydration of neutral salts and the power their addition to a chrome liquor has of increasing the amount of alkali which can be added without causing precipitation.

Each solution represents 10 cc. of solution A plus the stated number of gram molecules of the *anhydrous* salt. Where a salt was added in excess of its solubility, the excess readily dissolved in the first portions of standard alkali added. Only neutral salts were used and they were the purest obtainable. Each salt was tested by dissolving in water and introducing strips of litmus paper. Both red and blue litmus remained in each solution without changing color.

TABLE I.

Solution composed of 10 cc. of solution A plus	No. cc. tenth-normal NaOH required to start precipitation
(No salt added)	3.7
0.02 gram molecule of potassium bromide	3.9
0.02 gram molecule of potassium chloride	4.0
0.02 gram molecule of potassium nitrate	4.2
0.02 gram molecule of ammonium chloride	4.5
0.01 gram molecule of sodium chloride	4.5
0.02 gram molecule of sodium chloride	5.4
0.03 gram molecule of sodium chloride	6.2
0.04 gram molecule of sodium chloride	6.8
0.02 gram molecule of magnesium chloride	6.2
0.02 gram molecule of magnesium sulphate	10.5
0.02 gram molecule of sodium sulphate	11.4
0.02 gram molecule of ammonium sulphate	11.6

The evidence in support of the view that the property of salt noted by Dr. Klaber is due to hydration is very strong. G. M. Smith[3] calculates that at infinite dilution a potassium ion would have 9.6, an ammonium ion 10.7 and a sodium ion 16.9 molecules of hydrated water. Our results for the chlorides of these metals are in the same order; for 0.02 gram molecule of salt, we get for potassium chloride 4.0, for ammonium chloride 4.5 and for sodium

[3] *J. Am. Chem. Soc.*, 37, 729 (1915).

chloride 5.4. The figures given by Smith must not be compared with the number of molecules of water of crystallization of a salt. His figures are calculated for ***infinite*** dilution and decrease rapidly as the concentration increases. On the other hand, while the number of molecules of water combined with *one* molecule of the dissolved substance decreases with increasing concentration, the *total* quantity of combined water of the system increases. Magnesium chloride which crystallizes with six molecules of water gives a higher result than the same number of gram molecules of any other chloride used. Next in line comes magnesium sulphate which crystallizes with 7 molecules of water and then sodium sulphate which crystallizes with 10. The highest figure of all is obtained with ammonium sulphate which crystallizes together with chromium sulphate forming an alum containing 24 molecules of water.

The importance of Table I lies in the relative and not the absolute values of the results. The relative order of these salts ought to be practically the same for any chrome liquor, but the absolute values are affected by numerous factors. It will make some difference whether the chromium salt is a chloride or sulphate if NaOH is used to reduce the acidity, because the sulphate of sodium is more strongly hydrated than the chloride. The presence of strongly hydrated salts in a chrome liquor will affect the hydration of the salts added and chromium sulphate itself is very strongly hydrated and many liquors contain sodium sulphate in addition. Another important factor is temperature; the warmer the liquor the lower will be the results, because a rise of temperature decreases the degree of hydration. In his book Professor Jones gives a few examples showing that, with many salts, the number of molecules of water of crystallization is larger the lower the temperature at which the salt crystallizes. Some of these are reproduced in Table II.

No special precautions regarding temperature were taken with the chrome liquors in Table I, but all determinations were made at the same time and under identical conditions, the temperature of the liquors being about 33° C. The liquor containing no added salt required 5.0 cc. of standard alkali when at 25°, but after its temperature had been maintained at about 33° for 24 hours, only 3.7 cc. of alkali were required. All that Table I aims to do is to show that the greater the degree of hydration of a salt the greater effect its addition to a chrome liquor has of increasing the amount of alkali necessary to start precipitation. A more exact treatment would be of great value and ought to be undertaken by some university or other laboratory having the necessary time and facilities.

TABLE II.

Composition of crystals	Temperature of crystallization Degrees C.
$MnCl_2.2H_2O$	20
$MnCl_2.4H_2O$	15
$MnCl_2.6H_2O$	—21
$MnCl_2.11H_2O$	—21 to —37
$MnCl_2.12H_2O$	—48
$FeCl_3$	above 80
$FeCl_3.2H_2O$	80 to 60
$FeCl_3.2\frac{1}{2}H_2O$	60 to 40
$FeCl_3.3\frac{1}{2}H_2O$	20
$FeCl_3.6H_2O$	20 to —16
$MgCl_2.8H_2O$	above 20
$MgCl_2.6H_2O$	
$MgCl_2.10H_2O$	20
$MgCl_2.12H_2O$	—10 to —12

But even without any more exact data, the subject has a deep significance to both chemist and tanner. For the control chemist it is a warning not to place too much reliance on our provisional method for the determination of basicity of one-bath chrome liquors, without taking into consideration the amounts and kinds of electrolytes present in the liquor. It is possible to have two liquors having the same concentration of chromic oxide and both just at the precipitating point, and yet by the provisional method they will show different degrees of basicity due to difference in salt content. The danger of adding to a chrome liquor an amount of acid calculated from total acidity only is made clear by noting the concrete case of aluminum chloride, which is typical of the strongly hydrated salts. In what we call a twice-normal solution, about five-sixths of the water present is in a state of combination, so that the solution is really about twelve times normal. In this case, if we had calculated on the basis of the total volume of solution how much acid to add to produce a given increase of concentration, we should have an amount which would produce at least six times that increase in concentration. In one-bath chrome liquors we are dealing with solutions of very strongly hydrated salts.

The practical tanner will find it of interest to experiment with salts of different degrees of hydration. By adding certain salts to his chrome liquors, he can produce the effect of an increase in acidity without the necessity for neutralizing later on, since neutral salts are more readily washed out of the leather than strong acids. The nature of the subject invites both tanners and chemists to assist in increasing our knowledge of the rôle of neutral salts in chrome tanning.

DISCUSSION ON THEORIES OF LEATHER FORMATION

at the Atlantic City Meeting, June 9, 1917.

THE PRESIDENT: The next feature of the program is a formal discussion of some of the recently advanced ideas on the theory of leather formation. Three papers relating to this subject were published in our JOURNAL in the April number, by John Arthur Wilson, who has had the experience of working under Professor Procter. Mr. Wilson will open this discussion.

MR. WILSON: It was originally intended that I should read to you my recent paper on Theories of Leather Chemistry, but that will hardly be necessary in view of the fact that it has been in your hands for nearly two months.

I regard the discussion which is to follow as being of very great importance in emphasizing the direction of the service of the chemist to the leather industries. Until such time as we had obtained some good working methods of analysis, it was necessary to devote time to their perfection, but our chief service to the tanner should lie in our ability to assist him to make better and less costly leather. It is not to our credit to have to admit that as regards the manufacture of leather, the practical tanner is far in advance of the leather chemist, and it behooves us as chemists to do more to advance our science and its application to leather manufacture. I hope that the present discussion will prove to be a good start.

I have been asked to comment on the paper by A. W. Davison on "The Adsorption of Chromium Oxide by Hide Powder," reprinted in the June JOURNAL. Since the author states that this is only a preliminary to some extended work on the theory of tanning which is to be carried out at the University of Cincinnati, I should hesitate to offer any criticism that might possibly be discouraging were it not that I feel sure that Mr. Davison, like the rest of us, is concerned only with getting at the actual facts.

Mr. Davison appears to be under the erroneous impression that he is dealing with chromium compounds present only in two phases. If he will refer to the recent papers by Prof. Procter and myself, he will find that in the case of gelatin and HCl solutions at equilibrium, we dealt not only with the concentrations of acid in the solution and in the jelly phase, but with a further portion of acid which had been removed from solution by the gelatin. In the case of chrome tanning we have chrome present in at least three phases: That present in the solution surrounding the hides; that present in the solution absorbed by the substance of the hide; and that portion "fixed" or removed from solution by the hide. In Mr. Davison's work, the chrome fixed by the hide powder is included in the so-called "concentration of chrome in the solid phase."

To add to the complications, the fact has been neglected that with increasing concentration of the various salts present there will be a diminution of volume of the solid phase of the system. Furthermore, the author seems unaware that his figures would have been altered entirely by a change in the basicity of his liquors.

I think I need not go further in citing what is quite obvious, but would point out that in my opinion, Mr. Davison's greatest mistake lies in his assumption that no compounds between hide powder and tanning agent have been formed merely because he has obtained a smooth curve resembling an adsorption isotherm. I have been able to prove in the case of a colloid jelly, that if the colloid molecule combines with a dissolved electrolyte after the manner of NH_3 and HCl, the curve representing combined acid will be of the nature of a so-called adsorption isotherm.

I hope to be able to present this to you in some later publication.

THE PRESIDENT: While he is not on our program, we have here with us Dr. Arthur W. Thomas, of Columbia University, who has recently been associated with Mr. Wilson. I will call on Dr. Thomas to continue the discussion.

DR. THOMAS: Mr. President:—I came here to-day as a colloid chemist, much impressed with the work that Mr. Wilson has published during the last two years. The present popular notion of colloid chemistry, or of those who are thinking of taking up colloid chemistry, is that they are dealing with a subject that is full of mystery, entirely different from the chemistry we have been familiar with. This is a notion which I wish to dispel.

Before I mention a few points in Mr. Wilson's paper, I wish to add to the criticism of the paper by Mr. Davison, of which Mr. Wilson has just spoken. In this paper, Mr. Davison states that an inspection of his curve—the adsorption curve of chrome by hide powder—will reveal the fact that no breaks exist, and he further states that according to the Phase Rule, since no breaks occur in the curve, no compounds between the hide powder and the tanning agent have been formed. He concludes that in the case of chrome tanning, the contention of the physical theorists that the first step is one of pure adsorption has been verified.

Now that is the sort of thing we are getting not only in leather chemistry but in all branches of chemistry at the present time—the mysticism of the adsorption isotherm. Let us do the same experiment that Mr. Davison has done, but let us use charcoal instead of hide powder, and analyze products and plot concentrations. We shall get the same smooth curve, a parabola, or if we plot the logarithms of the numbers, we shall have a straight line, and since we get the typical adsorption curves, we proclaim that we know all about what is going on. The fact of the matter is that the adsorption isotherm shows us very little. It is merely the expression of an equilibrium relationship between the substance dissolved in the liquid phase and that dissolved in the solid phase, like the partition say, of benzoic acid between water and ether, where ether could be considered an adsorbing substance, if you wish to put it so.

Within the past year our ideas have been rapidly turning over, and the purely physical theory of adsorption is being discredited, due to the fact that some of our adsorption reactions are not reversible; therefore they are not purely physical; some chemical reactions must have taken place. Some of the more radical chemists are insisting that chemical compounds are formed. It is my impression that chemical compounds are formed in tanning by means of chrome. Now do not think for a moment that I am discrediting colloid chemistry, the science I am working in and teaching, for colloid chemistry appears to be the only kind of chemistry that is going to tell us just what reactions take place.

Consider the chemical reactions between molecules; for instance the mystery of copper sulphate having 5 molecules of water combined with it. According to our older ideas of valence and chemical affinity, there is nothing there to bring about a combination, but nevertheless we get such, and the familiar blue crystals. Such phenomena are leading us to the idea of molecular affinities. Hence, in the tanning of hide, consider the hide fiber as a mixture of chemical compounds, not one individual, but a mixture of exceedingly complex chemical compounds, reacting with another chemical compound. We have there action between molecules, and the statement by Davison that there are no chemical compounds formed, is too sweeping. He does not prove it. He merely shows that it agrees with the adsorption curve.

The argument may be raised against the chemical theory, that we do not have a combination of simple whole numbers, and according to our theories of chemistry, only simple whole numbers of molecules will combine. Fractions cannot combine, and it may be argued that since we have fractions concerned in the case of hide powder and chrome the union must be physical. There is no ground for such a conclusion, for our hide substance is composed of a mixture of very complicated compounds of high molecular weights, and how do we know that the apparent fractions may not be simple whole numbers? There is absolutely no way to prove it, so far as our present knowledge goes.

In regard to the work of Mr. Wilson—he has been pointing out the chemical relationships in tanning, and some of you who have read a few of our present books on colloid chemistry are probably inclined to criticise some of Mr. Wilson's statements; but if we consider, as I have pointed out, that our adsorption reactions may be chemical reactions, we come around to Mr. Wilson's theory. He has probably been a little ahead of his time in the development of the theory of colloid chemistry in leather manufacture.

THE PRESIDENT: I will call on Dr. Balderston to continue this interesting discussion.

DR. BALDERSTON: My strongest feeling in getting into this discussion is that I do not belong. My work has been more technical than scientific, and it is rather ridiculous for me to say anything on this topic in the presence of men who have been at the front, so to speak, in colloid chemistry investigation. Permit me at least to ask some questions. We have had quite a lot in print during the last few years in regard to tests for the completeness of chrome tannage, and figures have been given for the minimum quantity of chrome which must be present in chrome leather in order that it may be considered to be completely tanned. A recent paper by Lamb and Harvey, referred to in one of Mr. Wilson's papers, gives a minimum figure of about 3 per cent. Mr. Wilson speculates in regard to the possibility that 3.8 per cent. of Cr_2O_3 in a chrome leather may represent what you might call a monochrome salt of gelatine and chromium, the first of a series of chrome leathers, winding up with a polychrome leather. I suppose at the other end of the series we may place the sample which Seymour-Jones tells about, which remained for years in a wheel, and when taken out and analyzed showed 84 per cent. of chrome.

It is very difficult to exhaust a chrome bath by means of hide. If fresh pickled hide be placed in a chrome liquor which has only 0.08 per cent. of chrome, and left in two days, the amount of chrome will be reduced only about one-half, in spite of the fact that we have at least five times as much hide as could be tanned by the amount of chrome present in the liquor. Such facts suggest that the formation of chemical compounds between the chrome and the hide is at least open to question. In many instances it is necessary to have large excess of one constituent in a reaction in order to bring all of the other constituent into combination, but the excess in this case seems very heavy.

I am glad to have heard what Dr. Thomas said in regard to the present trend of belief about these reactions which are in the borderland between physical and chemical processes. It is encouraging to one who feels very ignorant about the theory of these things to find that those who know most feel that there is something yet to learn.

Of course Mr. Davison's conclusions are untenable, we will have to admit that, but it is scarcely surprising that on a first approach to the problem of chrome tanning (and it is evidently a first approach on his part, as he did not even know how to make the analyses) he assumed that there are only two phases present, one solid and one liquid. As a matter of fact there are no doubt several solid phases, and this is no doubt largely the reason he was led into an untenable position.

One of my regular tasks when I was a teacher, in criticising students' work, was to cut out from their note-books such statements as these: "it is thus proved," "we have therefore demonstrated," and substitute such words as "these results make it seem probable that." More than one series of experiments is necessary to prove anything, in leather chemistry or elsewhere.

I wish to ask two questions of Mr. Wilson and Dr. Thomas. First, whether it is possible that our failure to exhaust the chrome bath, the almost impossibility of exhausting it in practice, may be due to the passing over of a portion of the chrome which was originally in the solution in colloid form, into the crystalline modification of chromium sulphate, which, as Procter has shown, does not tan. I have often noticed that when strong light falls on the low strength bath in the chrome tannery, a distinct violet color shows in the bath, while in the stronger baths the color which shows is only green. So I have wondered whether our failure to exhaust the bath was due to the process being one of adsorption, so that an infinite excess of hide would be necessary to cause complete exhaustion, or whether it is because a part of the chrome has passed over into a condition in which it cannot combine with hide.

The other question is this—Do Mr. Wilson and Dr. Thomas consider that if the co-precipitation of colloidal hide-substance and colloidal tanning agent, due to electrical attraction, be established, this fact of co-precipitation will constitute sufficient proof of actual chemical combination?

MR. WILSON: In Seymour-Jones' piece of leather, the greater part of the 84 per cent. of chrome oxide was probably precipitated in the leather and not chemically combined with it.

When a piece of hide will not take up chrome from a weak liquor, it is generally due to excessive acidity, and if this be reduced sufficiently, the hide will probably then take up the chrome. By a proper control of acidity I have been able nearly to exhaust chrome liquors without ever reducing the acidity to the point where basic chrome salts begin to precipitate. In chrome tanning we are dealing with hide, which acts as a very weak acid, and chromic hydroxide, a very weak and slightly soluble base, and for this reason small changes in acidity produce great differences in the amount of chrome which a hide will take up.

The only explanation I can give as to why a hide will not take out the last traces of chromium is something of a speculation. As a liquor becomes more dilute and nears the neutral point, there is a tendency for the chrome molecules to polymerize, thus forming colloidal particles which are positively charged. Since all chrome tanning takes place on the acid side of the neutral point, the hide molecules likewise will be positively charged and, therefore, would repel the colloidal chrome particles.

In regard to your last question, it is our opinion that vegetable tanning is a chemical reaction, consisting of the combination of oppositely charged colloids followed by co-precipitation. On page 79 of the March JOURNAL you will find a formula representing the differences of potential concerned and therefore a measure of the forces tending to cause combination. Leathers of all different degrees of tannage can be produced, but we believe that these are really mixtures of different compounds. Different degrees of tannage might be considered as representing different degrees of saturation of the hide by tannin.

MR. YOCUM: Mr. President, I happened to be in England in 1908, and Mr. Jones showed me a sample of the leather that he had had analyzed by Prof. Procter, showing 80 per cent. or more of chromium oxide. This sample—I do not care to go into a discussion about how it got there or why or because or underneath or overhead or around, but he had put a sample of leather on the drum that he was using for tanning his skins. This piece was about 12 inches square, 12 by 16, I think it was, and was put near the axis of the wheel, and it stayed there for two years. Subsequently it was taken out and the Professor got a sample of it analyzed and made this report of 84 per cent. or something of that sort. I saw another piece and it was just like a piece of bone; it wasn't leather any more.

Now it is not quite fair to use that, because that was an exception. It is not quite fair to use that as a measure of the total result that ultimate chroming or chrome tanning might result in; and I think that also indicates that the possibilities of gain in weight, and so on, in the chrome have not as yet been arrived at. In other words, everybody here has been talking about how quickly you can do things; the facts are that time is an element that has not been quite well regarded, and time in chrome tanning, as well as time in bark tanning, must be considered.

THE PRESIDENT: Dr. Klaber, will you continue the discussion?

DR. KLABER: Mr. President—I am not going to take up very much time, because I find myself exactly in Dr. Balderston's position. I find myself very much at sea. However, I have reviewed some of the theories that have been propounded in regard to tanning, those of Fahrion and Moeller and Sommerhoff, and lastly the theory of Professor Procter and Mr. Wilson. I do not wish to take time to go into detail about these. I may state that Fahrion's original theory was one of oxidation. Moeller's theory is one, the point of which, I must say, I fail to get. Fahrion criticises it on the basis that it is a purely chemical theory. He rather sneers at it as a chemical theory, whereas I find that he depends very much on a chemical reaction for the basis of his theory. It seems to me that Professor Procter and Mr. Wilson have certainly played safe in saying that tanning is a colloidal co-precipitation. I notice Mr. Wilson says they believe that compounds are formed, but I judge from what Mr. Wilson has said also that these compounds are formed subsequently, and that at first the action both in bark and chrome tanning is colloidal co-precipitation. I must say that as I read over the literature on the subject and think about it, the more I realize that the full truth has not been discovered.

MR. KELLY: I wish to ask Mr. Wilson whether the presence of inorganic salts has any effect on the adsorption of the chrome?

MR. WILSON: I should say yes, because they affect both the volume and the electrical charge of the hide substance.

DR. KLABER: I should like to ask whether the salt which is added in one-bath tanning does not merely preserve the colloidal solution and prevent precipitation?

MR. WILSON: I do not see how the presence of salt can preserve the colloidal solution.

DR. KLABER: Very basic liquors can be used in conjunction with salt, whereas if they were used alone the chrome would precipitate out of the solution. Evidently there is some action of the salt in maintaining the solution.

MR. WILSON: Are you sure that is the case?

DR. KLABER: Absolutely sure of it.

MR. WILSON: I shall have to think that over.*

DR. THOMAS: Of course, it is well known that salts aid in the swelling, and instead of having a preservative action on the colcoidal nature of the solution, it might be that the salt acts first of all on the hide, the colloidal chrome itself not having the property of causing the swelling of another colloid. On the other hand, it is probably because of precipitation.

In answer to the question that Dr. Balderston brought up as to whether mutual precipitation of colloids could be regarded as chemical, I would say "Yes," inasmuch as it is absolutely impossible to get a colloid free from traces of salts. A colloid owes its very existence to a small amount of electrolyte. For example, a colloidal chrome owes its stability—(consider it for a moment really a precipitate in solution, for that is what a colloid more or less is)—or its solution tendencies to small amounts of chromium ion from chromium sulphate, or if you want to put it so—chromium sulphate; and the chromium ion being positively charged, gives the positive charge to the particle.

On the other hand, if you consider a negative colloid, such as arsenious sulphide, it is always formed in the presence of a slight excess of hydrogen sulphide. That is borne out by the fact that when you analyze these colloids, you find that there is always an excess of some reagent such as the H_2S or S in the As_2S_3 colloid.

THE PRESIDENT: I will ask Mr. Robert W. Griffith to add to the discussion.

MR. GRIFFITH: I don't wish to detain the meeting any longer than necessary, but I have been very much interested in the work of Prof. Procter and Mr. Wilson, and I welcome the addition of a new investigator in Mr. Wilson, and also, I hope, Dr. Thomas, and I am sure they will contribute much valuable information to the subject.

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* The paper by Wilson and Kern, p. 445, is in answer to this question.

Going over the ground quickly, and dealing first with what Dr. Balderston has just said about chrome tanning, I would say that I happened to have charge of the tannery where this wonderful piece of leather was made. As Mr. Yocum has said, it happened as a result of a piece of hide being jammed in the tanning wheel, and was found there after a considerable period, and after many tanning solutions had passed through. It was not a piece of leather at all; it was a piece of metal.

It is difficult to offer any constructive criticism on the researches of Procter and Wilson in the field of colloidal investigation, and many of their conclusions, while necessarily hypothetical, will find a wide acceptance. I would point out that there is a difference between a hypothesis and a theory. When we have established our theory, it will be proved in practice. A hypothesis will always remain a supposition and will not hold good until it has been proved. Theory and practice should always go hand in hand. At present in the tanning industry, there is no doubt that they are very wide apart, but it is just this kind of work and this kind of discussion which, I hope, will eventually lead to their coming close together.

Any scientific explanation of the complex process by which the union of tannins and hide substance yield leather must appear obscure to the non-technical mind. The chemical reaction involves substances whose chemical constitution is but imperfectly known, and the physical aspect introduces a process of reasoning which is difficult to apply in a practical way, yet it would appear that physical chemistry will contribute more to a proper understanding of our subject than the hypothesis of molecular reaction.

There is a certain mechanism in the combination of hide substance and tannin, involving the fibrous construction of leather, which renders it difficult to explain leather formation as a "salt" product. The compounds which enter into the combination are too susceptible to change to permit of chemical formulae being employed to express the result of their union, and even if such were possible, the proof of molecular reaction would be found in synthetical reproduction, and this presents a very remote prospect at this time. As one of the authors has remarked, it is doubtful whether an exact knowledge of the chemical constitution of hide fiber would be of great assistance in the art of tanning. There are, however, many features of the tanning process, the better understanding of which will contribute greatly to the scientific advancement of the industry.

The behavior of colloids, for instance, a study of which has been the subject of recent investigation by Procter and Wilson, cannot fail to contribute valuable data, particularly when these are studied under the conditions which obtain in actual tanning processes, and much remains to be done in this direction.

The study of the application of the law of osmose in the tanning process, of dialysis, of the various solubilities of colloids and crystalloids, and their relative diffusion, and the influence of mass action, are all fertile fields for investigation and research which will yield results capable of practical application.

Let us consider the product of rapid tannage and its tendency to yield too large a proportion of water-soluble matter in its first contact with wearing conditions. What are the conditions which govern the fixation of tanning matter in the production of good leather?

I have been very much interested in the theory of leather formation and have followed it for many years, and I am sorry that no reference has been made to the work of previous investigators. Nierenstein was the first, I believe, to advance the theory of salt formation, and it became the subject of considerable discussion, but was finally abandoned.

Stiasny, some years ago, reviewed the whole field of the theory of tanning, and his work was, I consider, a very valuable addition to the subject. Stiasny's conclusions were, although not definite, that tanning was divided into two divisions, physical and chemical. Primarily, he regarded tanning as an adsorption process, and there were secondary changes of a chemical nature which took place.

Fahrion advanced the theory that the secondary changes were confined to a process of oxidation, which was responsible for the fixation of the tannin.

Both latter theories have appealed to me very strongly. They hold good in both mineral and vegetable tanning. In connection with mineral tanning, I am inclined to the theory that there is a dialysis of the chrome salt, whereby the basic portion was adsorbed and the free acid liberated.

In the case of vegetable tanning, I have thought that the vegetable acid, which we call tannic acid, has a corresponding aldehyde and in the last analysis, I think that you will find that the fixation of all vegetable tanning matter depends upon the formation of aldehyde.

A study of the diffusion and the adsorption of crystalloids and colloids will contribute to an understanding of the conditions which operate in leather production. The rapidity with which tanning matter diffuses throughout the mass of hide substance varies under different conditions. Crystalloids are known to possess greater activity in this respect than colloidal solutions, but they do not enter into as permanent a combination or fixation as the latter.

An interesting problem is offered in a consideration of a method to overcome the resistance which the colloidal mass of hide substance offers to the penetration of colloidal tannin solution, by which such resistance is lessened by a preliminary treatment of the hide substance with a crystalloid possessing high ionization.

The problems of leather production are as varied as the uses to which leather is subjected, but the fundamental principles are common to all tanning processes, and such light as may be thrown upon one problem contributes to the illumination of the whole.

[This discussion was submitted before publication to Mr. A. W. Davison, whose paper on the adsorption of chrome by hide powder is criticised. He has not had time to prepare an answer, but one may be expected in the October issue.—Ed.]

NIGROSINE.*

By J. Merritt Matthews, Ph. D.

The Nigrosines are a class of grey or black dyes belonging to the general group of what is known as "induline" dyes. There are several varieties of nigrosines which will be explained as we go along. The general method of making nigrosine is to melt together a mixture of aniline oil, nitrobenzol, aniline salts and iron. The reaction is carried out in a large iron kettle provided with a good stirrer and suitable arrangements for heating to the required temperature and for properly regulating the temperature between certain limits. Provision must also be made in connection with this melt kettle for the condensation of the volatile constituents which are given off during the progress of the reaction. The exact reaction taking place in the preparation of nigrosines or other indulines is not known. A mixture of highly complex bodies is no doubt produced, the aniline probably being oxidized by condensation with the nitrobenzol with the formation of complicated phenylated anilide derivatives.

After the nigrosine melt has been finished, the excess of aniline oil which is always present must be recovered by a process known as stripping, and the dyestuff, which resembles a tar-like body must be isolated by proper treatment so as not to get it into a gummy mass which would ruin it for use. The product at last obtained is a black powder and is known as spirit soluble nigrosine, blue shade. This variety of nigrosine is not soluble in water, but has to be dissolved in such solvents as alcohol, benzol, solvent naphtha, etc. In color it is quite blue in shade and is not a true black. For present consideration this variety of nigrosine is not of any special interest to us directly as a dyestuff, but only as serving as a starting point for the preparation of another variety of nigrosine known as water soluble nigrosine. This latter dyestuff is made from the spirit soluble color by suphonation, which is the name of a process whereby the spirit soluble nigrosine is treated with concentrated sulphuric acid. This reaction requires great care and a skilful manipulation in order to produce the resulting dyestuff in the proper marketable form. The effect of the sulphuric acid is to combine with the nigrosine to make a new

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* Read at the Atlantic City meeting, June 8, 1917.

compound also of a bluish black color, but which is soluble in water, and partaking of the nature of an acid dyestuff. This dyestuff appears in trade in the form of small glistening lumps being cracked up in conchoidal fractures. This rather peculiar form is due to the method of parting it out from its sulphuric acid mixture and subsequent drying. Some might perhaps think that the dyestuff was in the form of crystals, but such is not the case; the presumed crystals are merely small irregular lumps.

The water soluble nigrosine is the product which is employed for the dyeing of leather. It is employed as an acid dyestuff. For the purpose of rendering the dyestuff solution acid, either formic or acetic acid may be used.

The nigrosine obtained in this manner, as already explained, is of a blue shade. In order to produce a jet black color, it is necessary to add to the nigrosine itself a suitable yellow dyestuff for the purpose of toning it to a neutral jet shade. Metanil yellow, a well-known acid dyestuff, is mostly employed for this purpose. In order to obtain proper results the yellow dyestuff should not be simply mixed in with the dried nigrosine, but must be skilfully added during the process of manufacture of the coloring matter, so that the resulting compound is not simply a mechanical mixture of the two dyes, but is really a combined and unified product. The jet shade of nigrosine is very similar in appearance to the blue shade, being in the same form of small cracked lumps, sometimes spoken of as crystals.

Nigrosines are apt to vary much in quality, strength of color and color tone. In testing a sample of water soluble nigrosine, it should first be noted whether it is completely soluble in water; poor grades of nigrosines will sometimes show a considerable amount of insoluble matter, which is not only useless but also detrimental for dyeing purposes. The color tone should be observed by comparison with a standard sample; this is also true for the determination of the color strength. A convenient method of testing is to dye two small silk skeins with equal quantities of the sample to be tested and the standard sample under like conditions, and then noting the intensity and tone of the color obtained. The jet shades of nigrosines will vary in tone depending upon the amount and purity of the yellow dye employed in shading. A clear neutral tone of grey is desirable, a reddish or muddy tone indicates an inferior quality of nigrosine. A rapid test which will furnish a fairly good idea of the quality of the sample is known as the "dip" test. Equivalent solutions of the sample under test and the standard sample are prepared and strips of filter paper are simultaneously dipped in and taken out of the two solutions. The strength of the solutions should be such that a moderate shade of grey is obtained. After drying the depth of color and the tone of the two paper colors are observed and compared. This method is not so accurate as the dyeing test, but furnishes a rough approximation of value. Of course, for purposes of leather dyeing the final and most conclusive test of the comparative value of two samples of nigrosine is to make representative test dyeings on leather.

There is another dyestuff known as nigrisine, which is sometimes confused with the foregoing, but which, however, is entirely different. Besides being spelled somewhat differently, being "nigrisine" instead of "nigrosine," it is also prepared in a totally different manner, being made by boiling an alcoholic solution of nitrosodimethylaniline hydrochloride. This dye is also known as methylene grey and malta grey. It is in reality a basic dye, and is used to some extent in cotton dyeing and calico printing, but has no especial use in leather dyeing.

Previous to the outbreak of the war nigrosine was made in this country to a considerable extent by several chemical factories, though not in sufficient quantity to take care of all our needs. Since the war, however, several other firms have taken up the manufacture of this product and at the present time I believe the full needs of our country in this respect are being adequately provided for. The nigrosines being produced are of standard quality and strength and are equal in every respect to the pre-war German product. Care, however, must be taken in discriminating between the different makes of this dyestuff coming on the market. While there are some that are inferior in quality, it will generally be found that such are the products of badly equipped and inexperienced factories. If proper selection is made, the very best qualities of nigrosines can now be obtained in any quantity and at reasonable prices.

SPECIFICATIONS FOR KAOLIN.

Discussion at the Atlantic City Meeting, June 7, 1917.

THE PRESIDENT: We will take up as the next committee report, "The Specifications for Kaolin." This is in the nature of a preliminary report by this committee, as the work was only undertaken since the spring meeting of the Council and has not been extending throughout the full year as is customary with committee investigations. Mr. Frey, who was assigned the duty of this investigation, is not present, and as he is one of Mr. Veitch's assistants, Mr. Veitch will make some remarks on this work.

MR. VEITCH: Mr. President, you have stated the conditions which have made it impracticable to make anything more than a progress report at this time, and I need add little to that, except to say that we have endeavored to get samples of kaolin from members of the Council who at the last meeting brought this question up and stated that they had had some difficulties with kaolin.

We received three or four samples. I think we would make better progress if we could get from the various members of the Association, samples of kaolin which are satisfactory and also samples which are not satisfactory. We could examine these, find the reason for the differences, and with this information in hand, draw proper specifications for kaolin and try to locate the deposit which we hope would run with regularity.

If any of you have, or during this year, run across unsatisfactory kaolin, unsatisfactory in any respect, as to clarity or water solubility or any other feature, I hope you will send us a sample, say half a pound, with full information as to what is the difficulty that you have encountered, and more especially, from whom the kaolin was bought and when. We can take the matter up with the dealer and get some information as to the deposit.

If you can help us to this extent, we can get along faster and have something worth while, possibly, before the next meeting. So far, our examination hasn't given us a lead as to a possible solution of the problem.

THE PRESIDENT: In way of explanation, I might say that the difficulty of obtaining proper kaolin has become acute during the past year or year and a half, and it was on account of this, that it was felt advisable to make an investigation of this subject, the feeling being that our present specifications would not indicate always when a kaolin was unsatisfactory for use in filtration work. If there is anybody here who has had any disastrous experience with the kaolin that they are obtaining on the market today, we would be very glad to hear from them.

MR. VEITCH: Mr. President, it occurs to me to ask if anybody has been giving the matter very much attention. Have they been using kaolin just as they have received it, or have they been in the habit of making examinations to see if the kaolin was within the present specifications?

MR. RIETHOF: We are washing our kaolin, because the water solubles are sometimes too high. I understood from Mr. Seltzer that he had received acid-washed kaolins with very high water solubles; since that time we have washed it. We never use it the way we get it.

THE PRESIDENT: You acid-wash it?

MR. RIETHOF: Yes, sir.

THE PRESIDENT: You are able to do that without any difficulty?

MR. RIETHOF: Certainly.

THE PRESIDENT: I understand from some who have attempted washing kaolin with acid that they obtained higher water solubles afterwards than before washing.

MR. VEITCH: I think it would depend somewhat on the kaolin and the source.

MR. RIETHOF: It would be interesting to know whether the difficulty lies in the water solubles or in some other aspect—or in other words—if the water solubles of the kaolin are the source of difficulty, or the fineness of the particles.

THE PRESIDENT: It is assumed that there is some difference, due to the colloidal nature of the kaolin, and it was thought that some information might possibly be obtained by making a "loss on ignition" test, but I believe that the preliminary work on this has given nothing but misleading information up to the present.

MR. MCCANDLISH: The results contained in the report of the Committee on the Comparative Analysis of Tannin Materials, representing the work of 23 chemists, indicate that the general supply of kaolin is fairly good. Variations from the average total solid figure, obtained without the use of kaolin, were almost as great in some cases, as the variations in soluble solids and non-tannin figures which involved the use of kaolin.

THE PRESIDENT: Maybe it is only the isolated case where the trouble has occurred.

MR. SELTZER: Some time ago we bought some acid-washed kaolin. We have a system in our laboratory whereby we always receive a works sample from the shipper of extract, and we check every shipment of extract by the tannery sample. As soon as we started to use this kaolin, I noticed that in the tannery analysis that had been made later, as compared with the works analysis made first, the non-tannins were very much higher, and that led me to be suspicious in regard to the kaolin. I tested the kaolin and I found 14½ milligrams of soluble matter to the 100 cc. of solution.

THE PRESIDENT: Did you get clear filtrates with that?

MR. SELTZER: Yes, sir. I took that kaolin and started to wash it in the meantime, because I had no other; and I tested the water soluble and found that I got a very low result, about ½ milligram, which is less than the method now calls for. In those days there was no method for determining the specifications of the kaolin, and since that time we have been washing every lot of kaolin received. Also, I find that it is important to specify that the kaolin should not be ignited. I found that the ignited kaolin I secured from one company did not prove satisfactory.

THE PRESIDENT: In what respect?

MR. SELTZER: It gave a cloudy solution. We wash ours first with acid, in about a 2 per cent. acid solution, let it stand a few days, then we wash with ordinary tap water. Our tap water is almost pure, containing three parts total solids to the hundred thousand, so we washed with that water by decantation. We have a decating jar with four openings on the sides and we let the kaolin settle and run off the water and fill up again and stir it. It takes very little time, you know. We prepare it a long way ahead of time, and we are always able to get good results. After using this city water, we use distilled water for about four days, and we find that our blanks are always ½ milligram or less.

MR. BALDERSTON: Mr. President, we had a rather curious experience some time ago in coming across a sample of unwashed kaolin that gave better tests for solubles than several of the acid-washed kaolins.

MR. SELTZER: I might add that we took the matter up with the party that sold us the material and they stated that they gave us unwashed kaolin by mistake and gave us the kaolin as a present because they had made the mistake.

MR. HURT: I certainly have to disagree with Mr. McCandlish as to the concordance of the results of 21 chemists. It seems to me, that we must not only examine the kaolin, but every detail of the methods used, and endeavor to find why there are such great differences in results reported.

You will notice on every page of this report, there are a number of analysts' results, which are omitted from the average, due to a deviation of over 1 per cent., and in many cases, 1¾ per cent., from the average. If we are to arrive at facts, why should any omission be made? And why 1 per cent. or 1¾ per cent.—why not 0.25 per cent. or 0.50 per cent.? It seems to me that we should look this matter straight in the face and include all the results reported in forming our conclusions as to the concordance of the results. The following table, which shows the greatest difference as reported by the Committee, compared to the greatest difference when all the results reported are considered, will no doubt be quite surprising:

Sample	Greatest difference Committee report	Greatest difference With no omissions
Chestnut	1.00	1.86
Oak bark blend	1.79	3.45
Hemlock	3.06	8.98
Myrobalan extract	0.91	2.92
Sulphite cellulose	2.70	4.53
Quebracho extract	2.72	7.92
Chestnut wood	1.54	2.89

In the Committee report, on the chestnut extract, one analyst was omitted from the average. On the oak bark blend, four analysts were omitted from the average. On the hemlock, four analysts were omitted from the average. On the myrobalan, two were omitted from the average. On the sulphite cellulose, six were omitted from the average. On quebracho, three were omitted.[1]

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[1] One of the greatest of these differences was due to an error in figuring, as explained in the correction, p. 360, August issue.—ED.

These results are anything but concordant and it seems to me, that with the ordinary care such as we should have, there should not be such a wide variation in results. There is something wrong somewhere.

I have found in one or two instances, that a great difference in results is caused by the cloth used in filtering the hide from non-tannin. Even after certain cloths were washed in hot water, a difference of 3 per cent. of tannin content was found, due to the fact that foreign materials in the cloth, not soluble in water, were soluble in the extract solution.

MR. McCANDLISH: The average deviations from the tannin figure, as given on the first page of the committee report, are not excessive when one considers the method of analysis.

MR. RIETHOF: I agree that the results are not so very good in these comparative analyses of tanning materials. I know I am very much off on some extracts. I will admit it, but I am in good company, I will say for consolation. I would be glad if I could lay the blame on the kaolin. It seems to me, that the results two years ago were better than this time.

THE PRESIDENT: The samples would have something to do with that.

MR. RIETHOF: That may be so in regard to the hemlock extract sample, but for instance on this oak bark blend extract—we have no excuse. We are off quite a bit on it. The average deviation, is not very high, but some of the co-workers are very much off.

THE PRESIDENT: Mr. Riethof, maybe you have some kaolin that Mr. Veitch would like to get hold of.

MR. WISDOM: I think the fact that Mr. Riethof was one of the two who used the rapid cooling, method may have something to do with it. There were only two who used the rapid cooling method.

MR. RIETHOF: That wouldnt' be in accordance with the results two years ago, for at that time we found that the way of cooling has no noticeable influence on the results.

MR. WISDOM: I disagree with you.

MR. RIETHOF: I think two years ago there was no difference whatever.

MR. WISDOM: I think, Mr. Riethof, on extracts having a considerable amount of insolubles, invariably the results showed there was quite a difference between the rapid and the slow methods. That was one reason why I didn't specify when I sent out the instructions. The analyst could use his own discretion in regard to employing the slow or the rapid, and most of them chose the slow—over 90 per cent.

MR. RIETHOF: That is very interesting, but two years ago there was no difference in hemlock extract between slow and rapid cooling. I chose the rapid cooling method because this enables me to run an extract, which I receive in the morning on the same day, as you know, this is sometimes of importance in factory control work.

THE PRESIDENT: If there is anybody here that has had experience with kaolin, it would be well if he would communicate with Mr. Veitch to help him solve this problem.

DISCUSSION ON DYE-TESTING

at the Atlantic City Meeting, June 7, 1917.

THURSDAY AFTERNOON.

THE PRESIDENT: The meeting will please come to order. The first paper on the program is the report of the Committee on the "Testing of Dyes for Leather," by Mr. Guy T. Creese, Chairman of the Committee.

(The report of this committee was printed in the JOURNAL in June, 1917.)

THE PRESIDENT: Have you some tests that you wish to show?

MR. CREESE: Yes. If this Association adopts the yarn method of testing dyestuffs, the Association ought to furnish the yarn to members at cost, because there is quite a variation in different grades of yarn, and they will give you different color results. Mr. Wisdom brought this out in his tests; and I will pass these samples around and you can look at them. There is also a difference in leather tests on chrome and bark-tanned leather, and that would have to be given consideration if we were going to adopt the leather method of testing dyestuffs.

THE PRESIDENT: It is well to bear in mind that what the committee was instructed to do was to find out if there was a possibility of developing a method for determining the relative values of dyes on leather. This report is a start in that direction, and we hope that it will be the ground work for future development, for future committees to pursue. There are men here who have had practical experience with dyes and I shall call on a number of them to give us their opinions regarding this question. One of the members of the committee is here, Dr. Klaber, and I should like to have him talk on it or give us some solution.

DR. KLABER: Mr. President, my experience in this work was that as far as the testing of the dyestuffs for commercial value was concerned, if you use the same yarn in testing, both the standard and the sample under consideration, you can get comparative tests. As far as leather was concerned, I personally was able to get no satisfactory results. In the case of the acid dyestuffs, I found that the results were fairly uniform. When it came to the substantive dyestuffs I found that by no method could I get uniform results whatsoever. I found that some of my results seemed to indicate that it was a question of surface percentage. On the other hand, others looked to me as if they ought to be based on the weight percentage; and I finally wound up in disgust with the leather test.

I should like to hear some of the people who were not on the committee discuss this question, for I certainly have not found any method of testing dyestuffs on leather that is satisfactory, either in my personal experiments or in the committee work.

THE PRESIDENT: Then you have no original suggestions to make that might solve the problem?

DR. KLABER: As far as testing on leather—no, but it seems to me as far as the buying and selling question is concerned, we can very well adopt a textile as a basis for testing.

THE PRESIDENT: As far as relative value is concerned?

DR. KLABER: Yes.

THE PRESIDENT: As distinct from color power?

DR. KLABER: As on a buying or selling basis, you can use the textile to determine relative tinctorial values. As far as the use of the dyestuffs on each man's individual leather is concerned, I think he will have to determine that for himself.

THE PRESIDENT: I understand. I should like to hear from Mr. Davies now.

MR. DAVIES: I can only say what my practice is in testing dyestuffs; that is, to make all tests for values on textiles. As regards the suitability of the dyestuffs for particular purposes, that, of course, can only be determined by making dye trials on the particular material you are going to dye. We find in practically all our laboratory work for value, the textile test is the best and only one. When you are dyeing textiles, you absolutely penetrate every fiber. When you are dyeing leather, you only dye on the surface or a little way below the surface. On account of the varying thickness of the leather you are dyeing, you spoil your dye test, as a test of value but you can determine the suitability of the color for a particular purpose.

All our work is done on textile fibers and we get results within 2 per cent. We very often make exhaust trials with substantive dyestuffs. After making the first dyeing, we wring those back, put a fresh skein of yarn in and completely exhaust the color. That is particularly important where two dyes are being tested which do not exhaust equally and the weaker dyestuff might appear stronger from the first dyeing than it really is, but the exhaust in that case would be weaker, so by a balance of the two, you can determine the actual strength of the dyestuff.

DR. KLABER: In handling dyestuffs, we find that some will penetrate leather, but there are some which do not. In the case of the substantive dyestuffs, they have very little penetration, and it would seem in that case that we ought to take the surface of the leather as the unit of test, rather than the weight. So far as certain acid dyestuffs are concerned, some of them penetrate completely through the leather and others do not penetrate at all, so we are more or less in a quandary in testing these products on leather, as to which unit to adopt, weight or area.

THE PRESIDENT: Mr. Lehmann, have you anything to add to the discussion?

MR. LEHMANN: Mr. Creese said that we should adopt a standard of yarns, that is to my mind not necessary. The point is that we have to take every individual dyeing by itself. For instance the chemist gets a sample of dyestuff into the laboratory and he only has to see how it compares in color value or tinctorial value with the standard of that particular dyestuff. Cotton yarns are spun in any numbers from 2-12 to 2-100. Woolen or worsted yarns are spun from 2-10 to 2-60, now even different lots of yarns which have the same numbers will dye differently in the same dye bath, therefore, it would be hard to adopt a standard for cotton or woolen yarns. It seems to me that the only standard we can adopt is the dyestuff standard and in dyeing out a new lot of color against the standard we must be sure to make all dyeings of the same yarn, reeled from the same lot.

It would be impossible for the Association to say that substantive dye tests should be made on 2-24 cotton yarn.

MR. CREESE: Mr. President, one of the reasons I spoke about the yarn was in the case of a dispute between buyer and seller.

MR. LEHMANN: I beg to differ from Mr. Creese. Any cotton mill in the country will tell you that they will not guarantee a 2-12 yarn or a 2-20 yarn or any kind of cotton yarn that you can buy to-day to be and to dye the same as the same kind of yarn a year ago.

MR. CREESE: It seems to me that this Association is large enough—it ought to buy yarn to last a year.

MR. LEHMANN: Even if it lasts a year, what are you going to do four years from now? The only thing you can do, when you buy dyestuffs, keep a sample of your standard. For instance, if a firm sells tannery dyestuffs, the principal thing for you to do is to keep 2 or 4 or 6 ounces of that dye that you are using, keep that corked, sealed and under lock and key, and if a year from now you want to buy some of that dyestuff, all you have got to do is take—say it is a substantive dyestuff—half a gram or 500 milligrams of the standard and 500 milligrams of the dyestuff you are buying; dye your 20-gram skeins reeled from the same lot of yarn and then compare your dyeings. You cannot go from one year to another and buy cotton yarn and think that you are going to have exactly the same shade on the same yarn number.

MR. CREESE: Of course, in testing dyestuffs, you have to test against your standard.

MR. LEHMANN: In our laboratory we test on paper first of all. We take 500 milligrams of dyestuff and dissolve it well in 500 cc. of water. In one bottle we dissolve the standard and in the other one the dyestuff in question, and then we drop both solutions side by side on filter paper. You can tell pretty near from this simple test if you are on the right track. After that you dye the different lots on textiles. The difference in worsted yarns of the same number, but of different lots is still greater than in cotton yarns. Supposing I buy 2-40 worsted yarn from the American Woolen Co., and Mr. Creese buys 2-40 from the U. S. Worsted Co., now these yarns are supposed to be spun from the same wool or grade of wool, but if we take a skein of each and dye them together in an acid dye liquor we will probably get two distinct shades from the same bath.

MR. CREESE: But you will agree that you can mordant large quantities of cotton yarn with tannin and get much more even results than with small quantities.

MR. LEHMANN: Yes.

MR. CREESE: If this Association had the yarn mordanted in large quantities it would get better results.

MR. LEHMANN: Yes, on basic colors for which you use cotton yarn mordanted with tannin, but we have got five distinct groups of dyestuffs to consider and then of course you have your wood dyes.

MR. CREESE: I wasn't taking up the subject of wood dyes.

DR. KLABER: In running these tests, the individual laboratories were requested in their preliminary work to use their own yarn. We did that and we determined on our own yarn the relative values of these dyestuffs that were furnished us. Afterwards we took the standard yarn which was furnished us by the committee, and we got the same relative test.

I really don't see the point of the discussion of the standard yarn, as long as the yarn is from the same lot.

MR. DAVIES: I think Dr. Klaber is right. We test a dyestuff on one yarn, and the mill that buys it dyes it on every kind of yarn. If the value is there, they get the value irrespective of the yarn they are dyeing. It is quite unessential that you have a standard yarn. The essential is to make dye trials against a standard dye. Every time a dye trial is made, a comparative dye trial of the standard is made. That is the only essential in dye tests—strictly comparative work.

MR. KADISH: I should like to ask the committee if they tried any dye test on split leather instead of grain leather.

MR. CREESE: No, sir.

MR. KADISH: It has been my experience that in a very crude way you can get a very much better exhaustion on a split leather than grain leather, even if the dye bath is not exhausted entirely. I find it possible to get very good comparative results on split leather, providing that adjacent pieces are used or the splits are made in the same way.

It might be well for the committee in future to do some work on split leather. If you have the pieces at the same temperatures, even if you don't get the same exhaustion, you do get a comparative idea of the shades.

MR. DAVIES: I should like to speak about the tumbling apparatus that you mention in your report. We have one in our laboratory which gave us very satisfactory results, and if the committee is interested in the design of that, I would be glad to furnish them with particulars of the type we adopted. We don't have any means of keeping the temperature up.

MR. CREESE: That is the point.

MR. DAVIES: But they are large enough to retain the heat, and we find we get very satisfactory tests so far as tests on leather are satisfactory in determining value.

MR. CREESE: Have you the jars covered with asbestos?

MR. DAVIES: No, but that would be very easy to do.

MR. CREESE: On those tests, do you put the leather in alone or do you put something in to aid in the pitch of the leather?

MR. DAVIES: Just the leather alone; and we generally make our leather tests by measure, not by weight.

MR. CREESE: How about you mordant colors? Those would penetrate more readily than the others.

MR. DAVIES: Not necessarily. You take a piece of leather of the type on which such colors are used, and you generally find that the measurement and weight are approximately the same.

THE PRESIDENT: I should like to hear from Dr. Levi on this subject.

DR. LEVI: Mr. President, the dye tests that we make are never made on leather at all. If we make a dye test on leather, we generally take two or three dozen skins and put them through. When we test the dyestuffs, we dye on textiles. We dye at 90°, not at 100°. I have found in my experience of twenty years in handling dyestuffs that this method will give me the best comparative result that I can get. When I make a mixture, before it goes to the factory I do the same way. I have dyed leather now for quite a while, and I don't think that the percentage of my failures is probably over 2 or 3 per cent. That does pretty well.

We dye all dyestuffs that way with the exception of nigrosines. With nigrosines, we simply dissolve 1 gram of nigrosine in 100 cc. of water, taking our type sample and making a comparative test. I have got samples from all the dyestuff manufacturers, probably, in the world. I keep them, so if we should buy dyestuffs from any of them, we have got their type samples there and that enables us, with very little trouble, to determine the money value.

I never dye at 100°, for I found out by experience, dyeing on textiles at 90° for one-half hour will give me pretty nearly an idea of the way it is going on our leather. Of course, if I should go over into leather, I should take our leather and dye that and should get a piece of John Smith's and Bill Jones' and Frank Brown's and I should get four different shades, always depending exactly on how the leather is tanned and prepared.

MR. H. C. REED: There is one point that should be brought out in the dye testing of logwood—I think it is the stumbling-block of a good many dye tests—and that is the question of oxidation. We have hematine and we have logwood and we have all degrees of hematine and, therefore, all degrees of oxidation. We might make a test of a logwood against a hematine on a 1 per cent. basis on wool, we will say. We might get a match. We will raise that percentage up to 5 or 6 per cent. The oxidized extract will be far better than the unoxidized. Now if on that 5 or 6 per cent. basis, instead of immediately discarding our bath and saying that is the end of it, we wring back the surplus dye solution into the pot and dye up, we will find very probably—in fact, quite probably, that the unoxidized extract will be far ahead of the oxidized extract. Therefore, it becomes a question really, for what purpose is the dye to be used? In certain cases you need an oxidized extract, the hematine; in other cases, you want an unoxidized; but you have always got to bear in mind in your dye testing that there is a wide variation between the oxidized and the unoxidized extract in the respect that I have mentioned.

MR. JOHN H. YOCUM: Mr. President, not being at all an expert in dyes, but having to handle them occasionally, it occurs to me that the dye test is the measure of the tinctorial power of the material purchased. There can be two causes for the reduction of tinctorial power. There is improper manufacture and the other is adulteration. It seems within the bounds of reason that some method of examining a given type of dyestuff for the amount of the adulteration might also be a measure as well as the dye test.

I know, of course, that batches of dyes as made are standardized by the addition of inert materials.[1] I would like to hear from some of these gentlemen as to the advisability of making examinations for materials other than dyes in dyes as received.

MR. LEHMANN: Mr. President, what the previous speaker said is absolutely not necessary. When you buy dyestuffs, you really make a contract with the manufacturer to furnish you an article to give you a certain amount of tinctorial power per square yard of leather; that is, in a tannery. In a textile mill you make a contract to give you a certain amount of tinctorial power per pound of either cotton or wool or silk. On either it is merely a matter of tinctorial power to the square yard, because no leather will ever absolutely dye through. You can cut any piece of leather and you will never find that the surface is the same color as the inside; it is always darker, no matter what shade you use.

For instance, acid colors are the ones that strike through the best, whereas the grain is a great deal darker than the inside. Basic colors only dye the surface and very, very little below the surface, especially if they are used on chrome leather.

The point Mr. Yocum was trying to bring out was that he would like to find out what adulterations are in the products we are buying. I believe Mr. Davies could explain this subject most clearly to you.

MR. DAVIES: I don't think there is anything in particular to say. Most dyestuffs are salted out from their solutions, and when they come from the works, they already contain a certain amount of adulterants. It doesn't really make any difference what is put in afterwards, salt is there just the same. It wouldn't do

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[1] **See abstract of Dr. Harold's paper on Standardization of Commercial Dyestuffs in this issue.**

any real good to determine the percentage of salt in the dyestuffs, because it won't show that it is an adulterant.

MR. YOCUM: I think that you have missed my point a little bit. The point that I was making is that I understand that dyestuffs are brought to standard by the addition of salt. Now, when you have standardized it and you have got a standard sample, isn't it one of the easiest determinations to make—to determine the excess of salt, whatever it may be?

MR. LEHMANN: No.

MR. YOCUM: You bring it to a standard, then you add more salt to it.

MR. LEHMANN: In the manufacture of a certain dyestuff the particular batch may come out wrong, there are just as many troubles in the manufacture of dyestuffs as you have in the manufacture of leather.

Supposing in salting out a certain dyestuff the powder is stronger in tinctorial power than the standard adopted by the manufacturing color firm. In order to bring it up to standard we have to add more salt; but the other lot of dye which you may buy from the same place may contain less salt, but is not of such a high tinctorial power as the product containing more salt.

The principal thing I was trying to bring out in the first place was this, when you made the contract for dyestuffs the first thing you want to do is to take an 8-ounce bottle of dyestuff which is offered you by a certain manufacturer at a certain price cork it up well put it away, if necessary under lock and key, and when you buy again 100 pounds or a barrel or 10 barrels of the same dyestuff, take your standard out, compare it with the lot received and put your first lot or standard away again, that is the only thing you can do in comparative tests for dyestuffs, because you buy tinctorial power and nothing else.

MR. SAXE: Are the standards of these large German concerns alike?

MR. LEHMANN: All these people were manufacturing dyestuffs for the last 40 years. The first dyestuffs that came out were basic colors, then afterwards came some acid colors, then came the direct colors, which were a great boom to the textile factories; but all these firms printed in the same shades, but they were called different names. You take chrysophenin—it was used little in leather, but it was sold by 15 names and probably everybody had a different standard.

MR. YOCUM: This chrysophenin is certainly a definite compound.

MR. LEHMANN: Yes.

MR. YOCUM: Then if you determine the adulterants in it, you would get its tinctorial value immediately.

MR. LEHMANN: No, you wouldn't. You can only get it by dyeing it out on cotton or wool or leather. By taking the adulterants in it, you can't get the tinctorial value; you can only get it by dyeing it out, for instance when a man manufacturers chrysophenin, he might get a batch which contains already in manufacturing, 20 per cent., and in order to bring it up to the standard of selling, he has got to add a good deal more salt.

MR. YOCUM: But he would have the pure stuff, wouldn't he; and wouldn't that be a measure of its tinctorial value?

MR. LEHMANN: No, it wouldn't. It is tinctorial value you are buying, not salt.

DR. KLABER: It is a very much easier proposition to determine the tinctorial strength than to look for all the possible adulterants.

MR. REED: There is a test, though, that I think might be a good one to have, and that is on the wood extract; take it on logwood. There is quite a little logwood on the market, adulterated with tanning extracts. It is not so bad in the case of cotton. It serves the purpose, perhaps, but this phase of it hasn't been touched upon, and perhaps it is not as pertinent exactly to leather as it is to wool. If an extract of hematine, for example, adulterated with a tannin extract, is used on wool, the tannin extract makes the wool harsh, and that is a matter that should be taken into consideration where hematine is to be used for wool. Therefore, the adulteration does enter in it, entirely aside from the question of tinctorial value.

DR. KLABER: On the subject of wood dyestuffs, I move that the committee be continued and that their work be concentrated on the valuation of the wood dyestuffs.

MR. CREESE: Mr. President, why don't you divide your committee and have a committee on natural dyestuffs and one on synthetic dyestuffs?

Dr. Klaber: We haven't gone into that.

Mr. Creese: There is considerable work that can be done on synthetic dyestuffs and considerable on natural dyestuffs, but one committee can't do it all.

Dr. Klaber: It is a problem for every individual manufacturer to determine on his own leather.

Mr. Creese: But there are certain tests that we can establish. There are tests that we can put a dyestuff through to show its fastness to color destroying agencies. Now, it appears to me that if we are going to continue with the work on dyestuffs, it would be more advantageous to divide the Committee and have a natural dyestuff committee and a synthetic dyestuff committee.

The President: I think that could be done without any duplication of effort; and while it is really not necessary to have a motion on that, because all this discussion goes to the Council when they are making up the work for the next year—they go over all this discussion which is valuable for directing the work for the next committees—I think the suggestion that the work be continued is a very good one and that it should be handled by two committees, one for the synthetic dyes and one for the natural dyes.

Mr. Lehmann: While we are talking about dyestuffs at the present time, there is a great deal of good to be done on one certain leather in which America has been the leader, and that is glazed kid. Everybody probably has worn a pair of glazed kid shoes, and he knows they are wearing very well, only when he walks on the streets, he finds out that just as soon as he stubs up against anything, the white shows.

Now, there is a certain class of dyestuffs which hasn't been investigated properly, to my mind, and that is sulphur dyes. Sulphur dyes are dyed or can only be applied on cotton as a textile fiber, or else on wool if you take proper precautions, and there is no doubt in my mind that if chemists would really set to work, they could also be applied to leather, because they are dyed with sulphide of sodium, as the ingredient to dissolve them or to keep them in a compound. I believe that this society ought to take that up as a special study; that is, to study how sulphur colors could be dyed on leather, perhaps before even the leather is tanned, and try to strike the leather absolutely through.

You see, sulphur dyes are rather cheap; that is, not at the present time, but when prices are normal, sulphur dyes are very cheap. At the present time, dyestuffs being high, people are used to paying quite a little for dyestuffs, and when sulphur colors come down to their normal price, they will be comparatively cheap. Of course, you would use more dyestuffs to cover a certain surface of leather, but you would strike through your leather; then if your leather should receive any damage on the surface, it wouldn't show so badly.

It is one of the drawbacks in glazed kid. I don't know how many manufacturers are here or are interested in it, but that is one of the great drawbacks, and I believe on calfskins, also. I believe that is one thing that this society ought to take up into, that is, as a problem. The individual men alone will not take it up, because it is mighty hard work, but when it is put onto them and a committee is appointed to investigate the matter, I think it would go much further. The reason why I bring that up is because glazed kid is an American manufacture and is recognized all over the world as an American leather, and I think it is up to us to find if sulphur colors could be properly used on any kind of leather.

SULPHONATED OIL ANALYSIS.

Discussion at the Atlantic City Meeting, June 7, 1917.

[The report of the Committee on Analysis of Sulphonated Oils was published in the June JOURNAL, pages 266-78. When W. K. Alsop, Chairman, was called on for his report, at the annual meeting, he gave a summary of the published report, and distributed reprints of it. The discussion on the report follows.]

DR. BUMCKE: I believe that the amount of SO_3 obtained in the treatment with HCl shows the correct amount of SO_3 contained in the sulpho-fatty acids, while the crucible method gives the total amount of sulphur, no matter in what form it may be present. As most oils contain small amounts of albuminous compounds, the sulphur contained in them would be found by the crucible method, but not by the HCl method. This perhaps accounts for the slightly higher figures obtained by the crucible method. Outside of this, the chances for losses by incomplete washing are greater in the HCl method than in the crucible method. This too may account for the higher results that some of the collaborators have obtained by the crucible method.

Mr. Yocum: I do not think that I expressed myself very well in my letter to Mr. Alsop. My experience indicates that the determination of the combined SO_3 is not a true indication of the emulsifying power of a given sulphonated oil. There is no doubt that it is brought about by the breaking up of the sulphonated fats, which emulsify with as much facility as the genuine sulphonated products; or it may be accounted for by the fact that two of the fatty acid radicals are compounded into one sulphonated radical. I do not know whether this is clear, but I am unable to express it any better.

Mr. Oberfell: What do you mean by emulsifying property, with water or with mineral oils?

Mr. Yocum: The capability of holding emulsion with mineral oil.

Dr. Bumcke: A year ago I mentioned that the total amount of SO_3 is not alone the figure by which the oil should be valued, but the other items of the analysis must be taken into account also. If an oil, for instance, contains very much neutral oil, it will not be able to carry so much oil in an emulsion as one which contains little. Excessive amounts of salt like Glauber salt and ammonium sulphate must be taken into account as they tend to hinder the formation of emulsions.

There is one figure which we have not considered yet, this is the amount of oxidized fatty acids. We mentioned it here a year ago but the committee did not take it up as the opinion about its usefulness or necessity was divided. There is some work necessary to find out what value the oxidized fatty acids have in the treatment of leather. May be the oxidized fatty acids have something to do with the emulsifying properties of the oil but to what degree cannot be decided at present.

Mr. Yocum: I do not think there is any question that oxidized oil will emulsify.

Dr. Bumcke: We have sulphonated cod oils, containing usually from 10 to 20 per cent. of oxidized fatty acids. There is no doubt that these have something to do with the emulsifying properties of the oil.

DR. KLABER: I should like to know whether there is any well recognized way of determining the source of the oil which is made into a sulphonated oil.

MR. OBERFELL: I do not think there is any recognized method. There may be some individuals who are able to determine that to a certain extent.

MR. DAVIES: I think that has been determined in some cases by an examination of the neutral oils.

MR. OBERFELL: Is that only true in some cases?

MR. DAVIES: Well, I do not know that it applies generally, but I know in some work we did in trying to determine just what oils were used in the manufacture of a product, we got a very fair idea by the examination of the neutral oil, though I do not think the amount of neutral oil is any fair indication of the value of the sulphonated oil.

There seems to be an opinion held by some members of this Association that by deducting the neutral oil from the total fatty matter they can work out the extent to which the oil is sulphonated, I think that ought to be condemned. It is a very unsatisfactory method.

MR. YOCUM: My experience indicates that this is a very misleading method of determining the source of the oil which has been sulphonated. If a mixture of oils is sulphonated, including an easily sulphonated oil, such as castor, and one more difficult to sulphonate, and then the neutral oils are separated and we try to get the constants of the separated oil, the castor oil does not appear in the reaction and the other oil does, so it is a question that I do not believe can be solved at the present time.

DR. BUMCKE: I know that the figures obtained on the neutral oil will give a valuable hint as to the material from which the sulphonated oil was made. But this neutral oil is obtained from an ether extract, and the evaporation of the ether and the heating and drying in the oven will produce some changes in the oil, so that it is not the same as the original oil.

For the fatty matter obtained from sulphonated castor oil, Lewkowitsch gives certain limits for iodine-saponification, and acetyl-value, but this applies only to castor oil. I have tried to obtain these figures from some other oils. Cod oil, for instance, usually has an iodine value varying from 140 to 170, and this goes down through sulphonation to about 65 to 100. The limits are so far apart that we cannot make any conclusion from it. These are the figures from the total fatty matter, not from the neutral oil.

MR. DAVIES: I think Radcliffe has already published a method for determining that; first of all, sulphonating a good many oils, then splitting the fatty acids from those oils and determining the constants. I do not think he will do it, because I think so much depends on the amount of sulphuric acid that is used in sulphonation.

DR. BUMCKE: I believe that we will encounter extreme difficulties when we try to find out of what oil the sulphonated oil was made. If the values of the original oil are within certain narrow limits, it seems possible to find out by numerous tests of the fatty matter separated from the sulphonated product how far these values will be changed for a certain oil. This seems possible for castor oil, olive oil and a few others, but if the limits of the values of the original oil are rather wide, like the iodine values of cod oil and other fish oils, a definite conclusion seems almost impossible. Such determination becomes much more difficult or perhaps utterly impossible as soon as the sulphonated product is made from a mixture of two or more different oils.

In Mr. Alsop's report, page 272, Mr. Yocum says, speaking of the total SO_3, "While this method does not, in my mind, determine all the combined sulphates, it is nearer to the truth than the HCl method." Will Mr. Yocum please explain why?

MR. YOCUM: It has been my experience that the HCl method has always been lower. I believe that there is no method of analysis which shows with any degree of accuracy the amount of sulphuric acid accepted and taken up by the oil. Consequently, all the analyses of combined sulphates in the oil are, to my mind, too low. That is a matter of manufacturing experience.

DR. BUMCKE: On account of the higher figures of the crucible method, you condemn the HCl method? Look at the differences, they are very small, indeed.

MR. YOCUM: When I wrote that, I had not seen these reports. I was dealing entirely with my own analyses. Anyway, if I had seen them, I would have dealt with my own analyses.

DR. BUMCKE: Mr. Fox and Mr. Cuthbert get identical results for sample A with the HCl method and the ash method, and my test with the HCl method is higher than two others made with the ash method, even a little higher than the ash method average. I think that in the HCl method, as I mentioned at first, the chances for loss are large, that is, if the ether solution of the oil, or the filter through which the acid water is filtered, are not sufficiently washed, there might be a loss, and that is what I think perhaps has occurred here. I cannot see, for instance, why it is that my tests are higher than some of the others obtained with the ash method. In Table B it is similar, my test with the HCl method is nearer the average of the crucible method than that of the HCl method.

And then Mr. Yocum said he thinks all these tests are too low and that we have no definite method to determine the total SO_3. I think we are pretty far advanced in this method. I am glad we have these methods. They seem to me to be as correct as anything can be in this line. The test for the inorganic SO_3 is fairly correct too, and we can well be satisfied with that. In order to show this, I have gone back over the last 24 analyses made in our laboratory, and I found that the average difference of the total is SO_3 is 0.045 per cent., and the average difference for the SO_3 in salts is 0.02 per cent. Now that is very, very small, and I think we may be satisfied with that method.

Mr. Yocum: Corroboration of results by any given method does not by any manner of means indicate the correctness of the method. It cannot be accepted in the case of any method that close results obtained by different collaborators give a reliable indication of the accuracy of the determination.

Mr. Boehringer: I believe with Mr. Yocum that the ash method is to be preferred. Our ash method always shows a higher result. In addition to that the ash is by far the quicker method, especially if you have to make the analyses in a given time.

Mr. Oberfell: This work will perhaps be continued another year by a new committee, and these matters will be considered.

Mr. Alsop: I think that in a number of cases analysts have found SO_3 in the fatty matter after the HCl treatment. Dr. Bumcke intimates or says that it is because it was not done carefully enough, and that is the reason that I recommended that it be worked on next year. Dr. Bumcke says (page 272), "According to a recommendation by Benedict, for the complete separation of SO_3, I dissolve the 4 grams of sulphonated oil in 25 cc. of water and add a little ammonia to make the solution slightly alkaline before I add the hydrochloric acid. Boiling must be continued until both layers, oil and water, appear clear. Complete washing of the solution of oil in ether in the separator and of the filter through which I filter all acid water and wash water is necessary to avoid losses. If this procedure is strictly adhered to, I do not think that any loss of SO_3 occurs, or that any remains in the oil."

MR. YOCUM: I have found that very thing that Mr. Alsop speaks of with the HCl method, and likewise I have felt that the sodium carbonate method offered opportunity for loss of sulphur, and tried out various other methods of oxidation, but was unable to carry them to a finale. I believe, however, that even the sodium carbonate method does not fix all the acid in the oil, and that there is an opportunity for loss.

DR. BUMCKE: On page 274 Mr. Yocum says "I think that the concentration of the brine solution should be specified in the method. As the method reads, 25 cc. of concentrated brine, may mean a solution containing from 15 to 20 per cent. of NaCl. I suggest that a 20 per cent. solution be used, as I do not think that saturated solutions will remove all the free or inorganically combined SO_3." I have always used a concentrated brine. That means a saturated salt solution, containing between 25 and 26 per cent. NaCl. This is done for the purpose of preventing any soap or soapy compounds of the sulphonated fatty acids from going into the salt washings. They are insoluble, with the exception of perhaps a little organic matter, but the oil itself is really insoluble. Sufficient time should always be given for settling.

At the first washing the brine will never be saturated even when a saturated salt solution is applied, as the water contained in the sample will dilute the brine to a certain extent.

It occurs sometimes, when the sample of sulphonated oil contains much water, that at the first washing with 20 cc. saturated brine, the brine settles out with yellow color. This indicates that a little sulphonated oil has been dissolved in the brine as it was too much diluted by the water contained in the sample. An addition of 20-30 cc. of concentrated brine will remedy the trouble and make the brine solution concentrated enough not to dissolve any sulphonated oil.

I do not see why that suggestion is made by Mr. Yocum and I should like to ask him why he thinks the saturated solution will not remove the inorganic compounds of SO_3. Salt solution, even if saturated with NaCl, is, as we all know, well able to dissolve any other salt. Its saturation is no reason why it should not dissolve any amount of SO_3, especially as the extraction is done 4 times and the amounts extracted from the oil are comparatively small and far away from the limit that this solution would be able to dissolve.

MR. YOCUM: Saturated salt solution depends on temperature, consequently what is saturated at 20° C. will not be saturated at 25° C. If a certain percentage is used, you have a standard solution for washing. As to the question of a saturated solution of NaCl being a satisfactory wash for the removal of free acids, I may say that experience has taught me that a saturated solution of any salt, whether it be sodium sulphate or sodium chloride or any salt I know of, is not nearly so good as one near to saturation but not completely saturated at the temperature at which it is used.

LEATHER AND GLUE.*

By Joseph T. Wood.

Director, Turney Brothers, Ltd., Nottingham.

In the tanning industries, definite steps in advance, due to the application of science, are extremely difficult to detail on account of the secrecy in which individual manufacturers have shrouded their work. Even in the case of new materials, directly introduced as the result of chemical research, the methods of application are kept secret, and vary in each tannery. This policy is a legacy of the time not so far distant when every master tanner, and, indeed, almost every man in the yard, had his little budget of trade secrets.

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* From *Reports of the Progress of Applied Chemistry*, Vol. I, 1916, issued by the Society of Chemical Industry.

Much of the work done during the past three years consists in the perfection of methods for exactly controlling the various tanning processes, and it is in this direction that the industry has benefited to the greatest extent. In all large works it is now the rule, rather than the exception, to find a chemist installed. The work of the International Association of Leather Trades' Chemists in Europe, and of the American Leather Chemists' Association in America, has been invaluable in standardizing methods of control.

In the analysis of tanning materials, although the method for the estimation of tannin is still an empirical one, namely, the measure of its absorption by hide, the technique is so worked out that the variation in the results of different chemists is now very small, whilst the tanner gets to know what he wants, namely, how much of the material will combine with hide. Until the chemistry of tannins is more completely known, we must be satisfied to use the hide powder method. A detailed account of this and other methods specially adapted to a tannery laboratory is given in *The Leather Chemists' Pocket Book* by Professor H. R. Procter and collaborators (Spon, 1912).

PREPARATORY PROCESSES.

Preservation of Hides and Skins.—The question of the cause and prevention of salt stains has received much attention during the past few years. On the Continent the use of certain denaturing materials has been found to cause salt stains. Abt[1] found that certain salt stains were caused by the presence of grains of calcium sulphate, which gave rise to a precipitate of calcium phosphate. In other stains, iron was an accessory cause. In others, again, he found bacteria which formed melanins. He recommends the addition of 4 per cent. of sodium carbonate to the salt as a denaturing agent.

In America, Yocum[2] investigated salt stains due to iron, originating from the blood. Lloyd[3] also contributes to the discussion. Becker[4] isolated several species of bacteria said to cause salt

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[1] *Bull. Soc. d'Encour.*, 1913, 119, 646; *Coll.*, 1913, 204; *J. S. C. I.*, 1913, 616, 667.

[2] *J. A. L. C. A.*, 1913, 8, 22; *J. S. C. I.*, 1913, 152.

[3] *Coll.*, 1913, 188; *J. S. C. I.*, 1913, 616.

[4] *Ibid.*, 1912, 408; *J. S. C. I.*, 1912, 829.

stains. In England the use of chemically pure salt[5] has been proposed and brought into use in some cases. For the preservation and disinfection of skins with special reference to anthrax, the process of A. Seymour Jones (formic acid and mercuric chloride) has been tried with some success. Much work has been done, especially in America, by Tilley,[6] who finds the Schattenfroh method, (hydrochloric acid and salt) gives somewhat more constant results. (See also E. Moegle, *Centr. Bakt.*, 66, 442; *Coll.*, 1913, 241.) A very useful account of the various problems which require dealing with in this section is contained in the Report of the International Commission on the Methods for the Preservation, Cure, and Disinfection of Hides and Skins, by A. Seymour Jones.[7] Mention should also be made of the important investigations into the ravages caused by the warble-fly (*Hypoderma Bovis*), by Professor George H. Carpenter et al., Dept. of Agriculture and Technical Instruction for Ireland, published in the *Irish Naturalist*, Oct., 1914; this J., 1915, abst. p. 196.

Soaking.—No great changes have taken place in this process, but it may be said that the advantage of assistants, such as small quantities of caustic soda and sodium sulphide, and of antiseptic methods generally, is fully recognized in all modern tanneries. A new process of soaking and softening hides and skins has been recently patented by Dr. Otto Röhm,[8] depending on the use of tryptic enzymes, but the process has not yet been introduced into general practice.

In the unhairing and bating process, the same chemist has proposed the use of proteolytic enzymes for removing hair or wool.[9] This process possesses advantages in the manufacture of chrome leather, but for vegetable tanned leather the fibers do not appear to be sufficiently split up. The process has been used in Germany and America, but so far has not been assimilated to English practice.

Liming, Including Felmongering.—Here again control of the whole of the processes has been the chief feature of the work

[5] A. Turnbull, *Leather Trades Year Book*, 1914, 181; *J. A. L. C. A.*, 1914, 412.

[6] *J. A. L. C. A.*, 1916, 131.

[7] *Coll.*, June, 1912 (Supplement).

[8] Ger. Pat. 288095, Nov. 12, 1914; *J. S. C. I.*, 1916, 372.

[9] Eng. Pat. 18870, 1911, *J. S. C. I.*, 1911, 1224.

done. Provisional methods of control were adopted at the London Conference of the I. A. L. T. C.[10] These methods have been also generally adopted by the A. L. C. A.

R. F. Innes[11] finds that in the preparation of lime-arsenic paints the highest percentage of sulphur in combination with the lime is obtained by allowing the latter to be as fully hydrated as possible, and yet as hot as possible, before adding the arsenic. It should then be stirred very thoroughly.

In a recent paper by J. E. Pickles,[12] a working formula is given for a sulphur paint which may be used as a substitute for sodium sulphide. Half a pound of sulphur is boiled with excess of lime, and 33 oz. soda crystals added to the solution. This gives the same unhairing effect, and the same alkalinity, or causticity, as 3 lb. sodium sulphide crystals ($Na_2S, 9H_2O$). When sulphur is boiled with milk of lime, a certain amount of calcium sulphydrate is formed, together with some polysulphides, the latter being rather advantageous than otherwise to the process. The sulphydrate has been shown to be the acting depilatory agent. By the omission of the soda an effect very similar to that of an arsenic lime is obtained.

The felmongering of sheepskins in New South Wales is fully dealt with in a paper by F. A. Coombs, E. Swinbourne, and G. W. Gabb.[13]

A. A. Schlichte,[14] in a thesis presented to the University of Michigan, deals with the alterations in the structure of skin due to the liming process, in which he shows that, contrary to general belief, lime will unhair in sterile solution.

J. T. Wood and D. J. Law[15] show that both ammonia and sulphur compounds are formed from the hair of skins in sterile solutions, and that these products take part in the unhairing.

Rogers[16] contributes some useful notes on depilating, and D. McCandlish and J. A. Wilson[17] describe a reliable method for the

[10] *Coll.*, 1913, 73; 1914, 305.

[11] *J. S. C. I.*, 1914, 578; *J. A. L. C. A.*, 1914, 416.

[12] *J. S. C. I.*, 1916, 456; *J. A. L. C. A.*, 1916, 318.

[13] *J. S. C. I.*, 1916, 227; *J. A. L. C. A.*, 1916, 286.

[14] *J. A. L. C. A.*, 1915, 526; *J. S. C. I.*, 1915, 1218.

[15] *J. S. C. I.*, 1916, 585; *J. A. L. C. A.*, 1916, 381.

[16] *J. A. L. C. A.*, 1914, 42; *J. S. C. I.*, 1914, 152.

[17] *Ibid.*, 1913, 28; *J. S. C. I.*, 1913, 153; *J. A. L. C. A.*, 1916, 318.

determination of alkaline sulphides in the limes, based on Blockey and Mehd's method (*Coll.*, 1914, 75). The causes of error in the different methods of estimating sulphides in lime liquors have recently been discussed by H. G. Bennett (*Coll.*, Lond., 1916, 219).

An exhaustive résumé of the subject of unhairing and liming by W. Eitner was published in *Der Gerber* in 1913.[18]

Puering and Bating.—In the puering and bating processes the use of artificial bates has increased very considerably during the period under review. Most of these bates are based on the researches of Wood,[19] published in the Journal of the Society of Chemical Industry from 1894 onwards. The most successful of these bates is sold under the name of "Oropon."[20] This is composed of the enzyme of the pancreas absorbed in sawdust or kieselguhr, and then intimately mixed with varying proportions of ammonium chloride or boric acid, according to the kind of work for which it is destined to be used.

A similar preparation is in use in France under the name of "Confit Wood." These enzyme bates have been very successfully used for sheep and glove leathers, and also for split hides for boot uppers and glacé kid. There are some difficulties in the puering of hard goatskins, and also sheep grains for skivers, the difficulty with the latter being due to the prolonged liming the skins undergo. The prolonged action of lime so changes the chemical composition of the hyaline layer, and of the fibers immediately underlying it, that the former is capable of being attacked by tryptic enzymes, whereas the compound formed on or in the fibrous structure of the grain renders it more resistant to the action of the enzymes. The result is that in practice the hyaline layer of the skin is damaged before the remainder of the skin is sufficiently reduced or "down." There is little doubt that further research will overcome this difficulty.

Wood, in collaboration with H. J. S. Sand and D. J. Law, has investigated the action of the puering or bating process on the resiliency of the skin, using for this purpose the apparatus devised

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[18] *J. A. L. C. A.*, 1913, 482.

[19] *The Puering, Bating, and Drenching of Skins*, Spon, 1912; *Das Entkälken und Beizen von Fellen, Vieweg, Braunschweig*, 1914.

[20] See Eitner, *Der Gerber*, 1912, 311; *J. S. C. I.*, 1912, 1193.

by Dr. Sand. By this means the degree of falling of the skins may be expressed numerically, and so recorded.[21]

The bacteriology of the bate has been further studied in America by William Cruess and Frank H. Wilson,[22] and John Helfrich contributes a valuable article on chemical control in the beam house.[23]

The following references to deliming, puering and bating processes may be mentioned:—

"The Acid Deliming Process," H. R. Procter, *Tanners' Year Book,* 1913, 75; *J. A. L. C. A.*, 1913, 350.

"Process for Bating Skins," Eberle and Co., Stuttgart. Eng. Pat. 22753, Nov. 19, 1914; *J. S. C. I.*, 1916, 430. See also Eng. Pat. 21202 of 1909; *J. S. C., I.*, 1910, 226.

"Improvements in the Preparation of Skins for Tanning," S. W. Cook, Eng. Pat. 24418, Dec. 21, 1914; *J. S. C. I.*, 1915, 1218.

"Process for Puering Skins," L. Krall, Fr. Pat. 469758, Mar. 18, 1914; *J. S. C. I.*, 1915, 42.

"Analysis of Material used in Beam House Procedure," C. R. Oberfell, *J. A. L. C. A.*, 1915, 252.

"Process for Deliming and Bating Hides and Skins," P. Schneider, *D. R. P.* 268236. In this process acid salts, such as sodium bisulphate, together with boric acid and sugar, are used. The process is more of a deliming than a puering process.

Pickling.—This process has come into increasing use year by year, not only as a preservative treatment, but more especially as a preliminary treatment in the manufacture of a great variety of leathers, principally chrome tanned, *e.g.*, split hides for boot uppers, sheep leather for gloving and for motor clothing, etc. No new methods have been adopted, but a great deal of light has been thrown on the theory of the process by the work of Procter and his pupils.

In the following references, the process is described and briefly discussed in 1 and 2. In 3 and 6 the control of the process in the works is described, and in 4, 5 and 7, the physical and chemical actions involved are fully discussed:—

1. "The Rising or Pickling of Skins," J. T. Wood, *Tanners' Year Book,* 1912, 115; *J. A. L. C. A.*, 1912, 409.

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[21] *J. S. C. I.*, 1913, 398; *J. A. L. C. A.*, 1913, 247.

[22] *J. A. L. C. A.*, 1913, 8, 180; *J. S. C. I.*, 1913, 617.

[23] *Ibid.*, 1915, 396.

2. "Note on the Pickling Process," Professor H. R. Procter, *J. A. L. C. A.*, 1913, 7.
3. "Chemical Data from the Pickle Solution," P. M. Randall, *J. A. L. C. A.*, 1915, 171.
4. "The Equilibrium of Dilute Hydrochloric Acid and Gelatin," H. R. Procter, *Chem. Soc. Trans.*, 1914, 313; *J. S. C. I.*, 1914, 326; *J. A. L. C. A.*, 1914, 207.
5. "The Acid Gelatin Equilibrium," H. R. Procter and J. A. Wilson, *Chem. Soc. Trans.*, 1916, 307; *J. S. C. I.*, 1916, 645; *J. A. L. C. A.*, 1916, 261.
6. "Felmongering and Tanning Sheepskins in New South Wales," F. A. Coombs, E. Swinbourne, and G. W. Gabb, *J. S. C. I.*, 1916, 227; *J. A. L. C. A.*, 1916, 318.
7. "Swelling of Gelatinous Tissues," H. R. Procter and D. Burton, *J. S. C. I.*, 1916, 404. Discussion, *J. S. C. I.*, 1916, 675; *J. A. L. C. A.*, 1916, 275.

TANNING PROCESSES.

(a) *Vegetable Tannage.*—This is still the most important tanning process.

Neradol.—The most striking advance in this section is the commercial production of a synthetic tannin due to E. Stiasny,[24] Neradol[25] is prepared by the action of formaldehyde upon phenolic bodies under such conditions that only water-soluble products are obtained. The original material was put on the market by the Badische Anilin und Soda Fabrik, but since the war, several English firms have begun to manufacture it with success. Their products are sold under the names of: Synthetic Tannin, Paradol, Cresyntan, and Syntan.

Used alone, neradol gives a white-colored, rather empty leather. The material strikes through the skin very rapidly, and it may thus be used as a preliminary tannage to shorten the time occupied in passing the goods through weak liquors; they can then be transferred direct to strong liquors of the usual vegetable tanning materials without danger of drawn grain or "case hardening." Great advances in our knowledge of the vegetable tanning process may be expected from the introduction of such materials, since the constitution of such synthetic tannins can be varied or modified in a controllable way; then the connection between con-

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[24] *Coll.*, 1913, 142; *J. S. C. I.*, 1913, 775; J. A. L. C. A., 1913, 208.

[25] Ger. Pat. 262558, Sept. 12, 1911, *J. S. C. I.*, 1913, 878.

stitution and tanning effects can be studied, and the question be answered how far the differences in the tannin molecule are responsible for differences in the leather produced.

References.—H. Dierdorf, *Coll.*, 1913, 366; Grasser, *Coll.*, 1913, 413; Eitner, *Der Gerber*, 39, No. 931; Moeller, *Coll.*, 1913, 487, 593; Stiasny, *Coll.*, 1913, 528, 597 (a reply).

J. L. Van Gijn and H. Van der Waerden, in Holland, have investigated the pentose content of various tannin materials, and described the method for the estimation of pentoses by precipitation of furfurol with phloroglucin. The method is useful in detecting the presence of quebracho extract and chestnut extract and also for the estimation of lignin.[26]

Electric Tanning.—The use of an electric current to aid tanning has been further investigated by O. J. Williams[27] and K. Rideal and U. R. Evans.[28] The conclusions drawn are that the direct current destroys the tan in a tan liquor, but that an alternating current has not this destructive effect, and may accelerate the tannage by cataphoresis

(b) *Mineral Tannages.*—The principal tannage in this class is by means of chrome salts. It has not only held its place, but largely displaced vegetable tannages for upper leather, and it is also coming into considerable use for sole leather. For the latter much ingenuity and long trials have at last overcome the difficulties due to the stretching of the leather and to its slippiness in use. Chrome tanning generally is very fully treated in the *Handbuch der Chromgerbung* by Joseph Jettmar (Schulze und Co., Leipzig, 1913).

R. F. Innes[29] has shown that the chrome content of a given leather gives no information as to possible causes of harshness, tinniness, or break, whereas a microscopic examination of the fibers often gives very useful information. The paper is illustrated by photographs of the fibers of chrome tanned glacé goat.

Procter and Wilson,[30] from an investigation as to the causes of undertanning with certain one-bath liquors, find this to be due to salts of hydroxyacids, which, when present in sufficient quan-

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[26] *Coll.*, 1913, 639; *J. S. C. I.*, 1914, 151; J. A. L. C. A., 1914, 109.

[27] *Coll.*, 1913, 76; *J. S. C. I.*, 1913, 373.

[28] *J. S. C. I.*, 1913, 633.

[29] *J. S. C. I.*, 1914, 579.

[30] *J. S. C. I.*, 1916, 156; *J. A. L. C. A.*, 1916, 173.

tity, entirely prevent the tanning. They further show that chrome tanning, unlike vegetable tanning, is a reversible process.

Procter has made several practical suggestions arising from a consideration of the research. One of these was that hides, or kips, could be partially chromed, and in that state can be split more readily than in the lime. The grain can be tanned out in chrome liquors, and the flesh split, which is best tanned in vegetable liquors, can be stripped of all chrome by means of a solution of Rochelle salt, or other salt of a hydroxyacid, and afterwards tanned in any way desired. A further use of the idea is that chrome pieces and shavings may be stripped of chrome and used in the manufacture of glue and gelatin.

Several other processes have been proposed for dechroming chrome-tanned leather for the preparation of glue. S. R. Trotman[31] treats the leather with sodium peroxide. Oxidation of the chrome to sodium chromate takes place. This is removed from the leather by washing and then recovered. W. Prager[32] uses 2 per cent. sodium bisulphate at 45° C., whereby the basic chrome salt in the leather is changed into the normal soluble salt. The latter is then washed away, and the leather finally neutralized with lime.

So far as my knowledge goes, there have been no changes in the alum tanning process, though here it seems possible to effect improvements by utilizing basic aluminium salts somewhat after the methods of one-bath chrome tanning. This was originally proposed by Bertram Hunt.[33]

(c) *Oil and Aldehyde Tannages.*—Oil leather dressing or chamoising has not undergone any change during the period under review, but Lewkowitsch and Wood[34] have shown that the use of neutral fish oils is not essential for the tannage, but that the free fatty acids can tan even quicker than the neutral oils, or glycerides. The process has not been successful commercially owing to the by-products—*e. g.*, sod oil—being of a different character from that produced from the original oils. The dis-

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[31] Eng. Pats. 5676, Mar. 7, and 12393, May 23, 1911, *J. S. C. I.*, 1911, 1462.

[32] D. R. P. 257286, June 15, 1912, *J. S. C. I.*, 1913, 501.

[33] Eng. Pat. 15607, 1884, *J. S. C. I.*, 1885, 747.

[34] Eng. Pat. 13126, 1911, *J. S. C. I.*, 1912, 597.

covery, however, throws a good deal of light on the chemistry of the oil leather tannage.

Tannage by means of formaldehyde, invented by Payne and Pullman in 1898,[35] has been improved and come into increasing use in the manufacture of white washable gloving leather. The skins used are mostly lamb splits or "linings." The leather is perfectly white, and improves by washing. The manipulation of the skins and details of the process are, more or less, kept secret.

Finishing Processes.

These are of almost infinite variety, including not only ordinary finishing of sole leather and dressing hides for the market and of upper leather in blacks or colors, but all kinds of fancy leathers, buffed, printed or velvet finish for bags, bookbinding, and leather goods generally. As a rule, the leather, especially sheepskins, is degreased before dyeing and finishing, although in recent practice it is frequently dyed before degreasing. Modern degreasing plants owe their origin to F. N. Turney.[36] The solvent used is generally petrol spirit or benzene, which is completely recovered by distillation. Other degreasing plants on a slightly different principle have been constructed by W. J. Sagar.[37]

Recently other solvents, which have the advantage of being non-inflammable, have been tried, the most promising being trichlorethylene (C_2HCl_3), sold under the name of Westrosol. It may be used in the dry way the same as benzene, but it has also been applied in admixture with soap to wet skins. The wet process has not come into general use in England, as it cannot compete with the dry process.[38] It may be noted that trichlorethylene has a toxic effect, and it is very probable that this would cause trouble if it came into general use.

Oskar Trebitsch has patented[39] the use of peptone and similar hydrolyzed albumins for the fixation of tannin in sole leather and

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[35] Eng. Pat. 2872, 1898, *J. S. C. I.*, 1899, 504. See also Meunier *Coll.*, 1912, 420.

[36] Eng. Pats. 8179 of 1893, 14978 of 1895, 1370 and 18360 of 1896, *J. S. C. I.*, 1894, 633; 1896, 589; 1897, 41, 677.

[37] Eng. Pat. 13778 of 1897, *J. S. C. I.*, 1897, 816.

[38] *Coll.*, 1913, 61.

[39] D. R. P. 265913, *J. S. C. I.*, 1913, 1121.

also for fixing the colors on dyed leather. Such products are stated to act better than albumin, which is generally used, since they have no hardening effect, but, on the contrary, make the leather softer.

J. T. Donald[40] contributes a useful paper on modern shoe polishes and dressing, in which the compositions required for various kinds of leather are dealt with.

In the older process of japanning with linseed oil the leather requires exposure to sunlight in order to toughen the varnish. It has been found that this effect is due to the action of the ultra-violet rays in the sunlight. As is well known, ultra-violet rays are absorbed by glass, but pass freely through quartz. A large plant for the treatment of enamel leather by ultra-violet light from mercury quartz lamps is at present installed in a German leather works. The effect is said to be exactly similar to that of sunlight and consequently, because of that, the manufacturer is independent of the weather. (See Eng. Pat. 10971, 1912, *J. S. C. I.*, 1912, 694; U. S. Pat. 1,099,378, 1910: also supplementary Fr. Pat. 443406, 1913, *Coll.*, 1913, 337.)

Collodion or nitrocellulose dissolved in amyl acetate and other solvents, alone or in mixture with oil products, has largely taken the place of linseed oil in japanning. The advantage of the process over the older method is that no ovens are required, exposure to sunlight is not necessary, and the leather retains its natural grained surface, which is visible through the transparent coating. The enamel has not the same tendency to crack as the linseed oil varnish.

Doerr and Reinhardt[41] have patented the use of ammonia vapor in the final drying of japanned leather. The vapor is produced by exposing ammonia solution, sp. gr. 0.950 to 0.960, in the drying stove during the final drying-off process.

Fat Liquors.—The use of emulsions of oils in water and soap solutions is an integral part of the chrome tanning process where the leather must be dyed and fat liquored before dried out. Fat liquors are also applied to vegetable tannages both before dyeing and also in the dye bath. The scientific aspect of these emulsions has already been developed by Meunier.[42]

[40] *J. S. C. I.*, 1913, 459.
[41] D. R. P. 267524, *Coll.*, 1914, 41.
[42] *Coll.*, 1910 222, 227; *J. S. C. I.*, 1910, 102.

The principal change has been in the increased use of sulphonated oils (sulphonated castor oil and sulphonated cod oil). These oils are now added to the dye bath, and are also used in the preparation of soft leathers, such as the jerkin basils for the lining of soldiers' winter clothing. They have the valuable property of emulsifying larger quantities of neutral and even of mineral oils. The increased use of these oils has necessitated new methods of analysis for their commercial valuation. Combined SO_3, total neutral oil, and moisture are the figures usually required. The method of analysis prescribed by the A. L. C. A.[43] is quite satisfactory for general control work. Other papers which may be consulted are as follows:—

"Developpement de l'emploi des huiles emulsionnables, et des emulsions en tanneries," U. J. Thuau, *Coll.*, 1913, 219 and 335; *J. S. C. I.*, 1913, 617; *J. A. L. C. A.*, 1913, 302.

"The Constants of the Fatty Acids from Sulphonated Cod Oil," L. G. Radcliffe and C. W. Palmer, *J. S. C. I.*, 1915, 643; *J. A. L. C. A.*, 1915, 434.

"Sulphonated Cod Oils," Dr. G. Bumcke, *J. A. L. C. A.*, 1915, 559; *J. S. C. I.*, 1915, 1214 (an excellent discussion of the various methods of analysis).

"Analysis of Turkey Red Oil," M. Herbig, *Les Matières Grasses*, 1915, 4316; *J. A. L. C. A.*, 1915, 437.

"Notes on Sulphonated Oil Analysis," W. K. Alsop and L. A. Cuthbert, *J. A. L. C. A.*, 1916, 364 (an interesting discussion on the constitution and analysis of sulphonated oils).

Waste Products.—The economical disposal of tannery waste has not received the attention in this country that it has in America. Meunier[44] recommends that the various effluents from the tanneries should be mixed together for settlement; the combination of tannin and lime, chrome, and dye liquors, when blended together, forms heavy and easily separable sediments. He also gives analyses of the various waste liquors from a sole leather tannery, using vegetable tanning materials only.

F. P. Veitch[45] gives particulars of sewage disposal plant at Gloversville, New York, where there are a large number of tanneries, and where the purification of the waste is largely a

[43] *J. A. L. C. A.*, 1914, 68; *J. S. C. I.*, 1914, 266.

[44] *Coll.*, 1912, 268.

[45] *J. A. L. C. A.*, 1913, 10; *J. S. C. I.*, 1913, 153.

problem of the purification of the tannery effluent. In a further paper[46] the same author states that the amount of effluent from tanneries varies from 100 to 375 gallons effluent per day per hide. The following figures on the character and distribution of the effluent from a tannery, handling about 3,000 horse and calf hides per day, are of interest: 4,000 gallons of spent soak, 1,200 gallons chrome liquor, 1,200 gallons of spent pickle, 1,000 gallons of spent bate, 7,650 gallons of sulphide sludge, 121,500 gallons of wash water, making a total of 136,550 gallons, of which about 15,000 gallons are what may be termed highly impure wastes, the remainder being wash water, which, from the nature of its use, can contain but little dissolved matter.

Sedimentation is absolutely necessary. The sewage on entering the filter should contain less than 300 parts per million of suspended matter. The lime mud from the unhairing pits should be kept separate from the other waste, and only the liquid portion mixed with the other waste liquors. It may be remarked that this is contrary to the usual recommendation, but it has been found that if the lime mud is mixed with the effluent, the volume of sludge is greatly increased, and its fertilizer value materially reduced, because so large a quantity of inert material is mixed with the nitrogenous matter, the most valuable constituent of the settled sludge. The lime mud should always be kept separate from the other waste, and sold or given away by itself.

Treatment of the effluent from the filters with hypochlorite at the rate of 5 to 10 parts chlorine per million, will make the material comply with all reasonable requirements as to purity. The total cost of purification plants, depending on construction and local conditions, may vary from about $35,000 to $75,000 for 1,000,000 gallons per 24 hours. Tables are given showing area, cost, and capacity of work for treating this quantity of sewage.

A. Roth[47] gives an account of the results obtained by the Massachusetts State Board of Health, in which it is stated that a bacteriological treatment of the wastes is possible, and that several plants are in operation. The preliminary treatment is a settling process, which is allowed to take place in a continuous flow tank of sufficient size, the length and breadth being so pro-

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[46] *Ibid.*, 1915, 126; *J. S. C. I.*, 1915, 437.

[47] *Ibid.*, 1914, 512; *J. S. C. I.*, 1915, 41.

portioned that the velocity of the sewage shall at no point be sufficient to disturb the settling action. In the Michigan Tanning and Extract Company's plant at Fremont (Mich.), working 300 hides per day, with a total waste water flow of 400,000 gallons per 24 hours, seven sedimentation tanks, 13 × 50 ft. and 55 in. deep, are used. In addition there are two small continuous upward-flow sand beds, with an area of 500 sq. ft. each. Alumino-ferric is used as a coagulant to aid in the sedimentation, and to discharge the color. No attempt is made to obtain a stable non-putrescible effluent by filtration, as the effluent from the continuous upward-flow sand bed is discharged directly into the creek.

The problem of dealing with the sludge is difficult, special drying devices, sludge presses, etc., being required unless large space is available for natural drying. Even after sedimentation, the wastes contain more dissolved organic matter than is present in ordinary domestic sewage. Further treatment of the waste is therefore imperative. Some form of filtration is necessary, as sewage farming requires too much land. Intermittent sand filtration has proved satisfactory if sufficient time is allowed for the aeration of the bed. The degree of purification depends on the condition of the bacteriological film and the supply of oxygen. The cost of treatment in the above-mentioned plant, for operation only, was about $5,000 per annum.

C. C. Smoot[48] gives analyses of partially dried sludge, and of the effluent from an American sole leather tannery. The solid matter was analysed by the State Department of Agriculture, and found to be particularly adapted for the manuring of fruit trees.

J. W. Phelan and J. H. Cohen[49] give details of a rapid filter system (Moore Slime Filter) to handle 1,000,000 gallons of effluent per day.

With regard to the attempts to produce a satisfactory effluent by the so-called "activated sludge process," important general papers by E. Ardern and W. T. Lockett[50] may be consulted.

MACHINERY.

Generally speaking, there has been a great change in the atti-

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[48] *J. A. L. C. A.*, 1914, 523; *J. S. C. I.*, 1915, 41.
[49] *Ibid*, 1913, 426; *J. S. C. I.*, 1913, 1024.
[50] *J. S. C. I.*, 1914, 523; 1915, 937.

tude of manufacturers towards the use of machinery, especially during the last three years, and great strides have been made in the use of machinery for all branches of the leather industries.

One of the chief advances has been in the introduction of the pneumatic roller fleshing machine, by the Turner Tanning Machine Company, of Peabody, Mass. The machine is constructed in a similar way to the modern type of fleshing machine, but instead of a solid rubber roller, there is a flexible hollow bed roller, connected with a pressure tank gauge, an automatic relief valve, and a constantly running pump. There is thus an open flow of air in and out of the bed, and the support is constantly and instantly varying in quantity as the width and thickness of the hide changes. The pressure of air on the support may be altered when desired without stopping the machine. By means of this improvement, the bellies and shanks are fleshed as clean as the backs, and the loss of weight by too clean fleshing of the heavy parts is avoided.

Another machine which has been largely introduced in America, also by the Turner Machine Company, is a power hydraulic press, in which the leather is placed on a table, and a platen brought down upon it with a pressure of about 75 tons. The result is a greatly improved feel of the leather—the elimination of growth wrinkles, and greatly increased cutting value.

The machine is also used for chrome sole leather, and can be used on cut pieces of other heavy leathers to good advantage.

A striking-out machine is now made in Great Britain capable of setting out the very thinnest skins, such as skivers, quite as well as thicker skins.

Blacking and seasoning machines have also come largely into use. Several new measuring machines, based on the principle of the old Sawyer machine, have been put upon the market, which are very reliable.

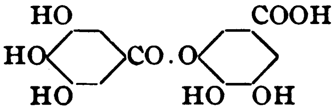
The National Physical Laboratory now standardize templates for checking the results of these machines, and after the war the whole question of the measurement of leather will be placed under the Weights and Measures Act.

CHEMISTRY AND ANALYTICAL METHODS.

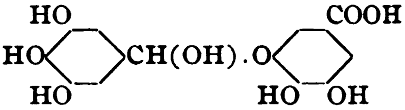
Some of the chemical problems involved have already been referred to, since it is not possible to separate the chemistry of the various processes from the practical work of leather making. The chemistry of the tannins has been the subject of continuous research.

Nierenstein and various collaborators at Bristol have continued to examine tannins and other products, such as ellagic acid[51] and catechins,[52] with a view of determining their chemical constitution. Nierenstein considers tannin, or gallotannic acid, to consist of a mixture of digallic acid (I) and leuco-tannin (II).

I.



II.



Emil Fischer,[53] after purifying gallotannic acid by solution in aqueous alkali, and extraction with ethyl acetate, as had been done by Stiasny and Paniker,[54] so that it contained no free carboxyl group, found it to yield on hydrolysis with sulphuric acid 7 to 8 per cent. of glucose, the other product being gallic acid. The conclusion drawn was that 1 molecule of glucose was combined with 10 molecules of gallic acid.

In a further paper Fischer and Freudenberg described an attempt to synthesize gallotannic acid by starting with the methylotannin of Herzig and his pupils. They obtained in this way a body which is shown to be pentadigalloyl-glucose, and which, if not identical with tannin, is so nearly related to it that the synthesis may be said to be accomplished. The structure of the tannin molecule may therefore be represented thus:

$$\overbrace{\mathrm{CHOR.CHOR.CHOR.CH}}^{\mathrm{O}}\mathrm{.CHOR.CH_2OR,}$$

where R = $(HO)_3C_6H_2.CO.O.C_6H_2(OH)_2CO$.

For an account of this work, see *Berichte,* 46 (1913), 3253, *Coll.,* 1914, 8. Fischer does not think his products can be of any

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[51] Nierenstein and Rixon, *Coll.,* 1913, 53; J. A. L. C. A., 1913, 172.

[52] Nierenstein, *Coll.,* 1913, 200.

[53] *Coll.,* 1914, 8; J. A. L. C. A., 1914, 280.

[54] *Chem. Soc. Trans.,* 1911, 99, 1869; J. A. L. C. A., 1912, 263.

use to the practical tanner, who can only consider much cheaper materials, such as Neradol.[55]

A large number of papers on analytical methods have been published, chiefly in connection with the estimation of tannin, but, as stated in the introduction, the hide powder method as specified by the I. A. L. T. C. and the A. L. C. A. still holds the field.

The attraction of a definite chemical method for the estimation of tannin still claims the attention of chemists, especially the use of copper and nickel salts. It may be pointed out that such precipitation methods are quite as empirical and unsatisfactory as the hide powder method, since in both cases we have to deal with colloidal precipitation, and the composition of the compound formed depends upon a number of physical relations, which it is extremely difficult to keep constant.

The following list of papers and notes will be sufficient to give an idea of the work done in connection with the analysis of tanning materials:—

H. G. Bennett, "Analysis of Tanning Materials," *J. S. C. I.*, 1914, 1182; 1915, 473 and 822. "Note on the Tannins of Valonia, Oakwood, and Chestnut Wood," *J. S. C. I.*, 1914, 1186.

A. T. Hough, "Notes on the Application of Tungsten Salts to the Analysis of Tanning Materials," *J. S. C. I.*, 1914, 847.

Puran Singh, "Nickel Tannates," *J. S. C. I.*, 1914, 172.

D. B. Dott, "Note on the Determination of Tannin," *J. S. C. I.*, 1915, 1124.

A. T. Hough, "Analysis of Tanning Materials," *J. S. C. I.*, 1915, 472.

F. A. Coombs and A. H. Dettmann, "Notes on Australian Pine Barks," *J. S. C. I.*, 1914, 232.

T. Callan, "Note on the Analysis of Guara and Guara Extract," *J. S. C. I.*, 1915, 645.

T. Callan, "Note on the Analysis of Tanning Materials," *J. S. C. I.*, 1915, 646.

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[55] Mr. F. C. Thompson points out that Fischer's attempt to synthesize gallotannic acid was by the condensation of glucose and the acid chloride of digallic acid, and the success of this attempt, according to Fischer himself, was not certain. He considers the preparation of gallotannic acid from methylotannin next to an impossibility. The methoxy groups could only be removed by the action of hydriodic acid, a procedure far too drastic for the stability of the gallotannic acid molecule.

Puran Singh, "Note on the Addition of Fat to Tannin Extracts," *J. S. C. I.*, 1915, 208.

Puran Singh and T. P. Ghose, "The Use of Nickel Hydroxide in Tannin Estimation," *J. S. C. I.*, 1916, 159.

The analysis of sole leather is dealt with very comprehensively by F. P. Veitch and J. S. Rogers,[56] and that of East India leathers by M. C. Lamb.[57]

SOME EFFECTS OF THE WAR ON THE TANNING INDUSTRY IN GENERAL.

The great change that has taken place has been the cutting off, by reason of the war, of supplies of oak wood extract, which comes from Hungary, the import of valonia from Smyrna, and, finally, labor difficulties. Practically no French extract came over for a long time. British tanners had, therefore, to draw increased quantities of mimosa bark from South Africa, myrobalans from India, gambier from Singapore, and quebracho extract from the Argentine. Supplies of chestnut extract were also obtained from the United States, and, although the quality is inferior to the French extract, it helped to keep the tanneries going. British extract manufacturers increased their plant, and came to the assistance of tanners by making a blended extract with quebracho and myrobalans. They also made an extract from mimosa bark, and the latter is now being made in South Africa. England is also getting myrobalan extract from India.

The probable result of all this has been that the British tanner has used more fiber in the tanning of his leather—in fact, has gone back to the process adopted 20 or 30 years ago, before extract was so plentiful and cheap. This has not improved the color of the sole leather, but probably the quality has been, if anything, better than it was prior to the war, because we have lacked the bleaching agents that tanners were using.

We have also been handicapped considerably by the price of such materials as lactic, formic, and oxalic acids. The two former are used for deliming, and oxalic acid is used to a certain extent in the early liquors to throw out lime salts and improve the color of the leather.

[56] *J. A. L. C. A.*, 1913, 286.

[57] *Coll.* (London), 1915, 111.

GLUE MANUFACTURE.

During the last three years there have been no striking advances in the methods of manufacture, but there has certainly been an awakening to the value of scientific control of the processes, and the control of raw and finished products. This has been largely rendered necessary by the difficulty of the bone market and the competition of the German combine. There has been an increasing tendency to concentrate on one product, and to pay more attention to by-products.

Owing to the increasing demand for gelatin, many who formerly only made glue are now producing this substance. This in itself has made it necessary to be much more careful about the details of manufacture, and thus indirectly the quality of the glue has also improved.

Many patent processes have been brought out, but none appears to be commercially successful. There is still a marked disinclination on the part of manufacturers to spend money on experiments.

Among the patents taken out is a process for treating bones with a solution of peroxide or percarbonate of sodium.[58] It is said to be much quicker than the usual treatment of lime, and a better colored product is obtained. While this process is too costly for ordinary glue, it is said to be effective in the manufacture of gelatin. Trotman's process for preparing glue from chrome leather pieces has already been mentioned, p. 495.

The testing of glue has received a good deal of attention during the last few years, and specifications for checking the quality of cabinet glue have been drawn up by the American Society for Testing Materials.[59]

There is also some interesting information on the chemistry and quantitative determination of gelatin by M. Berrar.[60]

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[58] H. Benzel, Fr. Pat. 460611, *J. S. C. I.*, 1914, 95; Eng. Pat. 24135, 1913, *J. S. C. I.*, 1914, 759.

[59] *J. S. C. I.*, 1914, 1021. See also "A Study of Various Tests upon Glue, particularly the Tensile Strength," A. H. Gill, *J. Ind. Eng. Chem.*, 1915, 7, 102; *J. S. C. I.*, 1915, 292.

[60] *Biochem. Zeits.*, 1912, 47, 189-214; *J. S. C. I.*, 1913, 37.

COLOR TRADE JOURNAL.

This new periodical made its appearance in August. It is a monthly, 64 pages and cover, with 10 additional pages of advertising. The cover is printed in colors, and the typography and illustrations are of high grade throughout. The publishers are The Color Trade Journal, Inc., 200 Fifth Ave., New York; J. Merritt Matthews, President; C. Cyril Bennett, Secretary. Dr. Matthews is Editor, Eugene C. Mayer, Business Manager and C. W. Butterworth, Managing Editor. The subscription price is $5 a year. Among the articles in the first number are the following: Present Status of the Dyestuff Industry, by C. C. Bennett; Standardizing Commercial Dyestuffs, by J. F. X. Harold; Color and Design in Primitive Art, by M. D. C. Crawford; Principles of Textile Bleaching, by Dr. Matthews; Color Card Independency, anonymous; The Truth about American Dyes, by Dr. Matthews; editorials; Giving Tone to the Liberty Bonds, anonymous; America's Opportunity, by H. Gardner McKerrow; Japan Rises to the Occasion, by Alcan Hirsch; Khaki, by L. DaCosta Ward; Making Cloths Impervious to Rain, by Herbert P. Pearson; Dyeing of Sulphur Blacks, by Dr. Matthews; Up Albany Way, by Elwood Hendrick; Progress with Natural Dyestuffs, by Edward S. Chapin. Nothing further is needed to show that the new Journal is a worth-while addition to the long list of trade journals. We are giving abstracts of several of the papers in the current issue.

ABSTRACTS.

Rubber Soles Up to Date. *Literary Digest*, Aug. 11, p. 20, from *Metallurgical and Chemical Engineering*, July 15, by Andrew H. King. This article asserts that the new kind of rubber soles (which the manufacturers assure us are "not rubber") wear longer than leather, beside having the advantage of being waterproof without treatment. Mr. King says that they are made of rubber and cotton or leather fiber, the fiber causing slight absorption of water and so preventing slipperiness on wet pavements. He also says that the specific gravity has been reduced from the high figures of the earlier materials by the addition of these fibrous materials. No actual figures are given.

Netherlands Hide and Leather Exchange. P. L. EDWARDS in *Commerce Reports,* August 21. Holland is an important producer of hides, goatskins and calfskins, but these have in the past been sold through London, Antwerp and Hamburg, even if they were to be tanned in Holland. At a meeting of tanners and other interested parties held at Rotterdam under the auspices of the Chamber of Commerce on July 12, 1917, a set of arbitration rules was adopted, and also the regulations which are to govern the new exchange. There will be two sections, one at Rotterdam and one at Amsterdam. It is expected that a royal charter will be granted within a few weeks, and operations will begin at once. Matters in dispute are to be referred to a permanent board of arbitrators.

Chrome Calf Leather. ANONYMOUS. *Leather Manufacturer,* August, 1917. Mechanical means of softening dry skins should be avoided, the skins being drummed only after they have become soft in the soaks. Addition of formic acid or sodium sulphide to the soaks hastens the softening, with some salt to prevent swelling. After 2 or 3 days' soaking, it is well to take the skins out and salt them down for a week or two, after which thorough washing prepares them for the limes. The first lime contains 5 per cent. of hydrated lime on the weight of the skins, water at 70° F. (This temperature is maintained through the liming.) After paddling for 24 hours in this the skins are withdrawn and another 5 per cent. of lime with 1 or 2 per cent. of sodium sulphide added. A similar amount of lime and sulphide is added on each of the next 3 or 4 days, and at the end of 6 days, the skins are drawn out, unhaired, washed in warm water and passed into the bating process. The bate liquor contains 8 ounces of oropon for each 100 pounds of unhaired skins, the temperature at the start being 100° F. The skins are turned several times, and allowed to lie in the liquor over night. They are then washed and pickled. Sulphuric or formic acid pickle is made up with ½ gallon of water for each pound of skin, to which are added 12 per cent. of salt and 1½ per cent. of acid, on the weight of the bated skins. The skins are drummed in the pickle ½ hour, and are then drained. If butyric acid is used, 15 gallons of water, 10 pounds of salt and 1 pound of acid make pickle for 100 pounds of skins. If the skins are to be tanned by the one-bath process, the deposition of sulphur in the fiber may be done by drumming in acid and salt and then in sodium hyposulphite solution. After tannage is complete, the leather should be horsed up for 48 hours to allow the chromium hydroxide to become fixed on the fibers. Fat-liquoring is done with an emulsion of sulphonated oil, soap and neatsfoot oil. An acid fat-liquor is much to be preferred to one made of oil and alkaline soap, since it gives softness and a well-nourished "feel" to the leather without danger of injuring the color or spewing.

Standardizing Commercial Dyestuffs. JOSEPH F. X. HAROLD, Ph. D. *Color Trade Journal,* August, 1917, pp. 14-16. While the standardization of the products of other industries has been progressing, nothing has been done to standardize dyestuffs, in spite of the fact that the dyestuff industry is based on scientific investigation to perhaps a larger extent than any other. The science has all been on the side of the seller. What the buyer lacked in science he made up in faith. The bribing of dyers who bought for the mill has been extensively practiced by dyestuff salesmen. "Like a pyramid, bribery rests on a substantial basis, looks well from both sides, and has an equally obvious point, no matter from which place it is viewed." The problem of standardization is difficult because of the complexity and variability of the materials concerned. The number of practical commercial colors is about 1,000, but many thousands of contaminants affect their shade, their fastness or their method of application. Most commercial dyestuffs are not chemical individuals, but are mixtures, reduced in dye strength by addition of diluents, mostly salts. The various batches of color produced from day to day do not run even, and the stronger batches must be reduced to a standard that can be maintained. The weakening of color may, of course, be carried to any extent, but this tendency is controlled by the competition between sellers. The stronger dye per unit price is preferred, if the buyer protects himself by making dye trials. Many buyers, however, are more alive to differences in price than to the matter of quality. "Simple Simon would be a philosopher to the man who haggles about the price he pays per dozen and then fails to count his dozen." A dyestuff of 5 per cent. strength selling readily at $2 per pound in a market where a 50 per cent. dye goes begging at $10 per pound illustrates the point. "The intelligent mill owner, equipped with laboratories for testing his supplies, may not believe the extent of the sale of such colors. * * * To such a purchaser, his precaution seems an obvious counsel of economy, but it is surprising how few buyers are similarly careful." Alizarine pastes and indigo pastes, where the difference in water content is easily observable, are sold generally on specifications in regard to water content. Dilution with solid matters is not restrained by any such check. "There is scarcely any explanation of this anomaly except the persistent trustfulness of human nature when its suspicions are not too sharply aroused." Another matter which enters into the problem is the fact that many colors as sold are mixtures of several chemically simple colors, beside whatever diluents they may contain. Sometimes the proportion of one color is very small, being put in for the purpose of modifying the shade (as in the case of nigrosines, see p. 463—ED.). In any case where the dye is made by mixing colors, the manufacturer has a legitimate objection to declaring the exact content of his dyestuff. There is no use for chemically pure colors in the textile industry, so long as the color strength is there, and the cost of purification would be wasted. Under normal conditions of competition it is not difficult to secure dyes which conform to standard in most respects, but under conditions which have prevailed during the last two years there has been little use of talking about standardization. The factors or constants of dyestuffs which determine whether they conform to a standard or type are many and varied. There is a natural tendency in the trade to standardize along certain lines. Among the criteria are the adaptability of the dye in question to a particular fiber and method of dyeing, its color intensity, its correctness of tone, and constancy in different lots, its fastness, and its chemical composition. When the dyer asks for bids from various firms for his colors for a year, both product and dyed samples are submitted to the color firms, and in most instances the reproduction of these colors by the color makers will conform to the types submitted in intensity, adaptability and tone, and will run true in subsequent purchases.

Giving Tone to the Liberty Bonds. *Color Trade Journal.* The Director of the United States Bureau of Engraving and Printing has ceased to worry about colors for his postage stamps, bank and treasury notes and Government bonds. This means that the American color maker has at last succeeded in making colors for these uses that will pass the extremely rigid tests imposed by the great Government plant. The supplies of German colors procured in 1916 by special arrangement with the British Government have not yet been used up, but the tests which have been made upon the American colors show that they will be satisfactory. The most important colors involved are Prussian blue, Chinese blue, chrome green, printing red and permanent red. The substitution of soda salts for potash salts in the making of the blues has been satisfactorily made. To print the 21,000,000 Liberty Bonds by the customary hand plate printing method would require the labor of 1,000 persons working in 8-hour shifts for a year. They are being printed by power presses. A great printing plant at Buffalo has been commandeered by the Government to help in printing the revenue stamps needed when the new revenue laws go into effect. Three cent stamps are being shipped to the post offices throughout the country at the rate of 100,000,000 a day, to be ready for the inauguration of 3-cent postage.

Japan Rises to the Occasion. ALCAN HIRSCH. *Color Trade Journal,* August, pp. 42-4. Description of the great development of chemical industry in Japan in recent years, with details of the formation of the Japan Dyestuff Manufacturing Company, and its plant.

Present Status of the Dyestuff Industry. C. C. BENNETT. *Color Trade Journal,* August, 1917, pp. 1-3. The chief obstacle to the rapid development of dyestuff making in America was the lack of the necessary "intermediates." Many of them are now being made by various firms. The general tendency has been for each manufacturer who entered the dyestuff field to aim at the kinds of dyes which could be produced most cheaply and easily. The result has been a somewhat one-sided development. At the present time the needs of the country in the matter of direct cotton colors are fairly well taken care of. There is, however, a scarcity of fast reds, and of developed blacks. Wool dyes are also pretty well taken care of. Blacks are chiefly supplied by logwood, though for high fastness against washing and light these blacks are not satisfactory. Blue wool dyes in good supply include indigo and gallocyanine. Not only is imported indigo available, but the synthetic dye is being made by the Dow Company. Alizarin blues are much needed, as many uses to which they are fitted cannot be supplied by indigo. The combination of makers represented in the recent merger should stimulate the production of the various types of dyes which are still needed.

The Truth About American Dyes. DR. J. M. MATTHEWS. *Color Trade Journal,* August. Manufacturers have in many cases refused to guarantee the fastness of dyes used since the war began. This has been popularly supposed to be due to the poor quality of the dyes being made by American makers. The facts are that much of the trouble was not due to American dyes at all, but to the use of odd lots of left-over dyes which were not considered fit to be employed so long as good dyes were available, but which were used when the supply of better colors became acutely scarce. There have been also cases where the American dye makers were to blame. The unprecedented demand caused lots of dye to be rushed into market without proper purification, and consequently there were disappointments in store for the users. In the main, however, the dyes put out by the American makers have been fully up to standard, being chemically the same as those formerly imported.

New Method for the Analysis of Rancid Fats. G. ISSOGLIO. *Annals of Applied Chemistry,* through *Les Matieres Grasses,* No. 111, p. 4766. The best actual criterion for judging of the rancidity of a fat seems to be to examine the odor and taste. Such an estimate depends on the individual, and is not capable of exact measurement. It has been proposed to measure the rancidity by means of the acidity. This, however, is misleading because some rancid fats have a very small and almost normal acidity. The acidity of a fat may be due to two causes, one of them the natural fatty acids, of high molecular weight and insoluble in water and therefore tasteless. In the rancid fat, there are added to these other organic acids of high molecular weight which are soluble in water and therefore easily perceived by the nerves of taste, even when present in very small quantity. It has been shown that moisture and oxygen are necessary for the development of rancidity. By the oxidation of fats susceptible of becoming rancid, by means of permanganate, for instance, the same products of decomposition may be produced that are formed when the fats become rancid in the natural way. Among these are the following acids and their corresponding aldehydes: formic, butyric, caproic, enanthilic and pelargonic. All these compounds are soluble in water and easily carried over with steam in distillation. These may be recognized by certain color reactions, but not quantitatively determined. The author has devised a method of determining a new number or index, called the index of oxygen consumption (l'indice d'oxydabilite) which shows to what extent rancidity has progressed. When a rancid oil is distilled with water, the material which comes over with the steam has the power of reducing permanganate or other oxidizing agents. The method therefore consists in distilling a quantity of the fat in question with water, and measuring the reducing effect of the distillate on a measured amount of 0.01 *N* solution of $KMnO_4$. The index having been determined for a given fresh fat, the excess due to rancidity is a measure of the change which has taken place.

L. B.

New Process for Obtaining Tanning Extract. CONSUL HOMER BRETT, LaGuayra, Venezuela, in *Commerce Reports*. A. J. Salinas, of Caracas, who is the holder of a concession for the manufacture of tanning and dyeing materials in Venezuela, has applied for a patent on a new "dry process" for the recovery of tanning extract from the divi-divi (also known locally as "nacasal" and "woutapana"). His application states that the process is new and unused in Venezuela, and that it has not been patented nor described abroad.

Origin of Chestnut Extract Tannage. "A TANNER" in *La Halle aux Cuirs*, June 24, 1917. M. Michel, a Lyons chemist, had a country place near the city, where there was hedge of chestnut trees bound together by iron wires. He noticed the black color where the iron came in contact with the chestnut. He was making a black dye for silk, in the manufacture of which "gall nuts" were used. The proof that the substance in the chestnut wood which gave the black color was the same as that in the gall nuts was easily made, and soon he had replaced extract of gall nuts with extract of chestnut wood in the making of his black dye. Mr. Michel suggested to a business acquaintance named Allegatiere, a tanner, that he should try chestnut wood as a source of tanning material. The leather produced by Allegatiere's experiments was gray in color, which discouraged him. After a time, however, he decided to use up some wood which he had left in storage, and the leather made with that was not gray. He found that the bad color was due to the discoloration caused by the damp wood acting on the steel of the cutters used in grinding the wood. The stored wood was dry, and so the trouble was removed.

The Tanning Material Industry in the Dutch East Indies. ANONYMOUS in the *S. and L. Rep.*, Aug. 18. Factories for the manufacture of mangrove extract were established by British capital in Borneo prior to the war. The imposition of tariffs on mangrove extract by both the United States and Germany was a severe blow to the industry. The lowering of the U. S. tariff improved the situation, and the extraordinary demand due to the war has made the business very prosperous. The price of the extract was as low as $43 per ton before the war. It has been as high as $180 since the boom began. The natives of the Dutch East Indies call the mangrove "bakau-bakau." There are several sorts, all of which can be used for tanning. The sort known as "toemoek" is in demand by the Chinese as a dyeing material, and brings several times the price of the others. The bark of the old trees is as much as 2 inches thick. It must be transported to the factory as soon as possible after being peeled, as it deteriorates rapidly. The percentage of tannin in the Borneo mangroves ranges from 30 to 40 per cent. The wages paid by the extract manufacturers are high, from the point of view of the region. The natives cut the trees, peel the bark and transport it to the factories in their small boats. No extract factories are in operation on the African coast, although the growth of mangrove there is abundant and of high quality. The writer attributes this to the lack of available labor. Two products of the Dutch East Indies which could be used in the manufacture of high grade leather are still unknown to the industry in this part of the world. They are "piang" nuts and "mangidstan" bark. (The former of these names suggests "pilang," a species of acacia, which grows in India and the East Indies, and the latter "mangosteen," an East Indian fruit, whose rind contains a high percentage of tannin.—Ed.)

PATENTS.

Fleshing Machine. U. S. Patent 1,235,697. John Kelling, Milwaukee, Wis.

Tanning Fish Skins. U. S. Patent 1,235,543. K. Bendixen, Copenhagen, Denmark. The skins are treated with an alkaline solution to remove a part of the oil. The remaining alkali is then neutralized with acid and the skins washed in water.

Production of Light Colored Leather. U. S. Patent 1,235,059. Sigmond Saxe, New York. After the hides have been partially tanned they are treated in a drum with a further portion of vegetable tanning material, to which has been added from 5 to 10 per cent. of iron-free aluminum sulphate.

Process of Stretching Leather. U. S. Patent 1,235,299. Irving M. Ellsworth, Orrville, Ohio.

Lignin and Lignone Derivatives. British Patent 106,493. E. Oman, Stockholm. Lignin and lignone sulphonates, present in waste sulphite-cellulose lye, are separated by saturating the lye with a salt such as sodium sulphate, which precipitates the lignin sulphonates and leaves the lignone sulphonates in solution.

Drum Tanning Apparatus. U. S. Patent 1,236,806. Edward Wilson, Liverpool, England. This patent covers additional features, extending the invention mentioned in patent 1,176,633 (p. 321, Vol. XI). The present patent relates to means of controlling the flow of liquor through the apparatus.

Tanning Material. U. S. Patent 1,236,468. W. Moeller, Hamburg, assignor to the Renner Company. Before tannage, skins are treated with acid-resin sludge, the free acid of which has been neutralized.

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PERSONAL NOTE.

The present Associate Editor will not, at least for some time, be connected with the JOURNAL of the A. L. C. A. after the present month. He has accepted the appointment of professor of the chemistry and technology of leather at the Tohoku Imperial University, Japan. The courses will be given at the College of Agriculture, which is situated at Sapporo, in the northern island, Hokkaido. The department is a new one, and the choice of an American for the place is a further proof of confidence in America and Americans on the part of official Japan. The appointment is for three years.

NOTICE.

CONCERNING THE DETERMINATION OF SULPHURIC ACID IN LEATHER.

The present methods for the determination of sulphuric acid in leather are far from satisfactory. Either a new method or radical modification of one of the present methods is necessary if entirely reliable results are to be obtained. In order that all valuable ideas and suggestions concerning possible methods may be available to the committee for consideration, it is requested that members submit any ideas as to new methods with available data and comments, and also suggestions for the elimination of errors in the Procter and Searle or other present methods.

It is urged that all members interested in this subject send their suggestions promptly to

JEROME S. ROGERS,
Chairman of the Committee on Sulphuric Acid in Leather.

Address:
Leather and Paper Laboratory,
Bureau of Chemistry,
Washington, D. C.

RESEARCH LABORATORY.

The following particulars in regard to Mr. Jesse Briggs Churchill, who is the newly appointed Director of the Research Laboratory, will be of interest to members of the Association.

Mr. Churchill was born in Chelsea, Mass., in 1875. His preparation for college was received in the Chelsea schools. He entered Lawrence Scientific School in 1896 and graduated in 1899. He was an instructor in the Chelsea High School for one year and then went to the Pennsylvania State College as an instructor. He was appointed Assistant Professor of Industrial Chemistry in 1905; became Associate Professor in 1910, and Professor in 1911, in which year he received from State the degree of M. S.

In November, 1915, he accepted a fellowship from Mellon Institute, conducting the work at the State College, until August, 1916, when he went on leave of absence to Pittsburgh. His training in chemical research began under Richards at Harvard while he was an undergraduate at the Lawrence School. In June, 1906, on leave of absence, he went to Göttingen and studied under Wallach, doing synthetic work on the terpenes. His work at Mellon has been concerned with pharmaceuticals, being about equally divided between laboratory research and plant practice in the Long Island plant of the British-American Chemical Company. He has had wide experience in general consulting and analytical work. For nearly ten years he was consulting chemist for the Pennsylvania Match Company.

NOTES ON THE ANALYSIS OF TANNINS. V.

By Louis E. Levi and Aug. C. Orthmann.

The analytical chemist employed in the tannery is often confronted with the proposition to determine the exact amount of tannin in extracts to which have been added coloring matters to disguise the real color of the extract or for the purpose of placing upon the market an extract of a decided color for use in making a leather for special manufacture. The usual method of analysis—that is with hide powder—does not give one the desired result. It is a well known fact that hide powder because of its porous nature will absorb inorganic as well as organic substances. This inherent property makes the analysis of tanning extracts, in order to determine the exact tannin content, of questionable value. In order to determine the value of hide powder analyses as compared with analyses made with reagent No. 33, using well known vegetable dyestuffs, we undertook this work.

In an article by R. Lauffmann in *Collegium,* Dec. 4, 1915, page 457, the author gives a resumé of his experience of analysis of tannins by the hide powder method as compared to our reagent No. 33 method.

Lauffmann's results as shown by his table of comparative analyses are in close proximity to those we obtained by the two methods. Lauffmann makes the assertion that the hide powder method was taken as a basis of calculating the value of tanning materials by the reagent No. 33 method; this, as proven by our previous papers, is incorrect. The basic factor was derived from the combination of pure tannic acid with chromium from reagent No. 33 and this was calculated to the hypothetical monoglucoside of tannic acid, it being assumed that tannins are varying combinations of these two substances.

This factor could, however, be eliminated and the factor representing pure tannic acid substituted; this would of course give a lower figure, but, at the same time a constant that could be applied in all cases for all so-called vegetable tanning materials. The idea that originated this method of tannin analyses by reagent No. 33 was to find the amount of *true tannin* present in these tanning materials, and not the amount of substance that would combine with hide, render hide imputrescible or be absorbed by the hide powder. This naturally recalls the old, old question: *What is tannin?* The sum and substance of our answer to this question is: "Tannic acid and its homologues, either separate or in combination, that will combine with hide fiber, either physically or chemically, to render the same imputrescible."

Our claim has been and is, that the hide powder method does not determine this factor, but determines each and every substance that will combine with it, and a great number of these substances do not contain or consist of tannic acid, many of which are mechanically or otherwise absorbed by the hide; not only can we place the chromium and aluminum compounds in this class but even the larger part of the so-called tanning extracts and vegetable or natural dyestuffs.

It can be safely assumed that nearly all vegetable tanning extracts contain more or less coloring matter, and that the natural dyestuffs contain more or less tannin. When making analyses of these materials by the hide powder method it will be noticed that the non-tannin solutions are in all cases practically free from coloring matter, this shows that in the case of tanning extracts the hide powder has absorbed all the tannin plus the coloring matter; the same holds good for the natural dyestuffs.

The natural dyestuffs such as logwood, hypernic, etc., etc., are as a rule only used for that purpose, *i. e.*, coloring, but upon making an analysis of substances of this nature by the hide powder method, we find that they are tannins! Many of these materials will render hide imputrescible and undoubtedly make good leather, but the question remains: Do they consist of true tannin plus coloring matter? With this question in mind, analysis of these substances by the reagent No. 33 method suggested itself and caused us to carry out the analyses as listed.

Name	Total solids	Soluble solids	Ins.	Non-Tan. by H.P. method	Non-Tan. by reag. #33 method	Tannin by H.P. method	Tannin by reag. #33 method
Archil extract	9.44	8.36	1.08	7.94	8.36	0.42	None
Fustic extract	95.23	87.83	7.40	25.32	63.08	62.51	24.75
Hypernic extract	71.10	66.42	4.68	45.59	55.27	20.83	11.15
Indigo extract	27.79	24.51	3.28	8.64	24.51	15.87	None
Logwood extract	93.61	88.05	5.56	39.28	64.00	48.77	24.05
Osage orange extract	95.01	89.18	5.83	21.76	69.30	67.42	19.88
Osage orange extract	57.71	53.79	3.92	11.82	40.96	41.97	12.83
Persian berries extract	51.46	49.77	1.69	39.07	48.22	10.70	1.55
Saffron extract	67.53	66.44	1.09	27.92	66.44	38.52	None
Turmeric extract	78.61	22.38	56.23	13.82	20.58	8.56	1.80
Quercitron extract	50.60	47.38	3.22	32.60	43.48	14.78	3.90

All of the non-tannin solutions from the above hide powder analyses were practically colorless and the color of the hide powder showed that the coloring matter was absorbed. The above materials are used as natural dyestuffs and for coloring only and not for tanning purposes, although some of them have tanning properties. Taking it for granted that these materials are coloring matters, how much coloring matter would the hide powder method show? Surely all that is absorbed by the hide is not tanning matter because coloring matter would not make tanned leather, nor is it all tannin, because if it were, how could we account for the depth of the color? The fact that the hide powder analysis does not show or give the correct amount of tannin present is shown by the above analyses. We can safely say that the non-tannins by reagent No. 33 (the difference between the soluble solids and tannin) contain the coloring matter and other non-tanning material. The amount of dyestuff could in this way be calculated by the difference between the soluble solids and the sum of the tannin by reagent No. 33 plus the non-tannin by the hide powder method, assuming that the hide powder non-tannins is correct. This, of course, would give rise to the question: "Must we have a factor for the different tanning materials when making the tannin analyses by reagent No. 33, other than the factor used at present?" The investigation of this factor and the absorption of non-tanning materials by hide powder will be the subject of a future paper.

In the above noted paper by Lauffmann, mention is made of the absorption of iodine by the non-tannins, especially sulphite-cellulose, thereby rendering the iodometric method for chromium determination inaccurate in connection with the indirect method for tannin analysis by reagent No. 33. We have experienced this difficulty of obtaining checks by the indirect method but found that this was due to the fact that not all the organic matter was removed by oxidization with peroxide. However, upon using more sodium peroxide, boiling longer, this difficulty was easily overcome. Furthermore, this chance of error would be entirely eliminated had Lauffmann determined the chromium by the direct method, *i. e.*, incinerating the filter plus precipitate and estimating the chromium in the ash.

Lying in the trenches of analytical methods and protected by the covering of usages of bygone days it is simply a question of time when the modern 75 centimeter guns of new methods will destroy the covering and place the defenders in position of easy capture. When captured by the enemy of inaccurate methods they will be taken into the country of their captors, where brought face to face with advancement, will simply absorb all that is good and use the methods in their own laboratories, when analytical work of this nature is done.

LABORATORIES OF THE PFISTER & VOGEL LEATHER CO.,
Milwaukee, Wis., August, 1917.

NOTE ON THE PROPOSED PROVISIONAL METHOD FOR EPSOM SALTS IN LEATHER.

By W. K. Alsop and W. A. Fox.

The proposed provisional method for the determination of Epsom salts in leather ash (*Journal,* current volume, p. 294), requires that both the iron and aluminum and the calcium precipitates be dissolved and reprecipitated, thus adding considerably to the time and manipulation required in carrying out the determination. That this method did not primarily apply to leather ash is shown by the note at the end of the first paragraph. The iron and aluminum precipitate is generally principally aluminum, and does not usually have the "characteristic appearance" mentioned.

The magnesia was determined in five samples of leather containing from 0.6 to 8.5 per cent. of Epsom salts. Several 10-gram portions of each sample of leather were ashed, the ash dissolved in HCl as directed in the method, the solutions mixed, and made to a definite volume. The number of cubic centimeters taken for each test was equivalent to the ash from 10 grams of leather. Two methods were used, one the proposed provisional method, and the other, called in the table "laboratory method," was the same except that the iron and aluminum and the calcium precipitates were not dissolved and reprecipitated. These results show that such solution and reprecipitation is not necessary, and it seems to us inadvisable to adopt a method requiring it.

Columns headed *a* are by the laboratory method; those headed *b* by the proposed provisional method. Results given are averages of good duplicates.

	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*v*	*b*
Per cent. total ash....	4.03	4.03	2.83	2.83	1.48	1.48	0.54	0.54	0.81	0.81
Per cent. insol. in HCl	0.19	0.19	0.28	0.28	0.03	0.03	0.02	0.02	0.11	0.11
Per cent. NH_3 ppt.....	0.19	0.19	0.26	0.26	0.12	0.12	0.07	0.07	0.17	0.17
Per cent. Ca ppt.......	0.33	0.33	0.10	0.09	0.12	0.12	0.10	0.09	0.03	0.03
Per cent. MgO from pyro-phosphate ppt...	1.38	1.40	0.66	0.66	0.44	0.45	0.31	0.31	0.10	0.10
Per cent. Epsom salts	8.41	8.53	4.03	4.03	2.70	2.77	1.89	1.87	0.60	0.61

LABORATORY OF THE ELK TANNING CO.,
Ridgway, Pa., September, 1917.

MIXING EXTRACTS.

By T. G. Greaves.

Although reducing extracts is simple enough, it is sometimes found to be elusive because of the different units in which measurements are taken and the different requirements.

A chemical engineer who had just figured out the more intricate conception of the specific gravity of the total solids of liquid extracts was temporarily at a loss to explain why it was that when he had mixed equal weights of 51° Twaddell extract and water, 22.7° was obtained instead of 25.5°, naturally thinking at first, that there was an expansion due to the mixing or that calculation could not accurately be based on the Twaddell scale. In the same way it seems that a formula which correctly reduces an extract from 27° Twaddell to 25° Twaddell should also reduce an extract of 27 per cent. tannin to 25 per cent. tannin, but it is found to only reduce it to 25.31 per cent. In making a dye test comparison between 51° and 42° Twaddell dyewood extracts, the equivalent weights are not in inverse ratio to the degrees as would at first sight be expected.

The explanation is that where the mixing is for specific gravity, the measurement should be by volume, and where it is for per cent. the measurement should be by weight. The definition of specific gravity, weight divided by volume as compared to water, depends on both measurements, but while the specific gravity itself implies the weight, the volume relation is not adequately provided for in mixings which depend on specific gravities, unless the measurements are in volume, because the volume implied by the definition, being unity, is the same for extracts of any specific gravity. In the case of mixing for a certain per cent. strength, weight only is involved in the definition, so volume cannot be used directly.

In the case of tanning extracts it is most convenient, usually, to measure in inches depth in a tub with vertical sides, and as this is proportional to the volume in the tub, the mixing is, in effect, made by volume. The results, however, are to be in per cent., so either per cent. must be converted to its equivalent in specific gravity, or volume converted to weight. The following formula can be used directly for either reducing or strengthening:

$$x = \frac{ab\,(c - \mathrm{P})}{m\,(\mathrm{P} - n)}$$

Or where water is used for reducing:

$$x = \frac{ab\,(c - \mathrm{P})}{\mathrm{P}}$$

Where

P = desired per cent.
x = inches to add
m = specific gravity of extract added
n = per cent. of extract added
a = inches of the original
b = specific gravity of the original
c = per cent. of the original

The above is derived from the statement:

$$8.33\,abc + 8.33\,xmn = (8.33\,ab + 8.33\,xm)\,\mathrm{P}$$

8.33 being the weight of a gallon of water. Any unit could be used as it cancels out of the equation.

In the case of dyewood extracts a certain specific gravity is the aim. For this purpose, let "S" = the desired specific gravity, and let both it and m and b (from above) be expressed in degrees Twaddell, then:

$$x = \frac{a\,(b - \mathrm{S})}{\mathrm{S} - m}\text{; or, adding water, } x = \frac{a\,(b - \mathrm{S})}{\mathrm{S}}$$

These last formulae are also used for per cent. where mixings are made by weight. For this purpose let

S = desired per cent.
x = weight to add
m = per cent. of the extract added
a = weight of the original
b = per cent. of the original

This is derived from $x\mathrm{S} + a\mathrm{S} = ab + xm$

In making "half" and "half," where equal tannin units of chestnut and chestnut oak bark extracts are guaranteed, the inches of chestnut extract to add to a given number of inches of chestnut oak bark extract are found by the following formula:

Where

a = inches chestnut oak bark extract
b = specific gravity c. o. b. extract
c = per cent. c. o. b. extract
d = inches chestnut extract
e = specific gravity chestnut extract
f = per cent. chestnut extract

$$d = \frac{abc}{ef} \text{ (from } abc = def\text{)}$$

If the gravities b and e are omitted, the error will be about 1 inch in 3 or 4 feet. It would then be, $d = \frac{ac}{f}$ which gives a little too much bark extract.

The tannin strength (T) of the mixture can be found from the following:

$$\mathrm{T} = \frac{ac + df}{a + d}$$

This formula is not strictly accurate, the gravities being omitted, but as it gives within 0.05 per cent. of the exact formula, it can be used in practice, for the sake of simplicity. If it is sold on a guaranteed 25 per cent. basis, the formula mentioned for reducing with water can be applied.

LABORATORY, JOHN H. HEALD & CO., INC.,
Lynchburg, Va., August 29, 1917.

THE WEAR RESISTANCE OF SOLE LEATHERS. III.

By Lloyd Balderston.

In two previous papers on this subject (Vol. II, pages 429 and 498), experiments were described in which pieces of leather about 1 inch square secured to the circumference of a wheel were worn by contact with another wheel having a rough surface of hardened steel. Many tests were made with this machine, and several well-known substitutes were compared with leather. The results were in every case very much to the disadvantage of the substitutes. The loss in 50,000 contacts with 40 pounds pressure was as high as 35 per cent., while a good vegetable leather lost 5 per cent. or a little more. Such figures are manifestly unfair to the substitutes, since it is common knowledge that there are several of them which wear very well.

It seems that the excessive wear of the substitutes was due to the overload to which they were subjected. Leather has high tensile strength, and when it is overloaded it simply wears faster, but not disproportionately faster, than in actual use. The substitute, whose tensile strength is low, when subjected to a heavy overload, breaks down. The actual surface of contact of the test pieces hardly exceeded 0.2 of a square inch, so the 40 pounds applied was equivalent to about 200 pounds per square inch, which is at least four times as much as would be exerted on the main portion of the shoe sole by an ordinary person in walking.

Having learned that the machine at the Leather and Paper Laboratory, described by J. S. Rogers at Atlantic City, gave results for substitutes indicating for them greater durability than for leather, W. K. Alsop and I concluded that this was due to the character of the wearing surface, which is an iron plate on which sand is sprinkled. The sand grains imbed themselves in the yielding material of the substitute, and during the slight twisting motion of the machine, they slide on the iron instead of cutting the sole.

We decided that in the present state of our knowledge, the only way to get results that would be reasonably sure to be such as actual wear would give would be to make a machine the action of which resembles the action of the foot in walking. The machine here described was built with that idea in view.

The sample of leather, 3½ by 7 inches in size, is secured to a cast-iron foot, (*a*, Fig. 1), a sheet of soft rubber ⅛ of an inch thick being interposed between the leather and the iron. This foot is bolted to a leg *b*, about 30 inches long, pivoted at *c*, just above the foot, to a lever *d*, which is held by a fixed pivot at *e*, and held down at the other end by a spring *h*. The leg is moved by the cam *f*, an Archimedes spiral, revolving as shown, and acting on the stud *g*. The foot rests on a platform *m*, called hereafter the sidewalk, and is curved in such a manner that as the leg moves all parts of the sample are brought into contact with the sidewalk, which moves as indicated by the arrow. When the stud *g* has been pushed as far as possible by the cam, the finger *k*, revolving with the journal *l*, lifts the lever *d* by means of the stud *j* and the rod *n*, so freeing the foot from contact with the sidewalk and permitting the spring *s* to push the leg back ready for another step.

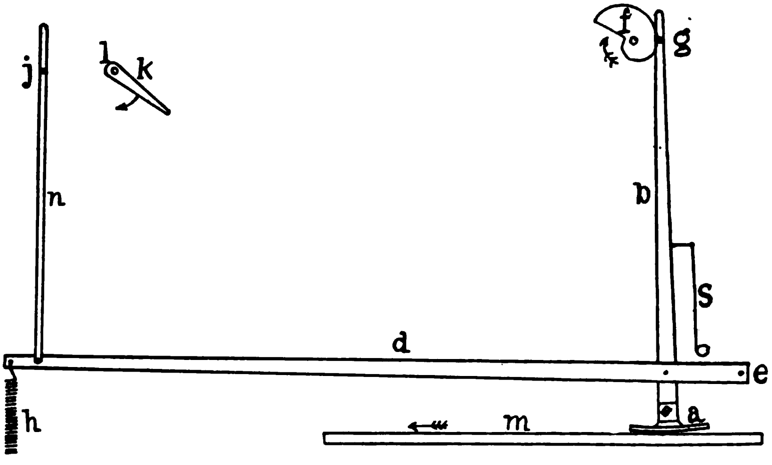

FIG. 1.

When the movable sidewalk has reached the end of its travel, a reversing device causes it to move in the opposite direction, at the same time bringing another cam into action to push the leg in the opposite direction, and shifting the shaft to which the spring *s* is attached so as to make it act toward the right instead of the left.

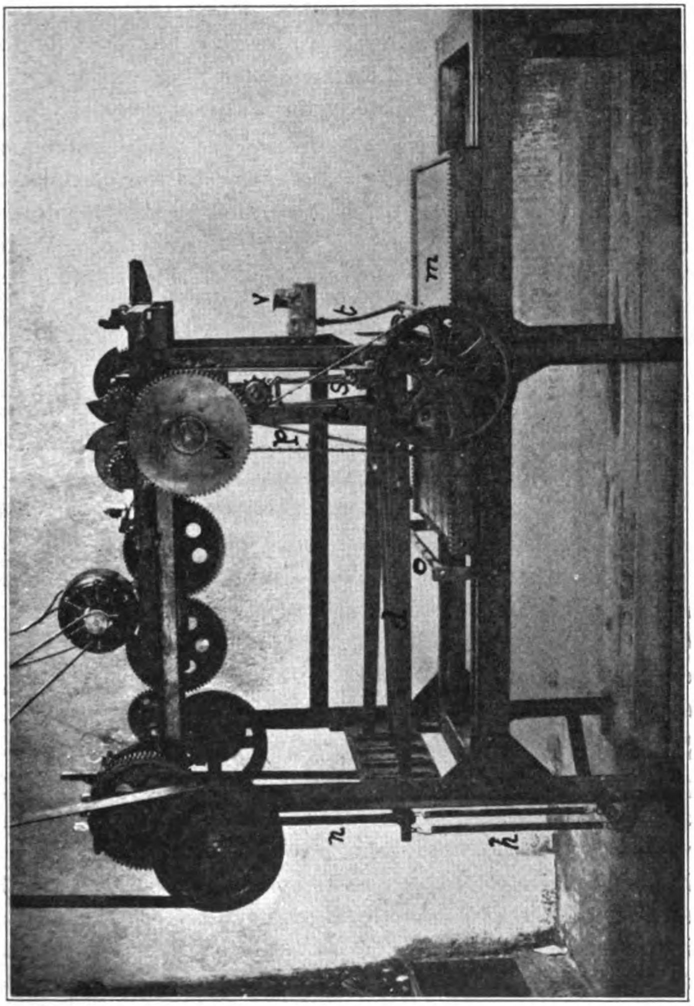

FIG. 2.

Figure 2 is a general view of the machine, which holds four samples. The sidewalk is about 20 by 33 inches, and the whole length of the machine is a little more than 6 feet. It is operated by a ¼ horse-power motor, operating through a countershaft overhead. An air-pump almost hidden behind the corner post at the left of the picture furnishes air to blow the dust off the sidewalk. This air is delivered through small holes in the pipe *o*, and another which is hidden behind the sprocket wheel.

The shafts on which the two sets of cams are set are carried on a frame which slides across the main frame of the machine so as to bring one or the other of the two pinions shown into engagement with the gear wheel *w*, which drives the sidewalk through the sprocket and the rack and pinion. The slanting line *p* is the edge of a lever which is actuated by a bell-crank under the sidewalk, which in turn is pushed by a bolt attached to the sidewalk, and the upper end of this lever being joined to the cross frame; when the sidewalk reaches the end of its journey the frame is pushed over and the feet walk in the other direction.

With the 44-tooth sprocket shown, the rate of motion of the sidewalk is slower than the motion of the feet so much as to cause a slip of about 0.1 inch in 7 inches, in each step. The cup *v* is so arranged that water may be made to run into it, the excess being carried away by a drain, and at definite times the cup is tipped over, delivering 125 cc. of water through the pipe *t* on to the sidewalk when it is desired to run wet tests. This is about at the rate of a rainfall of ¼ inch an hour.

The weight on each foot in the tests so far made was about 200 pounds. The joints by which the feet are attached to the legs are interchangeable, so that the feet may be shifted at equal intervals during a test and bring each foot in turn into each position, so as to discount any differences in the behavior of the different legs. The lift of the levers is so adjusted that the feet are lifted about ⅛ inch from the sidewalk at each step, and the action in dropping back and making a step is quite like that of the forward part of the foot in walking.

The machine is operated at the rate of 32 steps per minute for each foot. One run so far has consisted of 40,000 contacts for each foot, 10,000 on each leg. This is equivalent to about a 40-

mile walk, and on a concrete floor results in wearing away from 10 to 20 per cent. of the samples.

We have thus far been unable to make a concrete slab which is satisfactory. If the surface is finished like an ordinary sidewalk it is too smooth, and changes with wear. The slabs we have made were of 40-mesh round grained sand, and were uniform throughout. They wear down rapidly, and a new slab is necessary for each run. We are arranging for a carborundum sidewalk, 40-mesh, which we suppose will stand the wear and not change its character materially.

It is highly desirable that all those who are working at this problem should aim at finding out what kind of a surface is most dependable and how much difference small differences in the size of the particles of abrasive make. We may thus arrive at a standard surface, and eventually at a standard mode of testing.

The first measured run on this machine was made with a wooden sidewalk of smooth hard maple. The losses after 40,000 contacts were too small to measure with certainty, so the test was continued to 120,000. The largest loss was about 1 per cent., so I feel quite justified in saying that smooth hard maple is not suited to such tests. The second run used a concrete sidewalk. One of the pieces lost as much as 18 per cent. The third run was made with another sidewalk of concrete. Three of the samples were sole leather and one rough belting. The piece of belting was not from the best part of the side, but it outwore the sole leather pieces. This confirms previous results, and points to a possibility that we might save time and materials in making leather for soles!

In an abstract of the first article of this series in an English journal, the remarks on p. 433 about the difficulty of making a fair estimate of the relative durability of leathers of different tannages are criticised. The abstractor says that if the losses are expressed as percentages, differences in specific gravity are discounted. This seems at first glance to be correct, but when one attempts to make the computations for tests in which widely different leathers are concerned, he finds that the problem bristles with difficulties.

One kind of comparison which may seem fair is to reduce results to loss in grams per square inch. This discounts differences in thickness pretty well, if the leathers are of the same specific gravity. But if we compare rough belting whose specific gravity is 0.80 with hard sole of specific gravity 1.10, it is at once evident that the sole suffers a serious disadvantage. If we now reduce it to a percentage basis, this disadvantage is removed, but if the belting is 0.30 inch thick and the sole 0.21, there is another complication. If we now reduce the losses to percentage, on a basis of uniform thickness, say 0.21 inch, the belting percentage goes away up. This is not fair, because the belting is soft and loose, and much thicker than it would be if it had been subjected to damping and rolling, as the sole was. The net result is that if one has made a wear test of rough belting against sole, he can figure out the results to show anything at all.

Suppose a piece of sole, area 25 square inches, weight 100 grams, thickness 0.22 inch, lost 17 grams in a certain test. In the same test a piece of rough belting of the same area, 0.29 inch thick, weighing 91 grams, lost 13 grams. The losses per square inch are 0.68 and 0.52 gram respectively. The losses per cent. are 17.0 and 14.3 If now these percentage losses be reduced to the same thickness, say 0.25 inch. we have the figures 15.0 and 16.6 respectively. The value of the belting, compared to the sole leather, by these three comparisons, will be 131, 119 and 90 per cent. respectively.

In order to make a real comparison, we should have to know the comparative thickness of the same piece of hide tanned in the two ways, and this is difficult to estimate, with any data now at command. It is very probable that the piece of rough belting which was nearly 0.3 inch thick would, if finished in the same manner as the sole, have been no thicker than the sole. If we assume this, the belting wears better than the sole. By making a different assumption, some other conclusion may be arrived at. At any rate, the comparison of substitutes with each other and with hard sole leather may be made with reasonable fairness by the second method of computation, that is, percentage loss on a standard thickness. Chrome sole will have to be tried by yet another standard, because instead of being thicker than standard sole, it is thinner.

It is much to be desired that data should be accumulated in regard to the comparative thickness of leather tanned from the same hide by various standard methods. Perfect accuracy in such comparisons is not to be expected, but it will certainly be possible to get approximate figures.

ELK TANNING CO. LABORATORY,
Ridgway, Pa., September, 1917.

BORAX AND BORIC ACID IN THE TANNERY AND CURRYING SHOP.*

By H. L. Harris.

The early history of borax is vague and uncertain. The word is of Arabic origin, and, as far as known, dates back to the seventh century. Borax first came from the East. It is believed by many that it was brought by caravan from beyond China by way of Babylon and Palmyra to the Mediterranean ports, before the Christian Era.

Sir Edward Bulwer Lytton, in "The Last Days of Pompeii," bears testimony to the value of borax in the days of the Republic. "Borax," says Sir Edward, "was largely used by Nero and his slaves nearly 2,000 years ago and Pansa deeply regretted that he was not rich enough to buy borax to cover the arena after the death of the combatants in the fight between Lydon and Tetraides."

It is only within the last three centuries that the chemical nature of borax has been understood. The green flame imparted to alcohol by free boric acid was first noticed by Geoffroy, a celebrated chemist in 1732. In 1748 Baron discovered that borax was a sedative salt and soda. In 1818 Count Larderel discovered how to prepare boric acid from the lagoons of Tuscany and made a princely fortune by it. This boric acid was shipped to

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* Read at the Atlantic City meeting, A. L. C. A., June, 1917.

England and France and converted into refined borax by boiling in large pans and crystallizing in vats. About fifty years ago borate of lime was discovered in Chile; this also found its way to England. As far as it is known, borax is found in only three states in the Union, California, Nevada and to a slight extent in Oregon. The crude material as found in the United States is borate of lime. Upon eliminating the lime we have boric acid.

According to history, borax and boric acid have been used in the tanning of leather for centuries. It was used by the Egyptians and Romans ages ago in the process of tanning their bright colored leathers with mineral and vegetable tannins, and the utility of borax in the manufacture of leather is becoming more generally known as the years roll on, in the modern methods of the tannery and currying shop.

Mr. Andrew Torr of Boston was one of the early experimenters with borax and boric acid in the tannery. Regarding his first experiments, he says:

> "After the hide has been about one-half tanned all the following liquors should be free from its effects. If borax be used in the proportion of 5 pounds to 1,000 gallons of liquor and that proportion be kept up in every run of liquor from the leaches the whole yard will, in the course of two months, be under the influence of borax, extremely disastrous results following. My experience with borax in the liquors has proven to me that if it be used throughout the process the resultant leather will invariably be soft, spongy and of light weight; but, if it be used only in first stages, and in the right proportion, the resultant leather will possess a beautiful grain, and will, in addition to this, be turned out in the shortest possible time with the least expenditure of labor."

In the *J. A. L. C. A.*, June, 1917, there is the following:

> "Haenlein states that salt acts in two ways in the preservation of hides. First, it dehydrates the hide, the salt dissolving in water taken from the hide, a large part of the resulting solution escaping so as to leave the weight less than before salting. Second, salt acts as a preventive of putrefaction. Hide placed in solutions of salt containing from 10 to 25 per cent. according to temperature, does not decay. Weak solutions cannot prevent decay, but delay it. Solutions containing 2 per cent. or less of salt, however, have little or no preservative effect. It is sometimes stated that salt acts as a solvent of hide substance. The quantity thus dissolved is very small, so long as decay is not going on at the same time. Where a loss of hide substance occurs, the loss is due not to the salt but to the insufficient quantity used, which could not prevent fermentation."

Regarding the preservation of hides, Mr. Torr[1] says:

> "Borax has been used with excellent results to preserve hides and skins as they come from the animals' backs. Salting skins is necessary, but it is not always done with the requisite care and cleanliness and the resulting stains are a great inconvenience in making leather. One pound of borax will do the work of several pounds of salt. Two to 4 per cent. of the weight of the salt is a good proportion of borax and will prevent salt stains, even in the hottest weather. The borax and salt should be thoroughly mixed and applied to the flesh side evenly as in ordinary salting."

On this subject, Professor Procter[2] remarks:

> "There is no doubt also that, especially in fine leathers, boric acid is of great importance as an antiseptic and means of preserving the skins from putrefaction. We constantly keep raw skins months in a solution containing 2 per cent. of boric acid and 1 per cent. of carbolic acid and at the same time any traces of lime are completely removed, so that in some chrome leather tanneries this solution has been employed as a bate. It is necessary, however, in my experience, if hides and skins are to be preserved for any length of time in such a solution, that they must be frequently moved and the solution occasionally changed, so as to wash away dirt and allow the solution free access to all parts of the hide."

Professor H. Dussance[3] says:

> "The lime with which the interior of the skin is saturated, nothwithstanding all washings, forms with the tannin a tannate of lime, which takes away the suppleness of the leather."

Watt[4] says that the presence of lime, even in small quantities, not only produces a harsh leather, but it also prevents the free action of the tannin.

The removal of lime previous to immersion of the pelts in the tan liquors is absolutely necessary, especially for colored leather, and borax will be found to be a harmless and most efficient cleansing agent.

Flemming[5] gives the following directions for treating calf skins in arsenic limes:

> "Place the limed skins in warm water containing 8 pounds of borax to 1,000 gallons of water and the lime in the grain will be removed to some extent; the grain softened so that the fine hairs and scurf will come

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[1] In Borax and Boric Acid in the Tannery and Currying Shops.

[2] M.Sc., F.I.C. F.C. S., of Leeds University, in a treatise on borax and boric acid in the tannery.

[3] Treatise on the art of tanning, etc.

[4] Leather Manufacturer.

[5] Practical Tanning.

out readily when the skins are worked. Lime alone makes the grain rough and harsh. To place limed skins in cold water fixes the lime in the fibers and sets the short hairs so that they can be worked out only with considerable difficulty; therefore, warm water containing borax is recommended."

Procter says:

"Boric acid has considerable antiseptic properties, so that it is an ideal acid for use as a bate in cases where the object of the tanner is to remove lime with as little interference with the plumpness and toughness of the hide as possible. Thus, 5 to 10 pounds per 100 gallons, will remove lime from the surface of the hide and produce a better color. In dressing leather, employed in the same proportions after bating with the ordinary excrement bates, it will destroy the bacteria which have been introduced into the hide, checking any further destructive action of the bate and remove the last traces of lime, so that leather of a good color and sound grain can be produced."

For these purposes the hides and skins should be suspended or kept in motion, and a new bath should be made for each lot of hides, so the once-used bath may be safely employed as a preliminary wash and so exhausted. Hides and skins that have been treated with boric acid take a finer and milder grain when introduced into the tanning liquors, on account of some special action which the acid has upon the tannins themselves.

When leather is tanned by the chrome process, either by the one-bath or the two-bath process, the leather contains free acid. If the free acid is left in the chrome leather, it is very liable to interfere with the subsequent process of finishing. A 1 per cent. solution of borax in the water will free the stock from acid in from 20 to 30 minutes, or as mentioned by Professor Procter, 3 per cent. on the pelt-weight in ½ per cent. solution.

For any kind of leather that is tanned first in extract liquors and then retanned in a chrome process the following directions will be found of service:

After the sides have been split, mill the grains in warm borax water; 2 pounds of borax to 50 gallons of warm water for 50 sides. Let the grains run in clear, cold water for 15 minutes. Next prepare an acid solution by dissolving 3 pounds of sulphuric acid and 18 pounds of salt in 50 gallons of water. Drum the leather in an acid solution for 30 minutes, then drain this off and give the chrome liquor. Mix 4 gallons of concentrated one-bath liquor into 25 gallons of water. Run the leather in this solution 1½ hours, then place it in piles until the next day, then wash it thoroughly in running water. Press it well, and fat-liquor with soap and degras. After fat-liquoring the leather may be finished in any desired manner.

Flemming recommends the following fat-liquor for chrome glove leather.

"Olive chip soap	12 pounds
Glauber's salt	3 pounds
Borax	2 pounds
Sod oil	5 gallons
Cod oil	3 gallons
Neatsfoot oil	1 gallon

"Boil the first three ingredients for ½ hour; then add the oils and boil again for ½ hour; fill up the barrel to make 50 gallons of fat-liquor. Use 5 pounds of this fat-liquor for 100 pounds of leather. Dilute it with hot water and use at 125° F., drumming the leather in it for 40 minutes."

Procter says:

> "Finishes capable of being glazed to a high polish are made by dissolving shellac with a dilute solution of borax which has the advantage of being practically harmless to the leather, in small quantities; 5 parts of shellac digested warm with 100 parts of water and 1 part of borax is a good proportion. If the solution is used as a seasoning 'for glazing,' the waxy matter which separates on standing should be mixed by shaking before use. As a varnish a stronger solution should be used and the wax skimmed off. This finish is useful in lessening the tendency of iron blacks to smut or rub off."

Casein is largely used as a constituent for finishes and seasonings for leather. To make use of it a weak alkali like borax is necessary to dissolve it. Five gallons of good seasoning for colored leather can be made by boiling about 9 to 10 ounces of casein in 3 gallons of water to which about ½ ounce of borax has been added, and when cool the mixture may be weakened down to the viscosity required by the addition of a suitable quantity of milk and water.

A good harness dressing and filler can be made as follows:

Eleven pounds of borax dissolved in 15 gallons of water and brought to boil, 35 pounds of orange shellac are then added, cook for 5 hours and allow to cool. Next morning skim and throw the scum away. Then boil again for 2 hours. To the shellac already cut, add 1 pound flaxseed, 14 pounds of fish glue, 1 pound hypernic, 7 pounds extract logwood, 4 pounds contic castile soap.

Add enough water to make 45 gallons and boil 2 hours. Then you will have gained enough to make a barrel of dressing about 50 or 52 gallons total. Dissolve 4 ounces bichromate of potash in a gallon of water and add to the dressing slowly and stir (don't cook). After adding the potash add a little yellow, (say 2 ounces) and enough nigrosine to make a deep black, give enough ammonia to make it take hold. Two coats of this dressing will give a nice luster to the leather.

A little borax dissolved and added to annatto renders the latter more soluble and redder in color.

An operator writes as follows:

> "Glucose appears on the surface of sole leather. This matter must be gotten off the soles. How are we to do it? Suppose you put borax into warm water and work the leather thus treated within 24 hours after the wetting operation takes place. Did you ever try it? Although the above may be very good to do away with the sticky matter found in nearly all sole leather to-day, few know about this borax idea. When the shoes come to the buffing machines, this paste-like stuff sticks on the paper and renders its cutting or scraping qualities useless, and puts the workmen in a bad frame of mind. If any one has trouble in that direction, the above notes may be helpful. This glue is often found in the leather. Ask the Goodyear or McKay stitchers. They know. It causes the breaking of needles more than anything else. It is very hard to get good, nicely tanned sole leather, and the only way out of it is to use something in the shoe factory, or buy leather where they are using some kind of a composition to make leather convenient for the shoe factory, and for the kind of shoes that are to be made out of that leather."

To make an imitation English oak or to bleach dark leather, submerge same in a solution composed of 4 ounces of borax, 4 ounces of oxalic acid, thoroughly dissolved in 1 gallon of water.

A formula for white shoe dressing that has given satisfaction is as follows:

Bleached shellac	8	ounces
Borax	1½	pounds
Hot water	1	gallon

Dissolve the borax in the water and boil the shellac in the solution until it is entirely dissolved. Strain and add pipe clay or fine prepared chalk until a creamy liquid is obtained. The clay or chalk should be in the finest possible powder.

For other colors than white, dissolve the proper colored aniline in a little alcohol and add to the mixture. For example, a grey or drab color may be had by using a little black aniline with the white dressing, a brown with bismark brown or a mixture of red and black, etc.

For dressing skins a coating mass consisting of a mixture of sodium salicylate 5 parts, boric acid 1 part, and fatty matter 94 parts, the leather is rendered permanently pliable and elastic. Furthermore, this process shortens the time of dressing several days, it is simple in its application and not expensive.

In bating where a soft grain is desired as for box or the matte finish, the unhaired hides are placed first in a boric acid drench, and after a few hours, in a drench made from bran.

For a fine close grain boric acid makes an excellent drench for killing lime. It is a weak acid and neutralizes the lime without that injury to the hide which is liable to take place by the use of stronger acids. Boric acid arrests putrefaction and since for chrome tannage the object is to remove the lime without a loss of plumpness or hide substance, it is a very valuable chemical.

When making Russia calf shoes, if you use a solution of gum tragacanth, about the consistency of cream, taking care that the water used to dissolve the gum is perfectly clean and add ½ of 1 per cent. of boric acid, it will keep the flies away and prevent souring. If one has trouble with sour paste, dissolve boric acid in warm water at the rate of 1 ounce of dry acid to 1¾ pints of water; stir until the acid is all dissolved. Use this solution instead of water in mixing paste. This will prevent mold spores and souring.

If in using union and hemlock stock it is desired to have a still lighter color bottom than the original color, the soles should be dipped in a solution of boric acid in the proportion of 4 ounces of the powder to 1 gallon of water. Boric acid is so mild that it will not injure the fiber of the leather, nor will it eat away any coloring matter that is applied in after processes.

The following method of tanning fur skins is patented, according to *Chemical Abstracts,* March 20, 1917:

> R. Nasse. U. S., 1,210,968, Jan. 2.
>
> A solution formed from KAl sulphate 100 pounds, NaCl 80 pounds, Na borate 3 pounds and H_2O 25 gallons, is mixed with another fermented solution formed of wheat flour 100 pounds, brewers' yeast 1 pound, alcohol 1 pint and H_2O 28 gallons, and the mixture is used for tanning skins.

As a patent cleaner and to clean any kind of goods where the color will not run, the following recipe is said to be most excellent:

Castile soap	20 ounces
Borax	20 ounces
Gum camphor	16 ounces
Ether	5 fluid pounds

Dissolve the soap, borax and camphor separately in hot water and when cool add the ether and water enough to make 10 gallons. Keep tightly corked when not using.

A few years ago a shoe manufacturer sent us a sample of sole leather that was so hard and brittle that he could not use it, asking us to do what we could for him. We submitted the sample of leather to our research chemist, who soaked it in a 2 per cent. solution of boric acid for 24 hours, then washed it in clear water. When the leather was dry it was found to be materially softened so that it could be readily utilized.

THE SOL AND GEL CONDITION OF GELATIN SOLUTIONS.*

By L. Arisz, Utrecht.

As this important paper is not readily accessible to most readers, it seems desirable to publish a full English abstract. The experiments detailed were made on gelatin, previously purified by several days washing in water, and dried over concentrated sulphuric acid, and dissolved at a temperature of 50-60° in glycerin of specific gravity 1.176 containing 32 per cent. of water. The reasons for choosing this solvent in preference to water are not fully stated, but arise from the results of a previous investigation on viscosity published as an inaugural dissertation in Utrecht.[1] The solutions in each concentration were prepared in sufficient quantity for the complete series of observations, and were filtered. For viscosity determinations a set of seven Ostwald's viscosimeters were employed, selected so that the time of flow was in each case about two minutes, and the results are compared with those of water at 20°.

The gelatin solution, when heated to near 100° loses viscosity

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* Abstract by H. R. Procter, in the *J. S. L. T. C.*, No. 2, Aug., 1917. *Kolloidchemische Beihefte*, 7, 1915, Heft 1-3, 1-90. *Part 1, Gelatinisation.*

[1] *Sol en geltoestand van Gelatineoplossingen*, (*Utrecht, 1914*).

which it does not wholly regain on cooling, owing to a partial change into Nasse's β-glutin, one of the first hydrolization products of gelatin.[2] This permanent loss of viscosity is more rapid at higher temperatures, and below 65° does not occur even in 24 hours. Above 65° viscosities must be taken very rapidly to avoid change. This is shown in the following table:

TABLE I.

VISCOSITY OF 10% GELATIN-GLYCERIN SOLUTION HEATED TO DIFFERENT TEMPERATURES, AS COMPARED WITH WATER AT 20°.

Temp.	For 3 min.	15 min.	30 min.	24 hrs.
95°	71.0	68.3	65.4	—
85°	100.1	98.5	97.5	—
75°	147.0	—	145.2	—
65°	222.3	—	—	222.4

If a solution after cooling to any temperature below 65° be maintained at constant temperature, its viscosity gradually increases but at a rate diminishing with time, so that it apparently approaches an equilibrium value, which however at low temperatures is not reached in four days. Similarly if it be warmed from a lower to the given temperature, its viscosity slowly diminishes towards the same equilibrium value, which may be found by plotting and extrapolation, the change being completely reversible.

Fig. 1 shows the change of equilibrium viscosity with concentration and temperature. The viscosities above 65° are those taken in three minutes, given in Table I. The curve shows no break at the point of gelatinization, and the change which causes it appears in the 10 per cent. solution to have already begun at 55°.

We thus (below 65°) where we can neglect irreversible chemical change, have to do with two sorts of change of viscosity, both reversible. As is usual, viscosity diminishes with rising, and increases with falling temperature, and this change may be supposed to vary immediately with the temperature. There is also a change dependent on time, and taking place more or less slowly, but tending to a definite "inner" equilibrium-viscosity for each temperature. Thus if the change of temperature is infinitely slow, the viscosity will follow this inner equilibrium curve, and

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[2] *Zeitsch. f. Physik. Chem.*, 45, 75, 903.

have for any temperature one value only, while if it takes place infinitely rapidly, a curve will be followed *varying* only with the rapid change, but of which the absolute value will depend on the extent of the slow change already present when the rapid temperature change occurs. We may suppose that the slow change is from a more to a less viscous form of gelatin or *vice versa,* and obviously the actual viscosity of any solution will depend on the proportion of these two forms present. Thus for a given solution changing rapidly from T_1° to T_2° we may have any number of different curves *a,a'*; *b,b'*; and *c,c'*, which need not be parallel but cannot cross each other since the amount of the more viscous form present will always increase the viscosity due to temperature, but if the change is infinitely slow, the *N-N'* line of inner equilibrium will be followed; and if a solution be retained at constant temperature for a time it will always approach the viscosity *N-N'*, rising if below and falling if originally above it; its actual viscosity at the beginning of the time depending on its previous treatment.

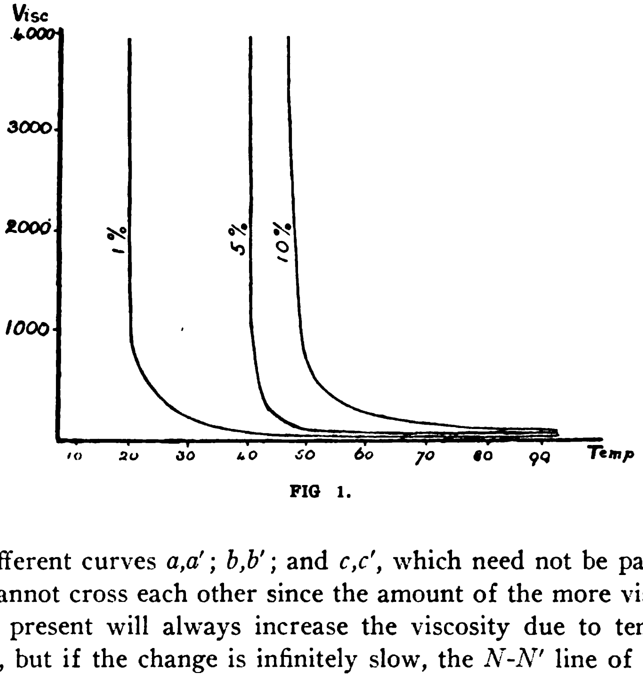

FIG 1.

By heating to 65° the whole of the gelatin is *at once* converted to the less viscous form. The lower the temperature the longer is the time required to reach the equilibrium viscosity.

§ 5. *Phenomena with rising temperature.*

If instead of increase of viscosity with falling temperature, its diminution with rising temperature is observed, some curious phenomena occur. The inner equilibrium temperature (with infinitely slow temperature change) for the gelatinization of the 10 per cent. solution is 44°, but if the temperature is kept for some days at 35° and then raised to 46° the gel does not at once melt, but after an hour is still *very* viscous, and many hours are needed before it ceases to lose viscosity. If on the other hand it is rapidly cooled and gelatinized at 35° and then at once heated to 44°, it first melts, and only gradually resumes the gelatinized condition. If cooled in the ice box, it may be kept as long as desired, and will always melt at 44° before re-gelatinizing, and at 20° it must be kept two weeks before it loses this property.

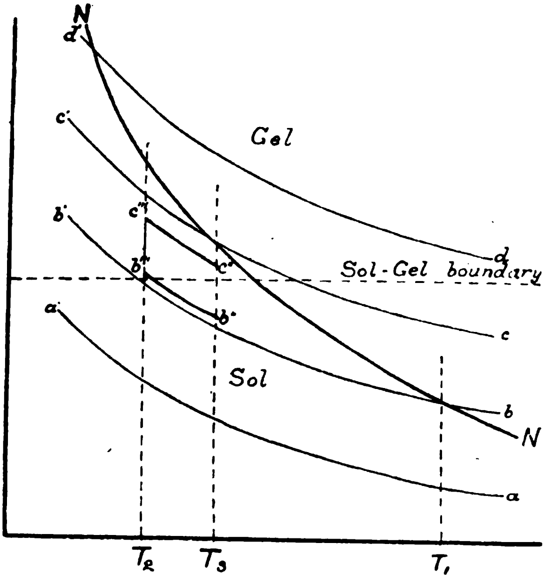

FIG. 2.

The causes of this behavior are most easily understood if we regard gelatinization simply as a point of rapid increase of viscosity. We can then in Fig. 2 (in which the ordinates are viscosities) draw a horizontal line as the limit of gelatinization, below which all solutions are liquid. If then one or more of the curves *a, b, c, d,* pass below this line the liquid will gelatinize and since at low temperatures the rate of change from the less to the more viscous form is very slow, the curve approaches very slowly, if at all, to the equilibrium line *N-N'*. Hence, at T_3° (Fig. 2) the curve *bb'* would be a liquid, but would more or less rapidly approach *N-N'* above the gelatinization line and solidify. At T_2°, however, *b* would at once gelatinize and would *at first* melt if raised to T_3°. At *O*° practically no change takes place in the proportion of the more to the less viscous modification, even in very long periods, so that a solution cooled rapidly from a temperature at which it is liquid to *O*° will always liquefy again at or below the equilibrium gelatinizing temperature.[3]

§ 6. *Relation between viscosity and temperature in solutions of different concentration.*

Experiments were made with 1 per cent. and 5 per cent. gelatin-glycerin solutions. As irreversible chemical changes take place rapidly over 70° and the reversible time change is very rapid, viscosity determinations were made as soon as the required temperature was attained. Below 70° the irreversible change is slow or none, and time changes were observed corresponding in character with those of the 10 per cent. solution, the equilibrium viscosity which was the more slowly attained the lower the temperature, being observed as before. These equilibrium curves were of the same type as in the 10 per cent. solution but with progressive dilution the point of rapid increase of viscosity occurred at lower temperatures, beginning with 10 per cent. about 55°, 5 per cent. about 50°, and 1 per cent. about 30°, the increase being almost vertical about 50°, 44° and 20°, respectively. Gelatinization ultimately occurred at the latter temperatures, but required one day with the 5 per cent. at 40°, and two weeks with 1 per cent. at 20°. (See Fig. 1.)

§ 7. If the temperature was kept, however, at 2° only the 2 per cent. solution gelatinized within 14 days and the 1½ per cent. and lower concentrations were still liquid after 14 days owing to the slowness or arrest of the "inner" molecular change.

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[3] Hence, in taking melting point of jellies it is necessary to retain them for some time previous at a temperature not much below their melting point. Compare also next section as to effect of concentration on melting point.—H. R. P.

§ 8. At temperatures below the gelatinizing point the viscosity curve in relation to time takes a peculiar course,[4] following for a time the type of non-gelatinizing sols which gradually increase towards a maximum, but soon rising at an increasing rate towards the gelatinized viscosity which can no longer be measured by a viscosimeter. As this viscosity must ultimately reach a permanent value the rate of the curvature must again diminish producing a curve of an S-type.

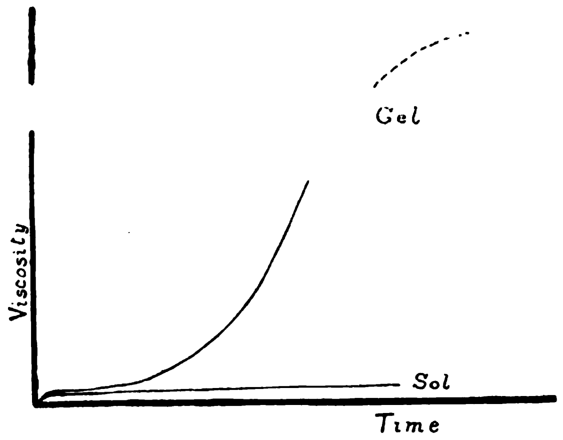

FIG. 3.

§ 9. *The effect of agitation.*

At low temperatures, the viscosity of solutions is reduced by mechanical agitation such as flow though a viscosimeter, the complexes, the formation of which causes the time increase, being evidently broken up. The effect is most obvious in dilute solutions near their gelatinizing point, and diminishes with temperature, and over 65° is no longer perceptible.

§ 10. *Tyndall phenomenon and temperature.*

The Tyndall-cone was produced by the light of a small Nernst lamp focused with lenses on the side of a plane parallel cell, and the light which it radiated at right angles was photographed. Exposure, development (Eder's ferrous oxalate), plates (Lumiere, etiquette violette), and fixation (thiosulphate) were constant in all experiments; and as an added check a surface illuminated

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[4] Wo. Ostwald, *Grundriss der Kolloidchemie*, 2. Auf., Dresden, 1911, 1912.

at an angle of 45° by the same light was photographed simultaneously, and plates were rejected in which this was found to have varied. An arbitrary scale for comparison was constructed, by using the same plates and developments, and photographing a surface illuminated by a light at various distances. The illumination of the cone was measured as near as possible to where it entered the cell. Both aqueous and water-glycerin solutions were used with similar results. The dispersed light increased on cooling from 70°-20° as 1 : 4 and increased in 12 days at 18° as 1 : 5.6 in liquid solutions. No break was observed on gelatinization. Thus the Tyndall effect is influenced in the *same directions* as viscosity by heat, time, and "previous history," but is quite unaffected by gelatinization. It increases with concentration, and in the higher concentrations is much more increased by lowered temperature.

§ 13. Rayleigh[5] gives the following formula for intensity of Tyndall phenomenon:

Intensity $= I = \phi \left(\frac{v^2 n}{\lambda^4 r^2} \right)$ where $I =$ intensity of scattered light, $v =$ volume of particles, $r =$ distance of particles, $\lambda =$ wave-length of light, and $n =$ number of particles. λ is pretty constant as the photographic plate is mostly affected by ultraviolet rays. It has been shown that intensity may increase eight times in a few days standing, and it is impossible to suppose that so large an effect can be due to mere approach of the particles as a function of temperature, and therefore, a volume-change of the scattering particles must also be assumed—that is, the particles coalesce. Bachmann[6] has noticed in solutions of 1—10 per cent. the appearance of undefined luminous places under the microscope with cardioid illumination, but not in higher concentrations, possibly because from the thickness of the microscopic layer the illumination became too general.

The size of the complexes is not only dependent on temperature but also increases with concentration. Wilke and Handovsky[7] have shown that light dispersed from a 20 per cent. solution is less blue than that from a 10 per cent. solution.

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[5] *Phil. Mag.* (4), **41**, 107, 274, 447 (1871).

[6] *Zeit. f. anorg. Chem.*, **73**, 125, 1911.

[7] *Drude's Ann.*, **12**, 1145 (1913).

§ 14. *Theoretical process of gelatinization.*

There is no kink in temperature curves of viscosity or Tyndall effect at gelatinization or melting point. Heat is evolved when dry gelatin is swollen in water and absorbed when jelly is dissolved in hot water, but not apparently when melted without addition of water.[8] It is possible, however, that a change in the curve might be overlooked as the process of gelatinization is gradual.

All properties of jellies seem more or less common to the liquid solutions. Elasticity of form[9] has been also detected in the liquid[10] near the gelatinizing point. Double refraction caused by stresses has been observed in dilute solutions when rapidly stirred.[11]

Microscopic structure is absent in jellies.[12] Ultramicroscopic structure seems common to both jelly and liquid.

Arisz considers that gelatinization must merely be considered as a great increase of viscosity of which he asks the cause.

§ 15. *Glycerin-water-gelatin and water-gelatin.*

Gelatin dissolves more readily in glycerin the more water is present. (It is questionable whether dry gelatin can be dissolved in dry glycerin without decomposition.) The gelatin swells with water and the swollen jelly melts and mixes with the glycerin. Probably the formation and division of large particles can only take place in presence of water. It is possible that the hygroscopic character of glycerin indirectly influences the relation between water and gelatin.

The gelatin-glycerin solution is far more viscous than a gelatin-water solution of the same concentration, and it usually solidifies at a higher temperature. Only in very dilute solutions is the reverse the case—a ½ per cent. glycerin jelly will never set, while

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[8] Wiedemann and Ludeking, *Wied. Ann.*, 25, 145, (1885). Frank, *Kolloidchem. Beihefte*, 4, 195 (1913).

[9] Bjerken, *Wied. Ann.*, 43, 817 (1891). Leick, *Drude's Ann.*, 14, 139. 1904. Fraas., *Wied.*, *Ann.*, 53, 1082 (1894).

[10] Rohloff and Shinjo, *Physik. Zeitschr.*, 8, 442 (1908).

[11] Metz, La double refraction accidentelle dans les liquides, Paris, 1904 Kundt, *Wied. Ann.*, 13, 110 (1881).

[12] Bachmann, *Zeit. anorg. Chem.*, 73, 125 (1911).

an aqueous solution of this concentration sets in about five days. The glycerin much delays or prevents the time changes which lead to the formation of larger particles and to gelatinization and to Tyndall effect. Consequently time changes are much more marked in presence of glycerin, but van der Heide[13] noted a rise in melting point when aqueous jelly was kept for some days.

Note by abstractor.—The foregoing experiments throw much light on the changes which occur during the heating and cooling of gelatin solutions, but fail to give any clear picture of the actual process of gelatinization, though the rapid change of viscosity at this point shows that it is not a mere continuation of the gradual increase which has preceded it. Without doubt there is a close connection between the size of particles and the viscosity. Einstein[14] concludes on mathematical grounds that when the molecule of the solute is large in proportion to those of the solvent, the viscosity depends only on the total volume of the dissolved substance, and not on its state of division; and if this were really so the mere coalescence of particles could not increase the viscosity, which seems contrary to the observations of Frank[15] and Hatschek,[16] but Einstein's reasoning is only strictly applicable to spherical molecules, while ultramicroscopic observation suggests that the gelatin coalesces into flocculent masses. The fact (§ 9) which is mentioned by Arisz that mechanical agitation lessens viscosity, coupled with the observation of Frank, that solutions near the setting point show evidence of elasticity of form, and that of Kundt[17] that, while very viscous solutions of sugar, glycerin, and dextrin (which do not gelatinize), show no polarization effects indicative of strain when rapidly stirred, such effects are shown strongly by extremely dilute and quite liquid solutions of gelatin, shows that some structure exists which can be sheared. Kundt does not seem to have repeated these experiments at higher temperatures, as the present writer proposes to do in the expectation that the phenomenon will disappear as the temperature rises.

Gelatinization has many resemblances to crystallization, and

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[13] *Inaug.-Diss.*, Strassburg, 1897.

[14] *Drude's Ann.*, 1906, **19**, 289; 1911, **34**, 591.

[15] *Kolloidchem. Beihefte*, 1913, **4**, 195.

[16] *Koll. Zeitschr.*, 1910, **7**, 301.

[17] *Weid. Ann.*, **13**, 110 (1881).

substances are known which if rapidly crystallized to ultramicroscopic crystals, have all the properties of jellies, but which spontaneously pass into ordinary crystalline forms. It is therefore a reasonable idea that jellies are networks of minute and very possibly flexible and threadlike crystals, and something of the sort has actually been observed in soap jellies.

Another plausible idea is that the gelatin particles as they cool become larger by increased hydration, until ultimately they touch each other and the solution passes at the point of gelatinization from an emulsion of hydrated gelatin in water to one of water in gelatin, but this is hard to reconcile with the recent work of Procter and Wilson, and begs the question of the nature and structure of the emulsified particles.

RAPID TANNING OF SOLE-LEATHER.*

By Alfred Seymour-Jones.

The World War has brought into prominence, through necessity, the problem of rapidly converting hides and the like into marketable sole or dressing leather, and numbers of patents have been issued claiming to bring this about. Also numerous machinery devices are offered for sale claiming to yield generous profits to those who will buy them. The schemes offer but little change over those already known to the trade. Extracts, either neat or diluted are employed, but in nearly every case some form of agitation is called for, either in enclosed drums or open pits. Wherever motive power has to be employed there must obviously be an increase in cost. There are two main factors which enter into tanning either by pit or drum methods: quality of leather (including weight), and interest on outlay. Apart from these may be cited less tannery space required when handling an equal quantity of hides; and probable saving in tannin and labor. Against must be put the problem of increased cost of motive power and repairs. Many tanners are not prepared to lay out capital in new ventures with the possible risks attending thereto. Nevertheless it must be admitted that some more rapid systems

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**Journal of the Society of Leather Trades' Chemists,* No. 1, July, 1917, pp. 2-3.

than those in vogue are being introduced with great success, and also that many of the systems which succeed in certain yards fail in others. Why? It is not possible for anyone to give an answer without first ascertaining the cause, but that a cause does exist must be admitted.

As the years go by, tanning becomes more and more rapid and the results more certain as to quality and weight. Whether the final success will be attained by the aid of machinery is yet to be seen, but it remains possible for a change to be made without calling in the aid of more machinery than that already in use, and I venture to suggest a method, for trial, which I know to have given excellent results. In making the suggestions I will not enter into details but enunciate principles, as obviously anyone experimenting will adapt the principles to local conditions.

Concentrated extracts do not appear to contract the grain surface, as is the case when strong dilutions are used, provided the hide is suitably prepared for receiving the tannin. If, instead of removing the lime by the suspenders, it is either neutralized or removed by means of a neutral salt, such as for example, hyposulphite of soda, and the hides then immersed in a neat extract, the tanning will be completed in about ten days to a fortnight, after which they should be laid away in a strong but diluted liquor for a few days before proceeding further. Extra weight may be introduced finally by any of the recognized methods, and the whole operation completed inside three weeks. If the extract be heated then the speed of tanning is increased proportionately.

Leather turned out by the above method is of good color and weight, being strong of fiber, enduring in wear. It may be done in any tanyard with pits. There is practically no loss of tannin.

RAPID TANNAGE.*

By Fini Enna.

To the Hon. Editor, J. S. L. T. C.

DEAR SIR:

Mr. A. Seymour-Jones has communicated to our Journal (Vol. I, p. 2) a method for the quick tannage of sole leather, which is the object of a German patent (Feb. 18, 1913, No. 275,454), granted to Mr. G. Durio, of Turin. May I be allowed, in the following lines, to outline another method of tanning sole leather?

English sole leather has always been looked upon as the best of the world's produce; this view is quite justified, as every continental leather merchant will tell his customer. It is moreover not a matter for surprise since great care and much time are expended in the manufacture. In Germany as in my own country, the pit system has been partly abandoned, and drums introduced instead, and although common sense will tell one that the pit system—and more so where bark is employed—will produce the best leather, and the better the longer the time expended, there is no reason why the other method should not be employed at such a time as this, when the outcry for sole leather is growing stronger with every day of the war. One is fully justified in trying to increase the speed of tannage, so long as the resulting leather is of good quality, weight and durability. I will endeavor in the following lines to describe as well as I can in a foreign language, a very good method which has been used with success in different German and Danish tanneries in which I have been working.

The hides, after soaking and cleansing, are given a lime made as follows:

Per 1,000 pounds wet weight (drained one hour over horse)

100 pounds lime.
12 pounds sulphur.
4½ pounds washing soda.

The sulphur is mixed with the lime, which is slaked with hot water in the ordinary way, and the mixture thrown into the pit (or paddle), whereupon the soda (dissolved in a small quantity of

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Journal of the Society of Leather Trades' Chemists No. 2, Aug., 1917, pp. 36-8.

water) is added. The lime is well stirred, the hides put in, and hauled each day for four days, 50 pounds of lime being added after each hauling, before setting again. The hides are then ready for unhairing. This being done, they are fleshed, and relimed for 24 hours, after which they are surface delimed in a paddle with N/20 sulphurous acid, the acid being evolved by the action of sulphuric acid and sodium bisulphite.

$$2NaHSO_3 + H_2SO_4 = Na_2SO_4 + 2SO_2 + 2H_2O.$$

The deliming on the surface can be omitted, and the hides simply well scudded and washed in a wheel.

The hides are then put in a pit containing 0.5 per cent. formalin (per cent. on volume), remaining there for three or four days, hauling being unnecessary; after this period they should be firm and white; if not, the formalin may be strengthened, but only slightly.

The hides are now ready for tanning; before drumming, however, it is necessary to fix the grain; the hides are therefore hung up in a pit on a frame (best fitted with hooks), in a liquor made from quebracho, valonia, myrobalans and wood pulp (5 per cent. of the mixture); probably a little mangrove extract would be useful. The liquor should be one that has been used in the drum, and should measure about 45° Bk.; the hides are hung head downwards, and a rocker pit is preferable.

Forty-eight hours is ample time in the pit, after which period the hides are transferred to the drum which contains sufficient liquor of 72° Bk. to cover the hides. The liquor may either be made from pure quebracho extract, or be a mixture, as, say, the above. A little Neradol or Syntan renders good service in that it lightens the color, but is of no tanning value itself, however much this property may be ascribed to it.

The same applies to wood pulp, which is used because it penetrates the hide easily and is just as easily replaced by the other tanning materials, which, owing to their (probably) colloidal state penetrate the skin with difficulty and are easily coagulated (dead tannage). The wood pulp helps to overcome this difficulty, but if employed in not too great proportion is valuable as an accelerator.

The liquor should not be at a temperature above the ordinary, since the movement of the hides in the revolving drum causes considerable heating. For this reason, and also because too much knocking about would loosen the fibers (the chief objection to drumming hides), the drum is run only for a short time.

It is customary to add a little oil of turpentine to the drum to prevent frothing, but I think this neither necessary nor beneficial. It is in my opinion, of very great advantage to add a bucketful (say three gallons) of any soluble oil. This increases the speed of the tannage, and I imagine that it keeps the grain smooth; at any rate it is beneficial to the resultant leather.

After the hides have been put in, the drum is set going for two hours; its speed of revolution should not be less than 8 nor more than 12 per minute. After this it is stopped and the lid taken off in order to allow the liquor to cool; after a rest of four hours it is again set going for three hours. The drum is then stopped and allowed to rest over night. Next morning the operations are repeated; the hides should then be tanned through.

The goods are now dried in a fairly warm drying room, equipped with a fan, until they are sammed; they are then scoured or struck out by machine, oiled off, and dried out in the cold. They are then retanned as follows, with the object of increasing the weight: the dried goods are wetted down in shanks and bellies only (to prevent them from absorbing too much extract) and put in the drum, in which they are run for a couple of minutes. Then some strong quebracho extract, mixed with a little wood pulp or Syntan (for the sake of color) is added, an ordinary fluid extract being employed, or, if preferred, a solid extract dissolved in its own weight of water. The drum is run for 15 minutes, when all the extract should have been absorbed. It is essential that no more extract should be added than what the hides can take up, and only experiments can decide the correct amount. After retannage the goods are oiled with sulphonated oil, on the grain side, of course, again struck out either by hand or machine (slicker system machine is the best, or the German "Trommel" machine made by Badische in Durlach), again oiled off, and hung up to dry in the cold. They are then brushed over with wax—ozokerite—and rolled, and are then finished.

In view of the fact that this method may appear rather "new" to some and as I have worked it myself for two years as stated above, I should be quite willing to assist those, who have the necessary courage to try it.

In conclusion, a few words about the method mentioned by Mr. Seymour-Jones. The method recommended by him is very applicable for inferior calf skins, intended for "wax" or similar dressing. I tried it at an English factory, where I had the good fortune to work last summer, on a large pack of calf, with good results. It is a curious fact that, as Mr. Seymour-Jones points out, the extract itself does not "draw" the grain as a strong solution does.

This could be explained with the aid of colloidal chemisty, but the explanation would be out of place in this communication.

I hope to have been of service to some tanner or other in writing this; with that hope, allow me to remain,

Yours truly,

FINI ENNA.

Nottingham, July 29, 1917.

THE ANALYSIS OF SULPHATED OILS*

By Ralph Hart.

INTRODUCTION.

The present methods for the analysis of Turkey-red oils have proven to be inadequate for the routine work of this laboratory where several such analyses have to be made every day. The determinations of importance in such products are the percentages of total fat and of combined sulphuric anhydride. The methods usually employed for total fat are (1) to extract with ether, or (2) to decompose with acid and to measure the volume of the oil which separates. Both methods were found unsuitable for our purposes; besides other reasons, the former was too tedious, and the latter consumed too much time.

The present method for the determination of combined sulphuric anhydride requires two gravimetric analyses, and, because of its length, its application for factory control is limited. It was noted, however, that this determination afforded an excellent

J. Ind. and Eng. Chem., Sept. 1917, pp. 850-2.

means of judging and controlling the manufacture of sulphated products, as is illustrated by the following case. A commercial Turkey-red oil, which was at first passed as satisfactory, was found on analysis to contain 40 per cent. less bound SO_3 than it should have. As a result, the oil was retested in a practical way, and found to be faulty in many respects. The cause of the trouble was later traced to hot weather, which caused the temperature of the unwashed sulphated oil to rise during the night.

To insure uniformity in shipments, this laboratory has made it a practice to estimate the amount of fat bound as soap, and the amount present as free fatty acids; the former was determined by titrating a water solution of the sample with H_2SO_4 in presence of methyl orange, and the latter by titrating the alcoholic solution with NaOH in presence of phenolphthalein. It occurred to the writer that it might be possible to saponify completely the rest of the fat by ordinary means. A few experiments proved that such was the case, and this fact was utilized to develop a new method for the determination of fat. A short method for combined SO_3 and ammonia was also worked out at the same time.

By our new procedure, we were able to determine, within a reasonable length of time, not only total fat and sulphuric anhydride, but also ammonia and caustic soda. Furthermore, this method makes it possible to estimate from the data obtained for the other tests the amount of fat present as soap, as free fatty acids and as esters, lactones, etc.; the only additional test required is for free fatty acids, which are determined as mentioned above.

Present Method for Fat.—The technical procedure[1] for the determination of fat in Turkey-red oils, Monopole oils, Sulpho Textol oils, etc., is to decompose with acid a sample contained in a special flask having a long neck graduated in cubic centimeters, and to boil the contents until the oil is clear. The latter is then brought within the graduation on the flask by pouring in a saturated salt solution. The per cent. fat is then calculated from the volume of the oil and its specific gravity which is assumed to be 0.945 at room temperature.

This method presents many difficulties; for example, during

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[1] "Examination of Hydrocarbon Oils." D. Holde, 1915 edition, pp. 409 and 410. English translation by E. Mueller.

the heating, the oil which spreads on the surface of the water prevents the latter from boiling freely, and, unless the flask is vigorously and constantly agitated, the contents are likely to spout out. Holde[1] says: "A disadvantage of the method is the fact that the layers do not completely separate, the deviation in results being as much as 1 per cent." Another source of error is that the contraction of the contents in the flask on cooling leaves behind a film of oil which is not taken into account. Finally, it has lately been almost impossible to obtain a flask of this type that will not break on heating.

A modified method is to heat the contents of the flask on the steam bath over night, or until the oil is clear. Hot salt solution is then added and the flask is immersed in the steam bath for an hour, or until the oil column becomes clear. The last procedure, if carefully carried out, gives fairly good results and was used to check our data.

New Method for Fat.—For our purpose, we may consider that commercial Turkey-red oil consists of the following substances: (*a*) ammonia or soda salts of the acids $HOC_{17}H_{32}.CO_2H$, $HOSO_3C_{17}H_{32}.CO_2H$, and polymerized acids; (*b*) unchanged castor oil, lactones, etc. Benedict and Ulzer[1] state that sulphoricinoleic acid is not decomposed on boiling in alkaline or neutral solutions, but is easily decomposed into ricinoleic and sulphuric acid by boiling with dilute mineral acids.

The determination of fat, as developed in this laboratory, is carried out in two steps: (1) a solution of the oil is titrated with $N/2$ H_2SO_4, in presence of methyl orange, and the alkalinity is calculated in milligrams of KOH per gram of sample; (2) in another sample the saponification value of the unsaponified oil is determined in the usual manner. The sum of the two results divided by the acid number of the original castor oil fatty acids gives the per cent. fat.

In case of samples whose acid numbers are not known, the average value of 190 is assumed. The acid numbers of castor oil fatty acids, as calculated from the saponification values given by Lewkowitsch,[2] lie between 186 and 194, or an average of 190.

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[1] "Analyse der Fette," Benedict and Ulzer, p. 348.

[2] "Chemical Technology and Analysis of Oils, Fats and Waxes," Lewkowitsch, p. 641.

In assuming this figure, therefore, the maximum error is about 2 per cent. of the fat, and since most commercial Turkey-red oils contain about 50 per cent. fat, the average maximum error due to this assumption is around 1 per cent.

The success of this method depends obviously upon the complete saponification of the oil, and upon the accuracy with which the alkali bound as soap can be determined. The saponification is carried out in the usual manner by heating with $N/2$ alcoholic NaOH, save that the heating is prolonged to 45 minutes. Check analyses are easily obtained.

The alkalinity necessary for the fat calculation must be that which corresponds to the soda (or potash) soap only and not to the ammonium soap, as the latter acts like fatty acids during the saponification, and consequently the fat corresponding to the ammonium soap is allowed for in the saponification value. To this end, the solution is heated with a measured amount of standardized NaOH, boiled to expel ammonia, and then titrated with $N/2$ H_2SO_4 in presence of methyl orange. With a little experience, the end-point offers no difficulty, and check analyses corresponding to 0.2 per cent. fat are easily obtained.

Even where no ammonia is present, it is best to proceed in this manner, in preference to titrating the original solution directly, that is, without the addition of alkali. The boiling with excess alkali serves as a blank on the saponification test, and avoids errors due to the partial saponification of the sulpho group, which occasionally occurs with some Turkey-red oils.

In case the sulphated oil was entirely neutralized with ammonia, a negative alkalinity will be obtained after expelling the NH_3, *i. e.*, the alkalinity will be less than the amount of alkali added. This is due to the fact that the NH_3 in the ammonium salt of sulphoricinoleic acid is displaced by NaOH on boiling; this displacement, which is quantitative, also occurs during saponification, and evidently must be subtracted from the saponification value. Such products can still be analyzed by this method with good results, as shown in the table on page 852 by Sample 1, which was entirely neutralized with ammonia.

The reliability of the fat determination, calculated from the alkalinity and saponification values, may be judged by comparing the percentage of fat thus determined (Col. III) with the fat found by the flask method (Col. II). Col. IV gives the per cent. yield in fat as obtained in large commercial batches, the fat being determined according to the new method. The average yield was 95.7 per cent., which compares very favorably with the theoretical yield of 96 per cent.

Ammonia.—To determine ammonia, two samples are analyzed for alkalinity; in one, the alkalinity is determined as described above, and in the second, it is similarly determined except that the boiling with caustic soda is omitted. The difference between these two determinations is evidently due to the ammonia, and may be used to calculate it. This is much simpler than the usual method of distilling with excess NaOH, and absorbing the ammonia in standardized acid. The results obtained by this method were very good, and are tabulated in Cols. VI and VII; where ammonia is reported as present, known amounts were added either to commercial batches or to laboratory samples.

Present Method for SO_3.—Sulpho-ricinoleic acid on boiling with dilute mineral acids, as already mentioned, decomposes, giving as one of the products, free sulphuric acid. The usual method for determining combined SO_3 is to boil the oil with hydrochloric acid. The fatty matter is then extracted with ether and the total SO_3 is determined in the water layer as $BaSO_4$. In another sample the SO_3 bound to alkali is determined by washing the oil dissolved in ether with concentrated salt solution, and analyzing the latter for H_2SO_4. The difference between these two gravimetric analyses gives the combined SO_3. The following is a much simpler method.

New Method for SO_3.—The oil is treated with a measured amount of standardized H_2SO_4, boiled until the decomposition is complete, and finally neutralized with standardized alkali in presence of methyl orange.

The following changes take place during the boiling:

$$2NaSO_3OC_{17}H_{32}.CO_2Na + H_2SO_4 + 2H_2O$$
$$= Na_2SO_4 + 2NaHSO_4 + 2HOC_{17}H_{32}.CO_2H$$

After heating, the original acidity of the solution, insofar as methyl orange is affected, is decreased by the formation of Glauber's salt, and is increased by the $NaHSO_4$. The net change in acidity, which is given by the titration, is equal to the difference

Sample No.	I Appearance of water solution	II Per cent. fat Flask method	III New method	IV Per cent. yield[1]	V Acid value of fatty acids	VI Per cent. NH_3 Added	VII New method	VIII Per cent. bound SO_3 Gravimetric method	IX New method
1[2]	Opalescent[5]	73.5	73.7	95.3	188	1.81	1.81	5.78	5.63
2	Opalescent[5]	77.0	77.1	96.0	188	None	....	....	....
3	White emulsion	73.8	74.2	95.7	188	None	....	4.12	4.09
4	White emulsion	78.5	78.3	96.3	188	None	....	....	....
5[3]	Clear soluble	36.6	36.0	95.4	188	0.740	0.733	2.04	1.87
6[3]	Clear soluble	32.6	32.1	95.5	188	0.375	0.385	1.75	1.64
7[4]	Opalescent	82.5	83.0	....	188	None	....	....	....
8	Opalescent[5]	60.1	59.0	....	Assumed 190		0.364	....	....
9	Opalescent[5]	68.5	69.0	....	Assumed 190	....	None	....	....
10	Clear soluble	40.4	40.1	....	Assumed 190	....	None	....	....

[1] Average yield 95.7%; theory 96.0%. [2] Neutralized entirely with ammonia. [3] Neutralized partly with ammonia. [4] Sulphated castor oil soap

[5] Changes to white emulsion on standing or on warming.

between the total alkalinity due to the soap and the acidity due to the $NaHSO_4$. The total alkalinity of the original sample is obtained as above. Hence, the acidity corresponding to $NaHSO_4$, or combined SO_3, can be calculated. It is to be noted that 80 parts SO_3 is equivalent, in this case, to 56.1 parts of KOH. Cols. VIII and IX give the results obtained by the gravimetric method and our present method, respectively.

Procedure.—Below is given in detail the analysis of a Turkey-red oil which was partially neutralized with ammonia. The solutions required are: standardized $N/2$ H_2SO_4, $N/2$ NaOH, and approximately $N/2$ alcoholic NaOH. All titrations were made in presence of methyl orange, unless otherwise indicated.

Total Alkalinity: Ten grams were weighed into a 250 cc. Erlenmeyer flask, balanced on a scale sensitive to 5 milligrams (all weighings were made in this manner), 150 cc. water added, and titrated with $N/2$ H_2SO_4. The titer of the acid was 27.02 milligrams KOH, and the titration required 17.2 cc.

$$\textit{Total alkalinity} = \frac{17.2 \times 27.02}{10} = 46.5 \text{ mg. KOH per g.}$$

Alkalinity after NH_3 was Volatilized: Eight grams were dissolved in 100 cc. water in a 500 cc. beaker, 25 cc. $N/2$ NaOH added, and gently boiled until litmus paper no longer indicated ammonia (about one-half hour). Water was added and the alkali titrated with $N/2$ H_2SO_4. The titer of the caustic was 27.30 milligrams KOH, the acid 27.02, and it took 31.85 cc. of the latter for the titration.

Alkalinity without ammonia

$$= \frac{31.85 \times 27.02 - 25 \times 27.30}{8} = 22.3 \text{ mg. KOH}$$

Should the sample contain a high percentage of fat (shown by the high viscosity and also by the fact that such samples give with warm water white emulsions) double the amount of caustic soda should be used.

From the above data, the ammonia was calculated as follows:

Ammonia $= 46.5 - 22.3 = 24.2$ mg. KOH, or, 0.733 per cent. NH_3.

Saponification Value: Eight grams were weighed into a 250 cc. Erlenmeyer flask provided with a long glass tube to serve as a reflux condenser, and 25 cc. $N/2$ alcoholic NaOH added. The flask was heated on a steam bath for 45 minutes, neutral alcohol added, and excess NaOH titrated with $N/2$ acid in presence of phenolphthalein. The blank took 23.4 cc. of acid, the titration required 9.95 cc., and the titer was 27.02.

$$\textit{Saponification value} = \frac{(23.4 - 9.95)\ 27.02}{8} = 45.4 \text{ mg. KOH}$$

The alcoholic caustic should be filtered to remove carbonate. The titration should be carried out immediately after saponification, as otherwise the absorption of CO_2 from the air makes the end-point indistinct. Double the amount of caustic should be used for concentrated samples.

The acid value of the castor oil fatty acid being known (188) the fat was calculated as follows:

$$\textit{Fat} = \frac{22.3 + 45.4}{188} = 36.0 \text{ per cent.}$$

Combined Sulphuric Anhydride: Eight grams were gently boiled for one hour with 25 cc. of standardized H_2SO_4 solution in a 300 cc. Erlenmeyer flask, provided with a condenser as for saponification. The flask was frequently shaken. Before disconnecting, the condenser was washed out with water by a spray from a wash bottle. The sample was then titrated with caustic soda. The end-point was best observed by adding excess alkali and finishing the titration with acid. It took 21.15 cc. of the alkali to neutralize the excess acid; the titer of the alkali was 24.48 and of the acid 31.4 (in the calculation, it should be kept in mind that the acid is partly neutralized by the alkali in the oil, which, in this case, is equivalent to 46.5 milligrams of KOH).

Combined SO_3

$$= \left(\frac{21.15 \times 24.48 - 25 \times 31.4}{8} + 46.5\right) \frac{80}{56.1} = 1.87 \text{ per cent.}$$

CONCLUSIONS.

I.—Turkey-red oils and similar products are completely or nearly completely saponified by $N/2$ alcoholic NaOH.

II.—Alkali bound as soap can be determined by titrating its solution with acid in presence of methyl orange.

III.—It is feasible to calculate the combined SO_3 from the increase in acidity due to the splitting of the sulpho group.

IV.—Based on these fundamentals a rapid method has been developed whereby sulphated oils can be analyzed for fat, ammonia and caustic soda bound as soap, and for sulphuric anhydride in the form of sulpho-ricinoleic acid.

Acknowledgements are due to Dr. F. Sonneborn and to Dr. F. W. Breth of this laboratory, for valuable suggestions and corrections.

LABORATORY L. SONNEBORN SONS, INC.,
New York City.

BOOK REVIEW*

By J. T. Wood.

THE METHOD OF ENZYME ACTION, by James Beatty, M. A., M. D., D. P. H., with introduction by Professor E. H. Starling, F. R. S. London, J. & A. Churchill, 1917. [5/-net.]

This is a very stimulating and suggestive book, remarkable in that it was written while the author was on active service with the Mediterranean Expeditionary Force, and so was not able to get access to original papers, as Professor Starling (now Lieut.-Col.) says in his introduction 'in this monograph Captain Beatty deals with a subject far removed from the more primitive problems now engaging the activities of this half of the civilized world, though it is one that has attracted and will continue for many years to attract the interest of a large body of workers in science. Like so many others of the riddles with which life presents us, the mode of action of ferments fascinates both chemists and physiologists. In this riddle lies hidden the mechanism of most vital phenomena, and until it is solved we cannot hope to penetrate further into the workshop of the cell itself, or to understand the various intracellular activities which in their sum make up the life of the individual."

Captain Beatty has carefully reviewed the whole of our knowledge of enzymes and discusses the physics and chemistry relating

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* *Journal of the Society of Leather Trades' Chemists*, No. 2, Aug., 1917, pp. 34-5.

to them in a very clear and concise manner. The sections on catalysis, colloids, adsorption, and chemical action, are all of great interest. As a result of this discussion the author formulates a working hypothesis of ferment action which, like most great ideas, has the merit of simplicity.

Enzymes are either colloids or attached to colloid molecules and in general appear to be optically active bodies. The characteristic properties of colloids depend on their enormous surfaces. An apt illustration of the effect of the subdivisions of matter in increasing the surface is given. A cubic centimeter in the form of a cube possesses a surface of 6 square centimeters, if divided into 1,000 cubes the surface becomes 60 square centimeters, if the subdivision is carried further until the edge of each cube measures only 10 $\mu\mu$., the aggregate surface is 60 square meters.

Now adsorption compounds are found at surfaces, and the quantity of substance adsorbed is proportional to the active surface. There is no doubt that enzymes form adsorption compounds with the substrate or body acted upon, and this part of enzyme action appears to be specific, *i. e.*, the particular ferment has the power of absorbing some particular substrate.

In addition all enzymes possess a general property, *viz.:* the power of attracting the H or OH groups in water. Thus, according to the author's theory enzymes have a dual composition, which in every case must be compounded of one substance exercising the specific and another the general function. Water alone can effect hydrolysis provided the concentration of the ions (H or OH′) can be raised to any considerable extent. Acids, bases, or salts can increase the concentration of either ion generally, and the author suggests that enzymes can increase it at the point of action, *viz.:* the surfaces of their particles, they themselves being either unchanged or else reformed in the course of the reaction.

Thus the enzymes will be indirectly powerful hydrolysers and will conform as regards hydrolysis to the definition of catalysts. The whole of the chemical action of enzymes may be reduced to the action of hydrogen and hydroxyl. In the case of the peroxidases, which are the most widely distributed of enzymes, the active agent is a colloidal hydroxide of manganese which gives up one hydroxyl group.

The composition of the hydrolyzing enzymes is not so well known as that of the oxidases, still analogy with the oxidases is in favor of a similar composition, and the fact that simple bases and acids can carry out hydrolysis in proportion to their ionizability is greatly in favor of the simplicity of the unspecific component. The author adopts Werner's theory of hydrolysis which is based on the assumption that molecular combination between solute and solvent, when the latter is water, occurs. He discusses this in detail for which the book must be consulted. From this discussion he deduces the hypothesis that this molecular combination loosens the internal bonds in one or both of the combining molecules, thus rendering the substances affected more reactive, in fact it is probably an essential condition of reaction. The action of the enzyme is to greatly increase the concentration of ions at the point of action. The concentration of ions is much greater than with acids and bases and consequently the action is more powerful; for instance boiling with hydrochloric acid for hours is needed to produce the same change in proteins that trypsin can produce in an hour or two at body temperature.

One may compare the effect to the action of nascent hydrogen as compared with molecular hydrogen in reducing processes. There are many illuminating facts about enzymes brought together in this book that it is not possible to mention in a short review. In conclusion the author says that if his hypothesis be the correct explanation of enzyme action it should be possible to manufacture enzymes. Some attempts have already been made in this direction.

July 30, 1917.

ABSTRACTS.

Waste of Hemlock Bark. J. H. Hamilton. *Industrial Progress and Commercial Record,* through *Hide and Leather,* Sept. 1. In 1916 the cut of hemlock in British Columbia was 100,000,000 feet. The bark from this lumber would be about 67,000 cords, the value of which for tanning purposes may be estimated at $670,000. The hides from the 25,000 cattle killed annually in British Columbia are shipped out, and leather corresponding to 50,000 hides or more is imported. Until a few years ago the market for western hemlock was very limited. Now that this lumber has become so important a part of the commerce of the province, the question of saving the bark is an acute one. The reasons why the western bark has not up to the present found a market are several. Logging conditions are so much more difficult in British Columbia than in eastern Canada that peeling the bark presents great practical difficulties. The loggers are unwilling to undertake to save the bark unless they are assured of a market. It is suggested that the forestry department of the government demonstrate to the loggers the feasibility of making the bark into extract on the ground. For such an extract the market is practically unlimited, and the freight charges on the concentrated product are not too high to permit it to be sold at great distances from the place of manufacture at a profit. Only from 6 to 8 per cent. of the timber cut in British Columbia is hemlock. If a market for the bark could be found, it is likely that a great increase in the cut of this timber would result. Analyses of hemlock barks from three localities by Mr. H. G. Taylor are as follows:

	Washington bark per cent.	Pennsylvania bark per cent.	Quebec bark per cent.
Tannin	17.0	13.3	10.1
Non-tans	6.4	7.5	10.1
Reds	1.6	3.5	1.9

In one tannery in Washington western hemlock has been used for a number of years, in the manufacture of skirting.

The Pulp and Paper Industry of Canada. O. F. BRYANT, of the Forest Product Laboratories of Canada, McGill University, Montreal. *Pulp and Paper Magazine,* through *Jour. of the Royal Soc. of Arts,* July 27 and Aug. 3, 1917. The two general classes of wood pulp are mechanical and chemical pulp. The latter is further divided into sulphite, soda and sulphate pulps. Mechanical pulp, or as it is commonly known, groundwood pulp, is made on a far larger scale than any of the others. In 1915, 53 per cent. of the total production was of this class. The woods most used are spruce and balsam. Spruce pulp is the best. For some grades of book paper poplar is much esteemed. The logs are cut into short lengths, and if the bark is still on it is removed by one of several machines. About 10 per cent. of the weight of the logs is bark, but the barking process removes about 20 per cent. of the weight. The barking drum is also used for the removal of bark, and avoids much of the waste. The logs are rolled around in a revolving slatted drum with continual water flow, and the bark rubbed off. The bark from the machines is at once used as fuel, while that from the drums is either pressed through rollers or piled to dry before use. Groundwood pulp is made by forcing the bolt of wood against a grindstone. About 50 horse-power is required to produce a ton of pulp in 24 hours. The quality of the pulp depends on the amount of water sprayed on the stone during the process. If the amount used is large, "cold ground pulp" is made, having fine and even fiber. "Hot ground pulp," in which the temperature rises to 150° F. or more, is uneven and coarse. The machines used for screening and dewatering the pulp are described.

In the making of chemical pulp the lignin is dissolved out and nearly pure cellulose is prepared. Sulphite pulp is made by cooking wood chips with calcium bisulphite. The methods of preparing the bisulphite are described at length. The essential thing is to lead sulphur dioxide through milk of lime. Some plants, however, make the bisulphite direct from limestone, over which a stream of sulphurous acid flows. Methods of chipping the wood and screening the chips are described. The cooking is done in cylindrical tanks from 40 to 50 feet high and 12 to 18 feet in diameter. Methods of construction of these tanks are described. They are now generally lined with brick. The cooking may be done in from 7 to 12 hours (quick cook"), or may take 35 hours ("slow cook," or Mitscherlich process). The wood for the soda process is prepared as for the sulphite method. The cooking is done in steel tanks 28 feet high and 7 feet in diameter. A solution of caustic soda at about 1.1 specific gravity is used. The time is about 8 hours. The soda is recovered by methods which are described, about 85 per cent. being recovered.

The wood for the sulphate process is prepared in the same manner as for the other two chemical processes, except that some mills do not remove the bark. This is poor policy, as it results in consumption of chemicals without producing any more pulp. The chemicals for this process are soda and sodium sulphide. This pulp is used in the manufacture of the "kraft" papers, strong brown wrapping papers. The cooking is done at a pressure of about 80 pounds per square inch, in steel tanks. The pulp is washed by the counter-current method, so as to make necessary the evaporation of as little water as possible in the recovery of the chemicals. The chips retain their shape after cooking, and must be ground up in a mill similar to those formerly used for grinding bark for tanning. The process of recovery of the chemicals is described in detail. Methods of bleaching the pulp are described at length, also methods of felting the pulp and making the various kinds of paper.

Mangrove Supplies in Porto Rico. *Jour. of the Royal Soc. of Arts,* Aug. 24, 1917. The variety of mangrove known as "mangle zapatero," or shoemakers' mangle, is considered the best for tanning and dyeing. It is also used as a preventive of boiler scale, especially where brackish water is used. The wood of this species is crooked, knotty and brittle. Two other species, known as "chifle de vaca" and "botoncillo" produce straight-grained wood which may be suitable for tool handles, etc.

Tanning Materials from British Malaya. *London and China Telegraph,* through *Jour. of the Royal Soc. of Arts.* Gambier is sold in bales and in cubes. The trade in bales is chiefly with European countries and the United States, where it is used in tanning. The value of gambier passing through the Straits Settlements in 1915 was nearly $1,500,000, and for the first 9 months of 1916, $1,300,000. Cube gambier is primarily used for chewing with the betel nut by the Oriental peoples. A part, however, goes into the European trade for tanning purposes. Betel nuts (areca) are a large item of trade in the Straits Settlements. This is classed among spices, but its astringent character suggests its use as a tanning agent. The yearly value of this article of trade is about $5,000,000. There has been some increase in the trade in mangrove extract since the war began. The annual value of this trade in these settlements is about $200,000.

Purification of Sewage by Aeration in the Presence of Activated Sludge. EDWARD BARTOW. *J. Ind. and Eng. Chem.*, Sept., 1917, pp. 845-50. The work described was done at the Sewage Experiment Station of the Illinois State Water Survey at the University of Illinois, Urbana. A continuous-flow plant was installed in the summer of 1916. The plant includes a screen chamber, a pumping pit, a grit chamber, an aerating chamber, a settling chamber, a blower room, and a laboratory containing sludge drying apparatus. A sludge drying bed and a pond to receive the effluent are also provided. The sewage treated is drawn from the main outlet sewer of the city of Champaign. A series of tests was made to compare the efficiency of three systems of aeration, filtros plates, baswood blocks and perforated pipes. The basswood plates furnish finer bubbles than the others. The removal of turbidity and the diminution in oxygen consumption were practically the same for all the tanks. In removal of ammonia nitrogen and production of nitrate nitrogen, the filtros plates were decidedly superior. The sludge from the tank with filtros plates also settled better than the others. The wood blocks, ½ inch thick, deteriorate rapidly and are hard to manage because of excessive swelling. The other problem studied was that of drying the sludge. Further experiments with sand beds were not satisfactory, partly because the sludge is difficult to separate from the sand and partly because the fertilizer value of the sludge was partly lost in the process. Experiments with a filter press were unsatisfactory because it was not possible to obtain cakes of sludge of satisfactory consistency. Further experiments in this line are to be tried. Various types of centrifuge were tried. The most satisfactory of these was specially designed for the purpose and was made by the Tolhurst Machine Works, of Troy, N. Y. It is estimated that one 40-inch machine will handle the sludge from 2,000,000 gallons of sewage per day, reducing it to 88 per cent. moisture, ready for the dryer. The author concludes that the prospect of making the sludge into a marketable product at a profit are good.

Discontinuous Extraction Processes. L. F. HAWLEY, Chemist in Forest Products, Madison, Wis. *J. Ind. and Eng. Chem.*, Sept., 1917, pp. 866-71. The first series of experiments involved glass beads which had been wet with a strong salt solution. The ratio, volume of liquid removed to volume retained, is called the solvent ratio. With any solvent ratio a, the amount of salt removed by a single washing is $\frac{a}{a+1}$ and the amount remaining $\frac{1}{a+1}$. Thus if the amount of liquid drawn off is five times that remaining on the beads, a single wash will remove five-sixths and leave one-sixth of the salt. After two washings, the amount remaining is $\frac{1}{(a+1)}$ 2, and so on. The table which follows shows the per cent. extracted with one, two, three and four washings, and solvent ratios from 1 to 10.

Solvent ratio	1 Wash	2 Wash	3 Wash	4 Wash
1	50.00	75.00	87.50	93.75
2	66.67	88.89	96.30	98.76
3	75.00	93.75	98.44	99.61
4	80.00	96.00	99.20	99.84
5	83.33	97.22	99.54	99.92
6	85.71	97.96	99.71	99.96
7	87.50	98.44	99.81	99.98
8	88.89	98.76	99.86	99.98
9	90.00	99.00	99.90	99.99
10	90.90	99.17	99.92	99.99

The rational method of making extractions is the multiple method, which applies the counter-current principle, in which a solvent which has been applied to a mass of material already partly extracted, and which therefore receives less dissolved material, is afterward applied to a fresh mass of unextracted material. The number of cells in such an extraction method may be as many as desired. The mathematics of the problem are much less simple than in the previous case. The table gives amounts extracted with solvent ratios of 1 to 6, and with from 1 to 6 cells, using the counter-current method.

Solvent ratio	1 Cell	2 Cells	3 Cells	4 Cells	5 Cells	6 Cells
1	50.00	66.67	75.00	80.00	83.33	85.71
2	66.67	85.71	93.33	96.77	98.42	99.21
3	75.00	92.31	97.50	99.17	99.73	99.91
4	80.00	95.24	98.82	99.71	99.93	—
5	83.33	96.77	99.36	99.87	99.97	—
6	85.71	97.67	99.61	99.94	—	—

Practical methods of extraction are discussed. Emphasis is laid on the importance of draining off each batch of solvent before applying another, as imperfect draining is equivalent to decreasing the solvent ratio. (The complications introduced by changes in the solubility of materials with increased time of extraction make the extraction of tanning materials very difficult to treat by mathematical methods.—ED.)

Foreign Markets for Imitation Leather. CONSUL FRANCIS B. KEENE, in *Commerce Reports*. Imitation leather is now practically indispensable to the continued operation of certain Swiss industries. Some of the uses to which it is put are upholstering motor cars, furniture and baby carriages, school satchels and bookbinding.

Rubber versus Leather Belting. *Hide and Leather,* Aug. 25. Some manufacturers of rubber belting have recently stimulated their salesmen to assert that the rubber belting they sell beats leather. This belting contains several plies of thin, closely woven and extra strong fabric, with a strong, high-grade friction firmly cementing the plies together, and vulcanized between the plates of a hydraulic press under great pressure. Among the claims for this rubber belting are ability to run at high speed over small pulleys without being damaged; very flexible, little or no stretch; can be laced or fastened, and does not pull out at the joints. The rubber people say their five-ply belt is 27 per cent. stronger than a single leather belt, used in a test, and the seven-ply is 18 per cent. stronger than double leather. Further, that the five-ply shows 54 per cent. less stretch than single leather, and the seven-ply 30 per cent. less than double leather. The rubber belt men claim that a light double leather belt is too thick to negotiate pulleys without becoming badly strained, so that the outside of the belt will check, crack and finally break. This rubber belt circular letter to salesmen is full of assertions that their special brand of rubber belting not only replaces leather, but beats it. A leather belting authority says this "Circular Letter to Salesmen" is very skilfully prepared. It makes the most of all that can be said in favor of the product, and judiciously omits all mention of the weak points. It emphasizes tensile strength, which is of minor importance because any good leather belt is many times stronger than is required by any strain which may be placed upon it in service; and it lays much stress upon the absence of stretch, but says nothing about the factor of elasticity which is so necessary a quality of a good belt, and which is so nearly absent in the rubber belt; it dwells heavily on the comparative cost of the rubber and the leather belts, but carefully omits any comparison of the cost per horse-power per annum. It also carefully avoids any mention of the power transmission capacity of the rubber belt, that being a feature that it is wiser to say nothing about, since rubber belting is notably deficient in its ability to transmit power as compared with the leather belt; and no mention is made of the impossibility of making repairs, and of the absence of any salvage value. We are informed that "it can be laced with rawhide or wire or fastened with any of the metallic fasteners on the market, and does not pull out at the joints." In this latter particular, this must be unique among rubber belts, for this is one of the characteristics of the rubber belt—its readiness to tear out at the joint, and the impossibility of making any permanent and satisfactory joint. It also omits any comparison of the length of life of the two classes of belts, and of the relative costs of the two belts in service. It is interesting to note the ingenuity of the effort to create a false impression about the extent of the increase in the price of leather belting, by quoting the advances which have occurred in the price of Chicago packer hides. There was a slump in the price of hides during February and March, 1916, and a recovery during April and May, and though it is true that hides were 22¢ in March, 1916, and 32¢ a year later, and that the increase between these figures is 42 per cent., this showing has been secured by searching for the periods of greatest difference. At both an earlier and a later date in 1916 the prices of hides had ranged from 27¢ to 29¢, and July 27, 1916, the price reported is 27¢, which compared with 33¢ for the same date 1917, and which is an increase of but 22 per cent., an increase, by the way, less than has occurred in the general average of commodities, but in this case the prices of hides is of no interest, as the question, if there is one, is of the increase in the price of leather belting, and as we all know, in four years this increase has been nearer 50 per cent. than 78 per cent., as stated. Attention is called to the prices at which this rubber belt is sold. The maker's price to jobbers is 50-10 per cent.—but it is understood that the most successful distributors are selling it at 30-10 per cent., making thereon a profit of 40 per cent. The writer is a believer in fair profits, and finds no fault with anybody who can sell an article at a profit of 40 per cent., but as this letter is mainly one of comparisons, it is fitting and proper to call attention to the fact that leather belting cannot be sold at any such profit, and disregarding the manufacturer's profit (which is probably quite sufficient on an article on which a dealer can make 40 per cent.) it would seem that in a purchase of this belt the buyer is receiving not more than 60 per cent. of belting material, whereas in leather belting he would receive (so far as the dealer's profit is concerned) from 90 to 95 per cent. of belting material. The concluding line is one of those statements which may be classified as "important if true." "It not only replaces leather, but it beats leather." The Leather Belting Exchange has just issued to its members a report from its Research Fellow, giving the result of some comparative tests between leather belts and rubber and canvas belts, which completely disposes of any such claims as those of this letter, and in the light of which these claims must appear to be ridiculous, and the members of the Exchange and their sales forces are now well qualified to meet any such claims.

Fish Skins for Glove Leather. *Shoe and Leather Reporter.* A good substitute for leather suitable for the manufacture of gloves has recently been discovered by the Bureau of Fisheries of the Department of Commerce in the form of seal gullets. Treated in a special manner, it is said, these seal gullets may be made into the finest kind of fine "kid" gloves, and they can be utilized for any number of other purposes. Samples of this leather were recently presented to Secretary of Commerce Redfield. Mr. Redfield has been very energetic in gathering together materials which have heretofore gone to waste and which are now believed capable of being so treated as to act as a substitute for some other raw material of which there may be a shortage. In this way the attention of the Bureau of Fisheries has been directed to the developing of aquatic sources of leather. For some time the Bureau has been handicapped in its efforts to develop the utilization of skins of aquatic animals for leather and other purposes because it lacked the services of a suitable man in position to devote his entire time to the solution of the various problems and difficulties which were arising. Funds were provided early in July and such a man as this, in the person of George B. Turner of Washington, D. C., was employed to take up the work. Mr. Turner will seek to bring about closer co-operation between fishermen and tanners and manufacturers who might be interested in the utilization of this product. This investigator is to endeavor to ascertain what the obstructive difficulties and problems are, and how they may be solved, and he will lend all possible assistance in the development of this industry. During the month of July, Wilmington, Del., Newark, N. J., and New York, Boston and various other points were visited for the purpose of getting in touch with tanners who are prepared to take hold of this work energetically and to learn something of the problems which confront them. As demands for the raw product develop, visits will be made to the fishing centers for the purpose of interesting fishermen to save and market the skins. The Bureau of Fisheries recently had an opportunity to examine some additional samples of leather tanned from fish skins, which indicate that considerable progress is being made in the tanning of these products. The steamer "Roosevelt" is now on her way from the Pribiloff Islands to Seattle, Wash., with about 5,000 seal gullets aboard. It is planned to tan these and use them in the manufacture of various articles. Seal gullets were formerly among those things thrown away as waste; hereafter, if the plans of the Department of Commerce materialize, they will be utilized to excellent advantage, and "seal throat gloves" will be among the coming season's novelties.

Successful Quebracho Company. CONSUL WILBERT L. BONNEY, in *Commerce Reports.* The Forestal Land, Timber & Railways Co., of London and Buenos Aires, reports another excellent year for its quebracho and other enterprises, located in the northern part of the Province of Santa Fé. This company is the largest exporter of quebracho extract in this district. The chairman of the board of directors at a recent annual meeting in London stated that during the 11 years of operation the company has paid an average of 11½ per cent. per annum on the preference shares and 16½ per cent. on the common shares, besides setting aside a reserve and depreciation fund of more than $9,000,000 (U. S. currency). Its quebracho extract factories are at Villa Guillermina, Villa Ana, La Gallereta, and Tartagal.

Philippine Hide Industry and Its Possibilities. COMMERCIAL AGENT C. E. BOSWORTH, in *Commerce Reports.* The hide and skin business of the Philippine Islands is absolutely unorganized and there is a tremendous waste. The hides and skins that find their way to the local tanneries are purchased from the independent operators who kill at the municipal or provincial abattoirs. There are no hide cellars worthy of the name. Most of the hides go immediately in pony carts to small tanneries in the vicinity of the abattoirs. There they are turned into a most indifferent leather, merely a rough tanned product, which the user has to dress and finish himself. The hides are good, light hides from the native cattle, which show definitely the influence of the blood of Indian cattle. The hair is so short that they give the impression of having been closely clipped. They are firm and exceptionally uniform through the whole spread of the skin. Only in the bulls of mature age is the characteristic hump developed to any degree, and it is only in the bulls that the neck wrinkles are noticeable. The hides of these native cattle, called "vacas," range in weight from 10 to 18 kilos of 2.2 pounds. A similar animal is imported from French Indo-China, but it is a little smaller and smaller boned; the hides average 13 to 14 kilos. All these hides are sold by the piece and are quoted at $6.25, with 25 per cent. additional for heavy hides. In addition to these hides are those of the carabao, a kind of buffalo, with a very thick hide, rather loose fibered but possessing great tensile strength. If the Australian buffalo will produce chrome sole and chrome belting leather so thick that a single layer is sufficient to replace double belting, these carabao hides will certainly do the same thing. Bark-tanned and waterproofed, the carabao hides produce sole leather superior in quality to ordinary soles, and with more modern tanning methods the leather would be still better. The tanners here do not even roll it. There is only one sole leather roller in the islands and this one does not work.

The horses here are ponies containing a mixture of the blood of ponies and small horses from northern China, French Indo-China, and Mexico, with a considerable admixture of Arab blood. There are some 243,000 horses in the islands. In Manila alone about 100 dead horses are collected every month, which are cremated, hides and all, though there is a great need of horsehides for razor strops and shoe leather. In the rest of the islands probably 2,500 horsehides are wasted every year because no one knows where to sell them profitably. A certain number of sheep and goatskins is available. In the Provinces the natives sun-dry these and also carabao hides, and make pails or basins out of them; but the methods used are very wasteful. The extra pesos that could be gotten out of a carcass would doubtless induce the Chinese butchers to skin their hogs. The hog kill is large for the size of the country and the hogskins are good.

The entire hide industry might be organized somewhat as follows: There should be a principal buyer in Manila, with an office and hide cellar for the proper care of the receipts. This buyer could make long-time contracts with the local killers to take their output at a reasonable price per piece. There are too many cut hides now, but if a premium were offered for free, clear hides, the percentage would be much less. The cattle are free from ticks and other parasites and there are no grubby hides. The brands are mostly on the flank and are reasonable in size; those on the butt are small. Provincial buyers who would act as collectors could be chosen from the Chinese, who are shrewd traders. They would act under the manager at Manila, carry on the buying in conjunction with their present businesses, and give the hides proper care until the accumulation was sufficient to ship to Manila. The Manila manager could easily make a contract with the municipal government for the hides from the dead horses that are collected by the city crematory. These horsehides carry two butt brands now—one for the owner and one for the Government—but it should not be difficult to bring about legislation transferring the brands to the flank, lower withers, or even the neck. The size of the brands also should be regulated; most of them are reasonable now, but some are large.

Effect of Hard Water on Tannin. DR. E. SCHELL. *La Halle aux Cuirs,* Aug. 12, 1917. (This article is published under the title "Small Causes, Large Effects.") The author has charge of analysis of chestnut extracts at a factory and by an accident to his apparatus was deprived of distilled water. As no more could be procured at once, and important work was on hand, he made some analyses with Paris city water, which has 20.5 "degrees of hardness," 5 temporary and 15.5 permanent. The plan was to correct the results by subtracting from the weight of the dry residues for total solids, soluble solids and non-tans an amount corresponding to the solids in the water used for dilution. The water was boiled for 20 minutes to destroy bicarbonates, and the residue from 100 cc. of the resulting water was 0.0108 g. per 100 cc., dried at 100° C. This water was perfectly neutral to the usual tests. To turn methyl orange to rose color required 1.1 cc. of 0.1 N acid per 100 cc. of water, corresponding to 0.004 g. of carbonate of lime per 100 cc. One would hardly suppose that such a small quantity of carbonate would have any effect on the tannin percentage, especially as the hide powder had an acidity four times as great as the alkalinity of the water. The analyses with the city water are compared in the table with analyses previously made with distilled water: (Values in percentages, column *a* analyzed with distilled water, column *b* with city water boiled and filtered.)

Analysis number	Tannin		Non-tannin		Reds	
	a	*b*	*a*	*b*	*a*	*b*
1	29.5	27.5	12.8	14.6	0.3	0.2
2	27.7	25.4	12.6	14.8	0.7	0.8
3	26.7	24.6	13.8	15.8	0.7	0.5
4	26.2	23.7	16.3	18.7	1.0	0.8
5	29.9	27.6	11.2	13.2	0.6	0.4

All figures in columns *b* have been corrected for the residues due to the water. These figures indicate in every case an important depression in the tannin figure. All the non-tannin residues have been very carefully tested with gelatin solution, and the discrepancy cannot be accounted for by presence of tannin in the non-tans. These results show clearly how important it is to use distilled water of good quality in analyzing chestnut extract. In order to verify the assumption that the differences were caused by the presence of carbonates, analyses were made with the same water, boiled and filtered and then acidified. The results were absolutely conclusive, the figures now obtained agreeing closely with those obtained with distilled water. The author concludes that elimination of the carbonates stops the destruction of tannin. The same extracts were analyzed with distilled water to which had been added, (1) precipitated calcium carbonate, 0.16 g. per liter, and (2) 0.14 g. magnesium carbonate per liter. In both of these cases the results agreed with those obtained with the boiled and filtered city water. The carbonate of magnesia caused a deepening of color in the extract from 2.5 red to 4.5 or more. Hard water therefore causes a loss, Dr. Schell concludes, of from 2 to 2½ per cent. of tannin. A factory using 500 tons of extract a month would suffer a monthly loss of from 20,000 to 25,000 pounds of tannin.

L. B.

Notes on Unhairing. "A TANNER," in *La Halle aux Cuirs,* July 29, 1917. It has been often said, and more often recently, that to secure a firm sole leather, the hides must not be violently agitated mechanically nor subjected to severe chemical treatment, especially in the soaks and limes. The writer is disposed to question the absolute wisdom of this long-established fear. He asserts that sodium sulphide in the limes is an aid, especially in winter, in keeping the liming uniform. It is true too that frequent renewal of contact surface between hide and lime liquor aids in the removal of the hair and is an advantage from all points of view. The writer, however, believes that from the point of view of loss of hide substance and also with respect to the firmness of the finished leather, it is better to secure the renewal of contact surface between hide and lime by agitating the liquid only, the hide being hung in place. It is only necessary to agitate the limes once or twice a day, by means of a paddle wheel which may be so arranged as to take but little space in the vat. In using sulphide of sodium the quantity should be varied according to the temperature of the season, and in no case should more be used than can be converted in the bath into sulphide of lime, since sodium sulphide is much more destructive of hide substance than sulphide of lime. To this end it is better to dissolve the sulphide in the water which is to be used for slaking the lime. L. B.

The Utilization of Tanning Extracts. "A TANNER," in *La Halle aux Cuirs,* Aug. 19, 1917. When extract is diluted for use there is often a considerable precipitation, more or less depending on the kind of extract and the method of manufacture. This precipitation is displeasing to the tanner because it represents loss of solids which might have been utilized. It is also objectionable because, unless great care is taken to settle the diluted extract well, or when as is sometimes done (a very bad practice) the extract is put directly into the liquors, the precipitate of phlobaphenes encrusts the surface of the leather, giving it a marbled and spotted appearance. The spots, commonly called lime stains, are often due to the deposit of these phlobaphenes. The precipitate which forms at the bottom of the tanks used for dilution is generally poorly utilized or thrown directly out as waste. It contains valuable substance, difficultly soluble, it is true, but which may be partly utilized by means of warm liquors.

Where mixed tannage is employed, part bark and part extract, the casks of extract may be emptied directly upon the leach of new bark. The head leach thus serves instead of a mixing tank, and the liquor produced may be taken direct from the bottom of this leach, if strong liquor is desired. The liquor obtained in this way is clear and *acid;* in good condition, therefore, for working to the best advantage. So far, so well, but do we get out of the leach all the tannin we put in? There is apparently a slight loss of tannin, which goes to counterbalance the advantages of the method. Sometimes, particularly in spring, the passage of extract over bark, in leaches not carefully cleaned, produces infected liquors, oily in appearance, and disastrous to use. To summarize, the advantages are: (1) Dispensing with dilution tanks and saving labor; (2) avoiding handling the precipitate, which simply goes to the fire with the spent bark; (3) partial utilization of reds; (4) economical acidification of the liquors; (5) avoidance of the stains on the grain of the leather commonly blamed on the lime. The two disadvantages are: (1) Probable loss of tannin; (2) danger of infection of the liquors. L. B.

PATENTS.

Production of New Tanning Materials. U. S. Patent 1,237,405. EDMUND STIASNY, Headingley, Leeds, England. In the August JOURNAL we published patent No. 1,232,620, the application for which was filed Dec. 13, 1912, issued to Dr. Stiasny for a new tanning material, and said that it appeared to be the original patent on neradol. *This* application was filed Aug. 20, 1912, and so far as appears it includes nothing not included in the earlier patent issued upon the later application. There are many things about the granting of patents which are difficult for the unofficial citizen to understand.

Leather Working Machine. British Patent 107,355. W. C. ROCHE, Beverly, Mass.

Leather Working Machine. British Patent 107,231. W. E. FAWSITT and W. F. STEVENS, London.

Hide Working Machine. U. S. Patent 1,238,235. R. F. WHITNEY, Winchester, Mass.

Fleshing Machine. U. S. Patent 1,239,748. ALBERTUS TRAVIS, Johnstown, N. Y.

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CHANGES OF ADDRESS.

Michigan Tanning & Extract Co. to Petoskey, Mich.
J. Houston Duffy to Taberg, Oneida Co., New York.
S. P. Sharples to 22 Concord Ave., Cambridge, Mass.
A. B. Cooper to 128 Montmorency Ave., Ridgway, Pa.
V. G. Lumbard to 263 Alameda St., Youngstown, Ohio.
I. F. Stone to 244 Madison Ave., New York City.
R. J. Bailey to Gleasontown, Pa.

PROPOSED CHANGE IN METHODS.

The following change has been proposed in writing to the secretary, in accordance with paragraph 22 of the by-laws of the A. L. C. A.

Under Chrome Determination, page 33 in the Methods of Analysis change reading as follows:

"After boiling gently 30 minutes, add water if necessary to keep the volume from falling below 15 cubic centimeters. Cool and dilute to 150 cubic centimeters, neutralize, etc."

The proposer explains that if the solution becomes too concentrated, especially in the presence of small amounts of organic matter, which are apt to be present in some chrome liquors, the addition of concentrated acid is apt to reduce some of the chromic acid.

TANNING AND DRESSING SHEEP PELTS.*

By A. T. Munroe.

After sheep skins have been de-wooled, the liming of the pelts follows. This is somewhat controlled in the first stages by the previous treatment of the skin to effect the removal of the wool. Some fellmongers, for foreign skins, adopt the quick method of sweating, which, by bacterial action, renders the wool easy of removal in the course of a few hours. The bacteria, under suitable conditions of heat and moisture, attack the roots of the wool, thus allowing the latter to be readily pulled out, but if the greatest care is not exercised by removing the skins from the warm stove just at the correct time, the bacteria, which develop at an extraordinarily rapid rate, proceed to attack the pelt. This means loss of tanning substance to the leather manufacturer. The latter prefers for this reason the loosening of the wool by means of a sulphide. This dissolves the wool, hence care is needed that the sulphide mixture shall not come in contact with the wool if possible. The skins are carefully painted with the sulphide paste on the flesh side only, and two skins are then placed flesh to flesh. The pelt is quickly penetrated by sulphide, and the wool roots are reached, which completes this work.

From the tanner's point of view the latter process is advocated as producing better pelts, but the wool buyer prefers the sweating, as giving wool of a better quality. Hence the fellmonger finds himself between two stools. Mention may be made here of several

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* *The Leather World*, March 15, April 12, May 17, Sept. 13, 1917.

points which need very careful attention. In summer time, with hot weather prevailing, when pelts after de-wooling are thrown on piles or stone floors which are warm, the heat is sufficient to cause an exudation of grease from the skin. This often occurs in patches, small or large.

The same effect is obtained during transit of pelts from place to place, even if care is taken to cover them well. If skins in this condition are put into lime, the grease spots in contact with the alkali form an insoluble lime soap on either flesh or grain, and the pelt is deprived of the useful action of lime, wherever these patches of lime soap cover the skin. Usually washing in cold water in a drum for a few minutes before putting into the pits will effect the removal of this grease, but the skins should not be allowed to lie about afterwards before lime treatment, or grease will probably again exude. The quantity of grease that appears on the surface is so small that unfortunately it is too often regarded as of no material consequence, and this neglect often provides a subsequent loss to the leather dresser.

The skins, as a preliminary, are thrown separately into an old lime, that is, one in which several batches of skins have already been treated. This latter does not swell the pelt so rapidly as a newly made lime, but its action is nevertheless equally as powerful; in fact, more destructive, if not carefully watched. The action of an old lime depends upon its bacterial activity, a new one upon its caustic alkaline qualities. Therefore the latter will rapidly swell the pelt, while the former tends to soften it by the solvent action of the bacteria, and which is mainly exerted upon the glutinous matters cementing the fibers together. It is beneficial to remove this medium to a certain extent which is entirely governed by the uses to which the pelt is to be afterwards put. For very soft, flexible leather, a prolonged treatment in old limes is advisable and necessary, but if a firm full-bodied leather that is mellow to handle be desired, then the old lime treatment must be curtailed.

It is impossible to give quantities of lime necessary with any degree of accuracy, as so much depends on the water used. Should any quantity of carbon-dioxide be present in the water, which nearly always is the case where the supply is drawn from a deep well, a quantity of chalk would be formed which, while neutralizing the effect of the lime, is a decided disadvantage to the skin, as will be seen later. Again, there are the sulphates of lime and magnesia in well water to watch.

Surface waters, as taken from streams which depend largely upon rain for their supply, are possessed of much softer qualities, owing to the greater absence of sulphates of lime and magnesia and carbonates, hence a smaller quantity of lime will be found in use to quite fulfil the requirements.

To preserve a good grain, care should be taken to scald the lime before using, and to mix it into a creamy consistency. This should be allowed to settle, and, in using, the portion at the bottom of the tub must be rejected. This will contain the sand or other hard matters which adhere to the skin, and in process of working in the pits will find their way into or on the surface of the pelt. The after working, as fleshing, scudding, &c., will often produce scutches or damaged grain from a neglect of this precaution.

The quality of lime is also a factor which must be reckoned in deciding the quantity to be used. It may be a common one, containing considerable portions of foreign matters, as stones, sand, &c., or it may be a fairly pure article. Less weight of the latter would naturally be used than the former. For reasons stated, it need not cause surprise to find in use the amount to range between 2 per cent. and 10 per cent., calculated on wet weight of pelt.

The objects in view for which lime is used comprise the production of soft leather, the easy removal of the short hairs or undergrowth, and the swelling of pelt for splitting, when the last operation is intended. The epidermis, or what is commonly called scurf, is not removed in pulling the wool, and acts usefully at first as a protective covering of the true skin, should the old lime be "too old," and thus contain destructive bacteria in too great abundance. This scurf is first attacked, and gives the skilled workman an opportunity to note effects and apply a remedy by disposing of a dangerous, stinking lime. Of course, under proper control, such a lime would not be in existence.

The new lime, containing very little bacteria, but very caustic qualities, is used last, and completes the swelling of the pelt. To obtain good results, the pelts should be drawn from the pits daily, and then replaced one by one, thrown flat on the freshly plunged lime liquor, and gently forced downwards with a light pole. In this way every portion of the skin is exposed to the lime's action. In some yards paddles are used, but it is a question if the saving of manual labor compensates for the damage often caused by the revolving dashers striking the skin when its surface is in such a delicate condition as to be so susceptible to be damaged by action of this sort.

Often, to get quick results in ridding skin of hairs, 25 per cent. of arsenic sulphide is added to the lime when in the creamy consistency. This will dissolve the hair to a great extent, but not completely. It does not swell the pelt, however. The addition of sodium sulphide will produce a caustic liquid with the lime, and swells the skin considerably. The use of lime from gasworks has often been practiced, because of the sulphide contained therein. Arsenic sulphide, it may be noted, produces a very soft, silky grain upon the finished product, while the sodium is found to give a rather dry, harsh feel to the grain.

Fleshing follows the liming, and is accomplished either by machine or hand work. The object is to remove all the flesh adhering to the under side of the skin. The skins also need trimming or rounding. Some prefer to do this before liming, and others afterwards. In either case it should be performed carefully with a sharp butcher's knife, and not with a flesher's knife; the latter is too large and unwieldy. It should be a separate job, and not more of the pelt should be cut away than is absolutely necessary. The trimmings make glue stock.

Following fleshing is unhairing, though this is taken first sometimes. It is working over the grain with a very clear-edged dull knife, of a semi-circular shape, by which means all the loosened hairs are pressed out.

Skins for splitting are piled one over the other, or put into "couch," as it is termed. The object is to obtain a surface as free as possible from wrinkles. The skin absorbs water, and thus becomes swollen in the limes. If left undisturbed in the pits, deep wrinkles follow the creases formed by the crumpled-up skins pressing one upon the other. These deep wrinkles are difficult, often impossible to remove; but even in the best limed skins some superficial wrinkles will appear in the swollen skins, which are more or less of a natural growth.

The pressure exerted in the pile or "couch" tends to distribute the water in the pelts more evenly, and to flatten the grain surface and wrinkles. The pelts also become harder, which promotes more level splitting, the firm substance presenting a more suitable condition for the knife of the splitting machine to cut an even substance in grain or skiver. The under or flesh side produces the raw product for chamois or washleather, and contains a large part of the fat cells and fat existing in the middle part of the pelt.

Usually the skins for splitting are selected in the limes. Those of a loose nature are thrown out for the purpose, while for basil or roan tanning the firm, well-grown skins are put aside.

Without diverging unnecessarily into the consideration of the different breeds of sheep, and when their skins are more suitable for different selections of leather, and why this is, it may be consistent to remark that for English sheep skins the best pelts for roan and selected basil work are those collected during September onward to February. After this date the quality changes, and the proportion of firm-grown skins is less in evidence. This goes on until after shearing, when a change for improvement will gradually become noticeable, and continue until September is again reached.

Following is the puering and drenching of the skins preparatory to tanning. From whatever source the idea came to use animal or bird excrement to effect the removal of lime in the skin, it may be said to be equally as successful as it is repulsive. Laying aside its objectionable smell and filthiness, it does work for the leather dresser which so far has not been surpassed by substitutes, and even some of the bacterial substitutes possess a characteristic odor which even the puerman dislikes. The object attained is not only the removal of lime, but a further separation of the fiber bundles to produce soft, pliable leather. If these fiber bundles are not divided, hard leather results, and as sheep skins are unsuitable for boot soling work, this result is not desired.

Here, again, so much depends upon the hardness of the water that quantities are difficult to give for puer to be used. Soft water, containing no carbon dioxide, will bring down limed pelts almost without the use of any puer at all; but if this element be present, then the forming of lime carbonate or chalk in the skin is dangerous to good results, and is to be avoided. Hard water may be improved by treatment with the requisite amount of lime, when the chalk formed will settle as an insoluble precipitate. This is a cheap and effective method to avoid forming chalk in the skins.

Generally, from 8 to 10 per cent. of the puer calculated on weight of wet skin is used, but the great ruling factor is the judgment of the puerman himself. He takes what he considers sufficient. If the work proceeds too slowly, he adds a little more. If too quickly, he adds water, or, if possible, more pelt. Temperature affects the work, and this must be allowed for. A great deal depends upon bacterial action, but not all, in obtaining the desired result. About one to two hours is sufficient to bring down the pelts to the desired silky state, but this again depends upon the thickness of the skin to treat.

When brought down low enough, the skins are scudded either by hand or machine, the object being to cleanse the skin. For skivers this work is relied upon to get rid of all the grease, although for stout splits it is better to rely upon degreasing than use excessive work with the scudding knife. When the operator has the skin thrown over his beam he can, by throwing a little clean water over the scudded grain, see if any short or fine hairs are present. The water draining off the surface allows the hairs to rise up, and by a glance down the skin they may be easily seen. These hairs may be shaved off by a clever man with the use of a very sharp knife, and without any damage to the grain.

The real cleaning of the skin is by the use of the drench. The puered skins are placed in a bath of warm water, containing 5 per cent. to 10 per cent. of bran well mixed in it. After the lapse of a few hours, depending largely upon outside temperature, fermentation becomes visibly active with the liberation of carbonic acid gas in considerable quantities. The skins are thus forced up to the top of the tank, and should be well moved about and forced down again, otherwise bad effects result in the form of dark patches, from the gas forming blisters in places.

Darkness is essential to good results in drenching, and the tanks are well covered for this reason, also to conserve the heat at one temperature. The vigorous and repeated stirring of the drench is also advisable to clean the skins, the particles of bran rubbing the surface of the pelts having a very beneficial effect in this way. Twenty-four to thirty-six hours is the usual time allowed, but this is much varied by the methods of working adopted by the skilled man in charge. Paddles are sometimes used to keep the drench in movement, and with satisfactory results. For some forms of leather the puer is dispensed with and the drench only is used.

The bran drench depends upon a certain amount of flour it contains to produce fermentation. With the advent of rolling machinery for milling wheat, it was early discovered that the bran produced contained much less flour than that given by the old-fashioned stone grinding, hence flour is added to the drench. War-time bran will contain less flour probably, and this must be watched in making up a drench.

Acids are produced in this process, mainly lactic and acetic, and these have the effect of again swelling the pelt, but it is a very soft, silky result, as compared with lime action. Mineral acids for deliming are frequently used, but not always with happy results. They are too rapid and violent in action, even in very small percentages, and attack the outer surfaces before the inner portion of the pelt has been penetrated, therefore their use is not to be recommended except in conjunction with other chemicals, where their rapidity of action may be controlled.

Sal ammoniac, or ammonium chloride, has long been used to remove lime. It depends upon the lime combining with the chlorine to form chloride of lime, a soluble salt, with liberation of the ammonia. The skin swells a little, but the chloride of lime and ammonia are easily washed out. If the object was only to get rid of lime, this process should be sufficient.

Boracic and lactic acids have been used with very good results, and have largely aided in removing grease from pelts. Probably the fat cells were sufficiently swollen or broken up to allow the grease to exude under pressure of the scudding knife; certainly a great amount of the grease can be got away by its use.

Before leaving the consideration of drenching, attention should be drawn to the very necessary precaution to practice the most stringent cleanliness in the tanks or tubs used for the process. They should be most scrupulously scrubbed and washed to remove every trace, as far as possible, of any colonies of putrefactive bacteria. These are always present in minor quantities, but if not removed will multiply at an alarming rate, especially if thunder is prevalent in summer. The precaution and expense of cleansing the utensils is amply repaid by the good results ensuing, which omission has abundantly proved.

Many firms now pickle skins before tanning, after the plan adopted by the American tanners. There are some advantages in treating skins in this way, amongst which may be mentioned the possibility of holding back raw stock for a considerable time if desired. Reasons may arise demanding a given selection of skiver to be pushed forward in advance of others, and where large quantities are handled, pickling opens the way for holding back stock not required so quickly. The same reason applies to unsplit skins. Pickling roans and basils permits of better pressing to remove grease, as the skins may be selected into sizes.

Dr. Procter, who has made a special study of this process, gives most valuable information on the subject in several published reports and books. He recommends 1½ ounce of sulphuric acid as sufficient for 100 pounds of wet pelt, with salt added to saturation. This requires more time but less acid to accomplish the work. The pelts from the drench are often placed in a solution of ¼ to ⅓ per cent. of sulphuric acid in water, where they remain about twenty minutes, during which time they become much swollen. This is followed by a salt solution of specific gravity (1.065), for twenty minutes, then into a saturated salt solution for one hour. The goods may then be drained and packed away where water cannot reach them. Other acids may be used, but the expense is greater, and much more time is required.

A quarter per cent. of formic acid will swell the pelt, if given sufficient time, and has valuable antiseptic properties. The swollen pelt may then be placed in a saturated salt bath. The action of the acid is to cause the pelt to absorb water, as was mentioned of lime. This hunger for water gives a swollen effect, which is counteracted by the salt, which in turn causes the skin to discharge the water absorbed. As a result, the skin becomes somewhat tawed, like alum-dressed leather, and may be dried out. If staked while in a suitable condition, it produces a white leather, which is, however, readily damaged by coming in contact with water. On the other hand, water containing salt to saturation does not produce any ill effects on pickled stock, hence for degreasing by hydraulic pressure, pickled skins have advantages over non-pickled skins.

Roans which are sumach tanned to obtain as white a vegetable tannage as possible are pressed from the drenches. In this condition they are in a very slippery condition, and great care is needed to make a pile of eighteen to twenty-four skins in the press without the whole collapsing. The skins are taken out of warm water, and placed flesh to grain in a pile, a liberal use of white wood sawdust being necessary to give the grip to the skins to avoid sliding. A copper plate is placed over the pile, and another pile of skins is built upon this plate. This is repeated until the required number of piles are obtained to fill the press. Pumping follows to force up the ram, and thus exert the pressure on the skins.

The pumping is not continuous, or the forcing out at too rapid a rate of the water contained in the skins would utterly ruin them. The pressure must be exerted gradually, with rest given repeatedly, to allow the water time to escape. When this is attained, the full pressure of two tons or more per square inch may be given.

Warm water is now used freely to wash the grease from the edges of the skins, also from the plates. The grease is conducted into a sunken receptacle, from which it is recovered and used, being a valuable raw product for soap making.

With a pickled roan, the pelt is not of a slippery nature in the least, but will pile readily and safely without sawdust. It is necessary, however, to use not warm water only to steep the skins, but a bath saturated with salt, in which some undissolved salt remains at the bottom of the tub, as a precaution against the neglect, in making up the bath for fresh supplies of skins, of adding water without salt. In washing away the grease, the same saturated salt water must be used.

Basils which are bark-tanned are usually given a short course in the tan pits or paddles, which gives them a rougher and more modified non-slipping surface. If, in pressing, the pile slips over, it is fatal to a satisfactory result; even if the pile is rebuilt, it is not so effective in removing grease. In pressing, the surrounding atmosphere should be at a high temperature, so that the skins may retain their warmth. The grease is not effectively removed when it is cold in the pelt.

When pressed, the blocks of pelts are placed in warm water, which in a short time enables the skins to be separated without any damage to the grain. Pickled skins must, of course, be soaked in a salt bath saturated as before stated. The skins soon swell out and recover their normal appearance, but a half hour in a drum will expedite the process if needed.

The removal of grease from skivers results from scudding the splits on the flesh side out of the puer, and they are never pressed.

Tanned skins and skivers are now often submitted to the action of grease-free petrol, which dissolves the grease in the skin, and effects its removal. It is accomplished in sealed tanks to avoid loss of spirit, the leather being submerged for a few minutes. The saturated petrol is drawn off and a fresh supply run into the tanks. Usually this suffices to clear away the grease. The leather is afterwards—while still in the sealed tanks—submitted to warm air, which passes in turn through the still, and thus the petrol is recovered. The saturated petrol is also distilled, and both it and the grease are separated and recovered for use.

Grease is also removed by swelling the raw pelt with formic acid, much after the manner of pickling, but with the use of hyposulphite of soda in a saturated solution instead of common salt, at a temperature of 100° F. Time must be given, and no hurry exercised, to obtain good results. It is claimed to be sure and effective by Mr. A. Seymour Jones, who is a most reliable authority, and was the originator of this method.

Tanning now follows, and here again it is difficult to obtain exact quantities of tanning materials used. The skilled tanner will say that so much depends upon the skins, their size and substance and that only careful handling to avoid any waste is possible. The tanning of grains for skivers is effected with sumach, usually in paddles, at a temperature of about 100° F. In practice the grains are carefully put into the prepared liquor by hand, each one separately, and opened out in the liquor, so that contact is made with every portion of the skin. The paddles are put in motion for a time, and then allowed to rest an interval. The tanner relies largely upon keeping the tanning strength higher than the tannin absorbed by the pelts, and claims this to be the condition prevailing so long as the sumach floats in a thick crust on the surface of the liquor during the periods of rest. If the sumach settles to the bottom of the paddle it is exhausted, and should the grains not be tanned, additional sumach is added to the liquor.

Though it is asserted that the sumach is exhausted, yet the tanner will use this same sumach with the addition of a very small quantity of fresh sumach for the purpose of sumaching basils in a tumbler with satisfactory results. About twelve hours is needed to tan skivers, but the time is varied by the thickness of the raw grains. The heavy ones require more time, while the thin ones less. Salt is much used in preparing the tan liquor, more being required when the raw stock is in the pickled condition.

After tanning, the skivers are drawn through clean warm water to wash off the adhering sumach, horsed to drain for the night, and hung up in the drying sheds next morning.

Fine ground sumach does not produce as white a tannage as the coarser, or half ground, but the finest particles of the former find their way into the fibrous construction of the skin during tanning, and give additional body and substance to the leather. The addition of salt may improve the color, but it certainly retards the drying, while by attracting the moisture from the atmosphere, it prevents the leather becoming hard or flinty. In the subsequent processes of dyeing, the salt is washed out.

Roans, after pressing and regaining the normal condition by treatment in water, or salt and water, are sewn into bags by machinery, each skin forming a bag. An opening is left where the two hind shanks meet, for the purpose of filling the bag with tan liquor. The liquor in the tan tub consists of sumach and water, and when used continuously will last for months. The practice followed is to make a strong liquor to commence operations, and to add sumach as required to keep up the strength. The skins, by inserting a funnel in the shank opening, and dipping below the surface of the liquid, are filled with liquor, the opening then being securely tied. In the first filling, about 3 pounds of dry sumach is put inside the skin bag. This prevents too rapid escape of tan liquor. The filled skin bags are placed in pile, and submitted to gentle pressure, during which the tan liquor penetrates the pelt, and escapes back into the tub exhausted. The bags are refilled again and again as needed, until at the end of the day leather is attained. The bags are opened, the loose sumach shaken out, and the skins usually thrown into a tan liquor for a few hours, then drained and dried.

Care is taken to always retain some sumach floating on the surface of the liquor in use, while with a suitable copper scoop the sumach is removed from the bottom of the tub. By this means the efficiency of the liquor may be retained for a long time to advantage, as a new liquor does not produce a leather so kind in handling as a carefully preserved older one. The formation of gallo-tannic acid in the liquor is to be guarded against, as this produces a darker color, which is not desired.

Basils are tanned in bark liquors or those made from tanning extracts. From the drench or pickle they enter a weak or sour tan liquor, with or without salt addition, depending on stock to be tanned. This is to obtain a level color as a start, and paddles are used to supply the required movement of the skins. Cold liquors are used, and the operation is much slower than the sumach one. Gambier enters largely into the tanning liquors, being added in solution as required, its use being more liberal as the end of the tanning stage approaches. The harsh feel and heavy color it imparts to the stock may be rectified by tumbling the goods afterwards in sumach liquor for half to one hour, or giving a sumach liquor in a pit for a day. Where sumach is not to be used, caution is required in the use of gambier, especially to see that it is dissolved before use.

Quebracho bark or extract is a valuable tanning material for basil work, producing a very mellow leather after sumaching. Should the red color be an objection, this may be very largely corrected by using myrobalan powder or extract in conjunction with quebracho. Some tanners prefer this method to using the de-colorized extract. So much depends upon the uses to which the basils are to be put, that the tannins used have to be selected to produce the color required.

Roller leather is required almost the color given by oak bark, which is principally used to produce this leather. In the finishing processes, a little color is added to the seasoning to give a shade to meet the fancy of the purchaser. If goods are to be dyed, it is advisable to get a regular clean color prevailing always, as this aids the production of good even colors. The time needed for tanning is usually three weeks to obtain a solid leather. Undue hurry produces a spongy leather, more like the sumach-tanned roan, and this is as a rule not the aim desired in bark or extract tanning.

THE EXAMINATION OF LOGWOOD.*

A Comprehensive Investigation of the Most Important of the Natural Dyewoods—Its Present Claims to Consideration—Analyses for Composition and Tests for Coloring Qualities under Variable Conditions.

The natural dyestuffs have long been forced to a position of secondary importance by the growth and development of the artificial colors. This has been accomplished not only by the invention of colors cheaper, more brilliant, faster, and more easily applied than the natural products, but a still more radical competition,—the artificial synthesis of the natural coloring principles themselves. Thus synthetic indigo and alizarine have been made more cunningly than in Nature's workshop, and the culture of the indigo plant and of madder seemed doomed to abandonment.

Logwood similarly suffered by the competition of artificial colors and, while their merits were not sufficient to urge a synthetic reproduction of its coloring principles, substitutes superior in many ways gradually restricted its use, faster acid colors reduced its importance as a wool and silk dye, and the sulphur colors replaced it largely in its application to the cotton fibers.

With the advent of the War, however, and the consequent dearth of synthetic colors, logwood recovered some of its quondam importance. Easily the leader among the natural dyewoods, it again competed with the artificial products. A product of the Western World, it was continuously available at our ports when rival products failed and the sharp stimulus of the War gave the logwood industry a hectic flush of health that must last until the native production of its substitutes equals the former imports.

SURFACE EVIDENCES OF ADAPTABILITY.

The crude wood as imported from Yucatan, Honduras, Jamaica, Domingo, or whatever source, gives hint, even on a general inspection, of its adaptability for dyeing purposes. A freshly cut surface should appear fresh and reddish. If the aspect is dull and gray the wood will yield little extract of value. Medium sized logs are richer in color extract than logs of extreme thickness or thinness. While mere observation can only be offered an approximate idea of the value of the wood, it is sufficient to surely distinguish the good from the bad logs. An exact estimation of the value of the wood can only be obtained after an extraction of it, or a decoction of the fermented material, for the wood in the original form has little color value. An extraction of a section of the wood is very slow and difficult, but if the wood be cut, rasped and then fermented the fermenting liquor extracts evenly and completely the coloring power of the material. Once the extract is obtained we are sure of having a mixture of a homogeneous character to examine.

In logwood the coloring matter exists as a glucoside of a constitution not yet fully established, and the process of fermentation splits up this into a sugarlike body and haematoxyline. This latter the source of the coloring power of logwood, is converted by the oxidizing effect of the fermentation to a second coloring matter, Haemateine, and this latter in turn, if the fermentation is not kept well under control, will be lost by conversion into humus bodies of no color power. The value of the fermented wood or of the extract is therefore immediately dependent on its amount of haematoxyline and haemateine, and its freedom from products of too prolonged an oxidation.

FACTORS IN DETERMINING VALUE.

The factors which determine the worth of a logwood extract are: color content, addition of foreign tanning or coloring matter, loading material, fermentation and reaction. Naturally the most important factor is the color content, and comparative dye trials only can afford an exact and definite estimate of the worth of a dyewood sample, but these test dyeings must be made with the utmost care and demand an intelligent comprehension of the peculiar and mixed nature of the logwood coloring matters.

Besides the test dyeing methods for arriving at the value of a

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* *Color Trade Journal*, October, 1917.

logwood extract certain colorimetric methods have been advanced in which the intensity of the color of the diluted extract serves as a measure of the dyeing power. In one of these methods ten grams of the aged wood, or a corresponding quantity of extract, are digested in alcohol and diluted with this solvent to one liter. Ten cubic centimeters of this solution are diluted with alcohol to 100 cubic centimeters and of this dilute solution 5 cubic centimeters are withdrawn and placed in a 50 cubic centimeter Nessler's tube or graduated cylinder treated with 5 cubic centimeters of a 1 per cent. alum solution and diluted to the mark. The color which gradually develops is compared under similar conditions with that produced from a sample of logwood of standard color value, using more or less of the standard material until the shades coincide in strength. The relative color power as compared with the standard can then be expressed.

Another colorimetric method is based on the reaction between logwood and copper salts. It is only approximate, but is quite rapid. A standard logwood solution is prepared from an extract of known strength containing 1/10 per cent. of the dried extract. 1 cubic centimeter of such a solution is placed in a test tube with 1 cubic centimeter of a 0.2 per cent. copper sulphate solution and 10 cubic centimeters of water. A little precipitated chalk is added and the glass shaken. The mixture is quickly brought to a boil, poured into a 100 cubic centimeter cylinder and diluted to the mark. The extract under test is similarly treated and carefully diluted in the 100 cubic centimeter cylinder until its depth of color matches that of the standard. The color is fugitive, lasting only from 10 to 15 minutes, so that the comparisons must be promptly made.

The water content of the wood or extract is determined by dehydrating a weighed portion of two samples at 105°-110° C. until constant weight. Owing to the slow drying of some adulterated samples of liquid extracts it is well to incorporate the sample with about an equal weight of pure ignited sand, to aid the exit of water by making the dried product more porous.

The normal ash of logwood contains chloride and phosphates of the alkalies. The quantity of ash is often an important proof of adulteration. It is determined by igniting a small sample of the wood or extract in a porcelain crucible at a low, red heat. The wood should not have more than 2 per cent. of ash, the extract not more than 3 per cent. Mineral adulterants, indicated in a higher ash, are alkalies which are added to promote a prompter oxidation. Common salt may be also looked for. Other adulterants, such as sand, clay and sawdust, remain undissolved in making up an aqueous solution, and they may be filtered off and weighed.

The addition of molasses may be detected and estimated by the addition of yeast to the solution of the extract, followed by fermentation, distillation and weighing of the resulting alcohol. Molasses and dextrine may be determined in the following manner: From 3 to 5 grams of the extract are dissolved in 50 cubic centimeters of water, 10 cubic centimeters of lead acetate added to precipitate the haematine and haematoxyline, then the mixture, diluted to definite volume, is well shaken, and after standing a short time is filtered through a dry filter. A definite fraction of the filtrate is polarized in a 100 cubic centimeter tube. Pure extracts do not, or only slightly, turn the plane of polarization, but never to the right.

For a quantitative estimation of the sugar content the entire filtrate is treated with hydrochloric acid until the lead is thrown down as chloride and there remains about ½ cubic centimeter of acid in excess. The mixture is heated for ½ hour in a flask provided with a reflux condenser and then cooled. Soda is then added to neutral reaction, the mixture filtered, and the sugar in the filtrate estimated grammetrically or volumetrically by Fehling's solution. For analyses of this character the haematoxyline and haematine may also be removed by hide-powder instead of lead acetate. Ten grams. of the extract are dissloved in a liter, warmed to 50° C. and a definite fractional portion treated with hide-powder by the digestion or filtration method. Any tannin matter present is also fixed by the hide-powder, and in the clear colorless liquid adulteration with sugar, molasses, starch, or salts may be readily proven. 100 cubic centimeters of the original solution, before treatment with the hide-powder, and 100 cubic centimeters of the filtrate after the hide-powder treatment, and carefully evaporated at 100° C. to constant weight. The first equals the total extract; the second—the evaporated filtrate—

gives the impurities. The difference between 1 and 2 gives the combined color and tanning matters removed by the hide. The hide-powder must be free from extractive matter, as these would be attributed in the analysis to the logwood.

Chestnut extract is one of the commonest adulterants of logwood, and it is rather difficult to detect its addition and that of other tannin matters. The poor solubility of chestnut extract in ether as compared with the high solubility of logwood is the basis of a method of detection and estimation. Pure dry logwood extract contains 87 per cent. of ether-solubles and 13 per cent. of alcohol-solubles. Chestnut extract being almost insoluble in ether and quite easily soluble in alcohol, any serious departure on analysis from these numbers points to adulteration by chestnut extract. Thus logwood containing 50 per cent. adulteration by chestnut extract would only show an extractive by ether of about 44 per cent.

COMBINED METHOD FOR DETECTING ADULTERATION.

Following is a combined method for the determination of gelatine, molasses and chestnut extract. Gelatine is indicated by a high nitrogen figure. Pure vacuum dried extracts run about 0.8 per cent. Nitrogen is determined by Kjeldahl's method. An aqueous solution of the extract is made, gently warmed and digested with gradual additions of coarse bone-black until the color of the logwood disappears. The solution is then filtered. Chestnut extract is proved present if there is considerable difficulty encountered in discharging the color of the solution. If the almost colorless extract gives at once a considerable precipitate on treatment with Fehling's solution chestnut extract is further proved. If the filtrate gives little reaction with Fehling's solution, but after inversion with hydrochloric acid, as in the former test, gives a decided precipitate, then the extract has been adulterated with molasses. If the nitrogen figure is above 1 per cent. adulteration with gelatine is probable.

Gross adulterations with this material above 8 per cent. can be detected as follows: From 3 to 4 grms. of the powdered dry extract are extracted two or three times with 95 per cent, alcohol at the ordinary temperature. The undissolved residue is taken up in warm water and precipitated with an excess of lead acetate solution. The blue precipitate formed is filtered off and in the filtrate the excess of lead acetate is brought down by the addition of soda. The lead is filtered off and the final filtrate which now contains gelatine is treated with a solution of tannin. If gelatine be present a precipitate or distinct turbidity develops.

Another method for the detection of tannin materials, such as chestnut extract, is as follows: A ½ per cent. solution of dry extract, or a corresponding strength of the liquid extract, is treated with 1/3 its volume of yellow ammonium sulphide. With pure extracts the solution darkens and a slight brown flocculent precipitate develops. With tannin-bearing extracts the solution becomes lighter and a heavy bright gray milky precipitate develops. With 1/10 per cent. solution of pure logwood only a slight dark turbidity develops, while with tannin adulterants a bright strong turbidity appears, which in a short time gathers in large, bright flocks.

As above said the most reliable method for testing logwood is by comparative dye trials, but these must be conducted in the most precise manner and with a special direction to using such a character and proportion of mordant as shall best develop the virtue of the logwood under test. The best recipe for dyeing one sample of logwood may spoil utterly another sample, and unless two samples are known to be of the same batch of logwood, and to differ only in dilution, they can never be properly compared by dyeing them by a similar formula.

As the prospective investigator has seldom this information about two extracts it will be seen that the comparative dyeing of logwood samples differs wholly from that of any artificial dyestuff. This is for the reason that in dyeing logwood some of the color already exists, and some of it is made in the bath by the mordanting, and the proportion of color that already exists and that which requires making may differ materially in two logwood samples. The problem is further complicated by the fact that the very assistants which develop the color which requires making in the bath are apt to spoil by overoxidation the color which exists already made.

In the analysis of a logwood extract two equally important questions must be decided, *viz.*, how much color value has the material, and in what form and degree of oxidation are the coloring matters present? The wood and extract contains varying proportions of haematoxyline and haemateine, and so we may have extracts rich in the one and poor in the other. We may have extracts yielding excellent results when dyed by appropriate recipes and well adapted to one class of fibers, but which are of little value when applied in a varying way or upon a different fiber.

The relation of haematoxyline to haemateine may be compared to yellow and red prussiate of potash. The former yields a heavy blue precipitate when combined with iron salts in a high state of oxidation, while the latter gives a similar heavy blue precipitate when combined with iron salts of no oxidizing power. Thus haematoxyline forms a color lake with oxidizing metallic salts such as ferric oxide, cupric oxide, chromic acid, etc., while haemateine requires no oxidizing action to develop its color lake and combines directly with metallic salts of no oxidizing power, such as alumina, ferrous oxide and chromic oxide.

The reaction between haematoxyline and oxidizing metal salts takes place in two phases. The metallic oxidizing compound oxidizes first the haematoxyline to haemateine, and is itself reduced to a metallic salt or oxide of no further oxidizing power. Then the second phase of the reaction sets in and the haemateine formed combines with the metallic oxide to form a lake. Thus the haemateine is indirectly the dyestuff, while the haematoxyline may be regarded as the leucobase, such as reduced indigo, needing only oxygen for its development. It is essential that these relations be exactly understood before we can make clear the functions of these two products of different degrees of oxidation in their mode of combining with various mordants.

We have then four variables in logwood dyeing, viz., haematoxyline, which must first be converted by oxidation to haemateine and then fixed by a metal mordant; haemateine, ready for fixation, needing no oxidation and damaged by conversion to brown oxidation products; metallic mordants, oxidizing in character; and finally metallic mordants not oxidizing. These variables are shown in the following scheme:

$$\begin{array}{r}\text{brown, overoxidized,}\\ \text{color overdeveloped}\end{array}\left\{\underbrace{\overbrace{\begin{array}{c|c}\text{oxygen} & \text{haematoxyline}\\ \hline \text{haemateine} & \begin{array}{c}\text{non-oxidizing}\\ \text{metallic salts}\end{array}\end{array}}^{\text{haemateine}}}_{\text{black}}\right\}\begin{array}{l}\text{underoxidized,}\\ \text{color underdeveloped}\end{array}$$

A mixture of haematoxyline and haemateine when acted upon by an oxidizing metallic mordant such as chromic acid, first has its haematoxyline oxidized to haemateine, which then combines with the metallic oxide to form a lake. The haemateine reduces the chromic acid to a non-oxidizing chromic oxide, and in doing so is converted to brown oxidization products leading to a waste of color and often to a brownish bloom on the logwood black. The chromic oxide formed then combines with the remaining haemateine. The production of this waste brown body is the greater the more chromic acid is employed, or the larger the proportion of haemateine is in the sample. A different action takes place with a mixture of haematoxyline and haemateine when a non-oxidizing metallic salt is employed. Here the haemateine at once combines with the mordant while the haematoxyline is left useless in the bath except for such gradual slow oxidation as it can get from an excess which partially converts it into useful haemateine.

COMPLICATED FEATURES.

The proposition is most complicated when we have to do, as is usually the case, with mixtures of haematoxyline and haemateine in the presence of mixed mordants of an oxidizing and non-oxidizing character. Here, unless a properly devised balance is secured, some of the haemateine is overoxidized to brown oxidation products, affecting materially bloom and appearance of the black dye, or by underoxidation some unused haematoxyline remains in the bath.

It will thus be seen that the course of logwood dyeing is more complicated than is usually believed, and much trouble is encountered by not keeping clear this relation between the mordant and the dyestuff of logwood. Time and again complaints are made that a logwood is weak or yields a brownish black, while in reality the trouble is with the mordant either in its character or its disproportion to the coloring matter.

If a fermented wood is to be given a comparative dye trial it must first be quantitatively extracted. From 10 to 20 grms. of finely rasped average sample of the wood is repeatedly boiled in a porcelain dish with renewal of water until no color is further extracted. The combined decoctions are then diluted to a definite volume. Solid or liquid extracts are at once dissolved in water and made up to a mark. These solutions are then ready for test dyeing, following the principles above exposed.

TESTS FOR COLORING MATTER PRESENT.

If the test is to establish how much coloring matter is present, including both the haematoxyline and haematine, a mordant is selected which shall combine with and fix both of these. This from the nature of the case must be a mixed mordant, made up of an oxidizing metallic salt directed to the haematoxyline, and a non-oxidizing metallic salt directed to the haemateine. The use of an excess of oxidizing mordants can destroy by overoxidation the haemateine, while non-oxidizing mordants can do no positive damage. They do not, however, develop and fix a black color with haematoxyline. By dyeing the logwood sample on various mordants of oxidizing and non-oxidizing character, and observing which of these is best adapted to the development of the color, we have an important guide to the color strength of the sample when we compare it with a standard, and, moreover, we are able to note the proportion of haemateine and haematoxyline in the sample.

The test dyeings for this purpose shall be made on wool skeins which have been mordanted in 5 different ways.

(1)—Mordant with chrome and tartar, 1 : 2.
(2)—Mordant with chrome and lactic acid.
(3)—Mordant with chrome and sulphuric acid, 1 : 1/3.
(4)—Mordant with chromium fluoride and tartar, 1 : 1.
(5)—Mordant with alum and tartar, 3 : 2.

The first two mordantings fix on the fiber a mixture of chromic acid and chromium oxide. The third practically chromic acid only, for very little chromium oxide is formed from the reducing action of the fiber itself upon the chrome. The fourth and fifth precipitate only non-oxidizing mordants on the fiber. In the greater number of cases both haematoxyline and haemateine are formed in the logwood and hence the mixed mordants of either recipe 1 or 2 above are best adapted. In cases where haemateine strongly predominates, the mordanting recipe 1 can be combined with 4 or 5. Where haematoxyline is in excess recipe 1 and 3 can be combined.

Weaker Trial Dyeings Advisable.

In test dyeings of this character comparisons are best made with weaker dyeings, and thus it is not well to employ the strong percentages of mordants such as are actually used in practice, while in dyeing black in the large way 3 per cent. of chrome is used it is best for the weak shades appropriate for these dye trials to use the above recommended weak bath of 1 per cent. chrome and 2 per cent. tartar. With samples containing a very great proportion of haemateine, ½ per cent. chrome, 3 per cent. alum and 3 per cent. tartar, or ½ per cent. chrome, 2 per cent. chromium fluoride and 3 per cent. tartar, may be employed instead of the larger percentage of chromium. The first of these weaker mordants yields a lighter ground and thus facilitates comparisons of weak dyeings. Before the final test dyeings an approximate qualitative dye trial can be made on wool mordanted with 6 per cent. of alum and 4 per cent. of tartar. On this bottom haematoxyline scarcely yields any tints and some conclusion can be gotten of the quantity of the haemateine present. The trials should be made with dyeings of a definite strength, between 5 per cent. and 10 per cent., reckoned on wood, 1 per cent. to 2 per cent. reckoned on the dry extract, and 2 per cent. to 5 per cent. on the liquid extract, varying with the strength of the sample. The dyeings should all be conducted under similar conditions of time and temperature. The better the exhaustion of the bath the more reliable is the test as exhibiting the full virtues of the sample. If the bath after dyeing shows a strong brown color we can conclude that over-oxidation has attacked the haemateine and that the mordant was a faulty one for the product.

If the results of the dyeings on the five different mordants above given are compared we will be able to discover in what form the coloring matter exists in the logwood sample under test, and consequently whether it is adapted for a certain purpose, keeping in mind the principles earlier laid down, and the fact that haematoxyline does not react with non-oxidizing mordants. The weak dyeings made on the mordants 4 and 5 in the foregoing are to be compared with similar ones made with pure haemateine or with haemateine extract of known strength. A good idea of the composition of the sample under test is thus gotten by comparison, and the haemateine content can be definitely determined by matching up to the standard.

The question then remains, whether haematoxyline is present, and in what amount. This is answered by the dyeings in the mixed mordants 1 and 2 which have developed coloring matter. The difference between the dyeings on the two orders of mordants, the comparison of 1 and 4 gives the haematoxyline content. In this manner can both the constituents of logwood be determined and the availability of the logwood for different fibers, or methods of dyeing or mordanting be established.

By Inductive Analysis.

The following inductive method of arriving at the proportion of haematoxyline and haemateine in a logwood extract has found much favor, although it is somewhat troublesome, but, from the mixed nature of the extract, there can be few short methods. In this method about to be described solutions of known proportions of the two coloring matters of logwood are prepared, and these being used as standards are compared in their dyeings with those made on samples under test. The following are the normal solutions to be prepared, the weights indicated being made up to the liter so that each 20 cubic centimeters of the solution corresponds to 1 per cent. on a gm. skein.

(1)—5 gm. 51° Tw. Ext. wholly consisting of haematoxyline.
(2)—5 gm. 51° Tw. Ext. wholly consisting of haemateine.
(3)—5 gm. 51° Tw. Ext. containing ½ haematoxyline and ½ haemateine.
(4)—5 gm. 51° Tw. Ext. containing 80 per cent. haematoxyline and 20 per cent. Tannin (Sumach).
(5)—5 gm. 51° Tw. Ext. containing haematoxyline with ½ per cent. chalk.

First Test:—Five 10 gram skeins of wool are mordanted with 3 per cent. chrome and 5 per cent. of tartar, yielding a mordant of a somewhat oxidizing character, and each of these skeins thus bottomed is dyed in one of the above solutions, using 140 cubic centimeters or 7 per cent. of the extract diluting to 400 cubic centimeters and dyeing for 1½ hours. The dyeings show the following results:

1—The bluish shade of haematoxyline.
2—Much darker, approaching a black.
3—Between 1 and 2.
4—Weaker than any of the above.
5—Darker than 1, the chalk favoring oxidation.

These tests show that oxidized extracts yield a darker color than the un-oxidized, and that extracts reduced with tannin give weaker dyeings.

Second Test:—Five 10 gram skeins of wool are mordanted with 10 per cent. alum, 2½ per cent. chrome, 2½ per cent. bluestone and 2½ per cent. tartar. The mordanting is kept up for 2 hours and after washing well the goods are dyed as in the first test, with the five separate extracts, but only 3 per cent. of the extracts are used,—60 cubic centimeters of the dilute solution. On comparison Number 1 with pure haematoxyline is now found the best of the series; 2, 3 and 5 are brighter than 1; while 4 is weaker than 1. If a non-oxidized extract is desired one should be selected which most conforms to the behavior of No. 1 in the two sets of tests given. If an oxidized extract is wanted such a one should be chosen as shall give the darkest color, as does the haemateine in the first test.

Third Test (for cotton):—Six skeins of 8 grams each are well boiled out and dyed respectively in the following solutions, the quantities indicated being diluted as above to one liter:

(1)—5 gm. 51° Tw. Ext. wholly consisting of haematoxyline.
(2)—5 gm. 51° Tw. Ext. wholly consisting of haemateine.
(3)—Solution 2 reduced with 20 per cent. water.
(4)—5 gm. 51° Tw. Ext. containing 80 per cent haematoxyline and 20 per cent. tannin (sumach).
(5)—Solution 4 just neutralized with chalk.
(6)—5 gm. 51°Tw. Ext. containing haematoxyline with ½ per cent chalk.

The skeins are entered in their respective baths containing 100 cubic centimeters of extract solution and 300 cubic centimeters of water at 60° to 80° C. and left to cool slowly in the bath for from 1 to 2 hours. They are then wrung out and worked for from 4 to

5 minutes in a bluestone bath containing 3 per cent. on the weight of the cotton. Such dyeings show results as follows:

1—Shows the gray tone of haematoxyline.
2—Darker than 1.
3—Rather dark gray, darker than 1.
4—Quite weak, tannin hinders dyeing logwood on cotton.
5—Darker than 4 but not up to 1.
6—Darker than 1, lighter than 2 or 3.

Extracts which contain tannin are recognized by their reddish gray tone. By comparison of these three series of tests it is easy to say how a product approaches any of these types in composition. It is somewhat difficult to make these pure types of haemateine and haematoxyline for one's self, but they can usually be procured. Comparisons can be quickly made of the relative oxidation of extracts by the use of cotton goods on which mordants of varying character have been printed.

How to Make a Quick Test.

For a quick test for fermented and unfermented extracts, and for tannin additions, the following is recommended. Extracts of about 1° Tw. are treated with stannic chloride. Strongly fermented extracts give a dark brown precipitate, weakly fermented extracts a light violet precipitate, while tannin bearing extracts give a dirty or yellowish precipitate. Neutral extracts are deep red, alkaline are violet, and acid extracts are light yellow, when weakly fermented and orange yellow when strongly fermented.—*J. H.*

A UNIFORM DYE TESTING APPARATUS.

Arthur M. Reeves.

After noting the report of the Committee on Dyestuffs in the June issue of the Journal, I thought I could offer a few suggestions on dye testing. My vocation is the testing of textile dyestuffs, but these suggestions are applicable to leather testing as well.

The drawings (see pages 600 and 601) are for an apparatus that will make uniform dyeings at a uniform temperature. One pint E-Z type glass jars can be substituted for my idea of a jar. The temperature of the bath can be regulated quite easily by the addition of salt petre to the water used in the bath. The rotation of the shaft will keep the sample well supplied with the dye solution.

Dyeings can be made to show less than 5 per cent. difference by making exhaust dyeings in the liquor remaining in the dye bath. A comparison made between two exhaust dyeings will reveal much.

The testing of dyes should be made at a less percentage than that at which the color is actually used. In using the method stated in the report*, one should dissolve one gram of the dye in two liters of water and use the same volume. This can be easily worked out at any definite temperature.

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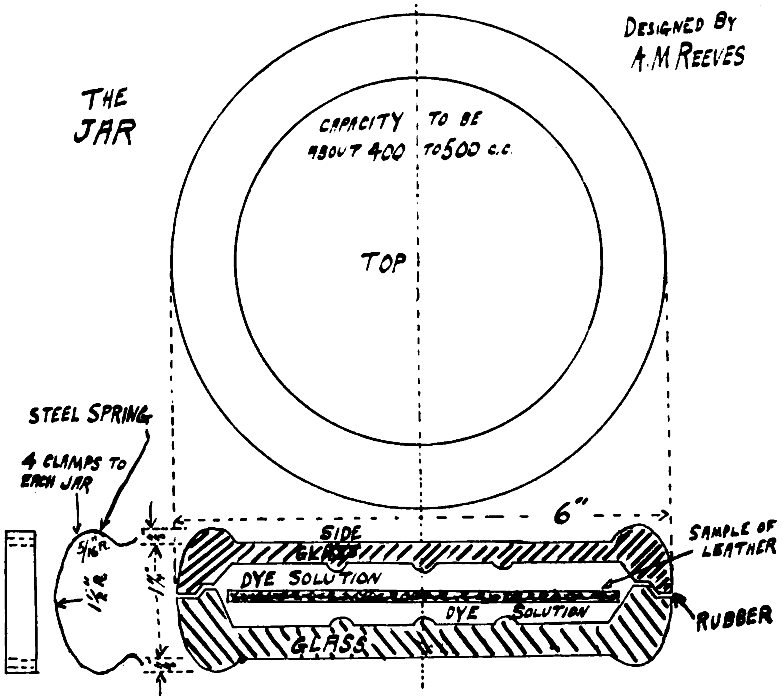
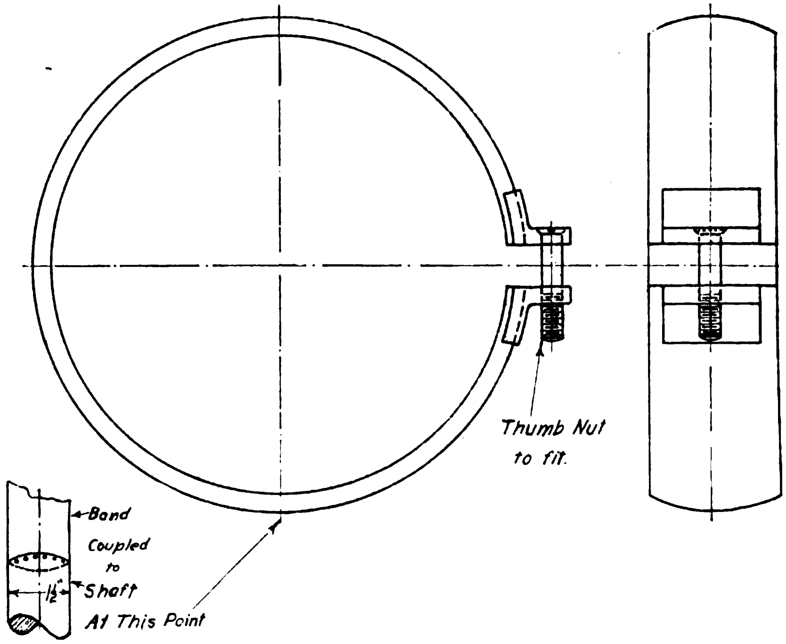
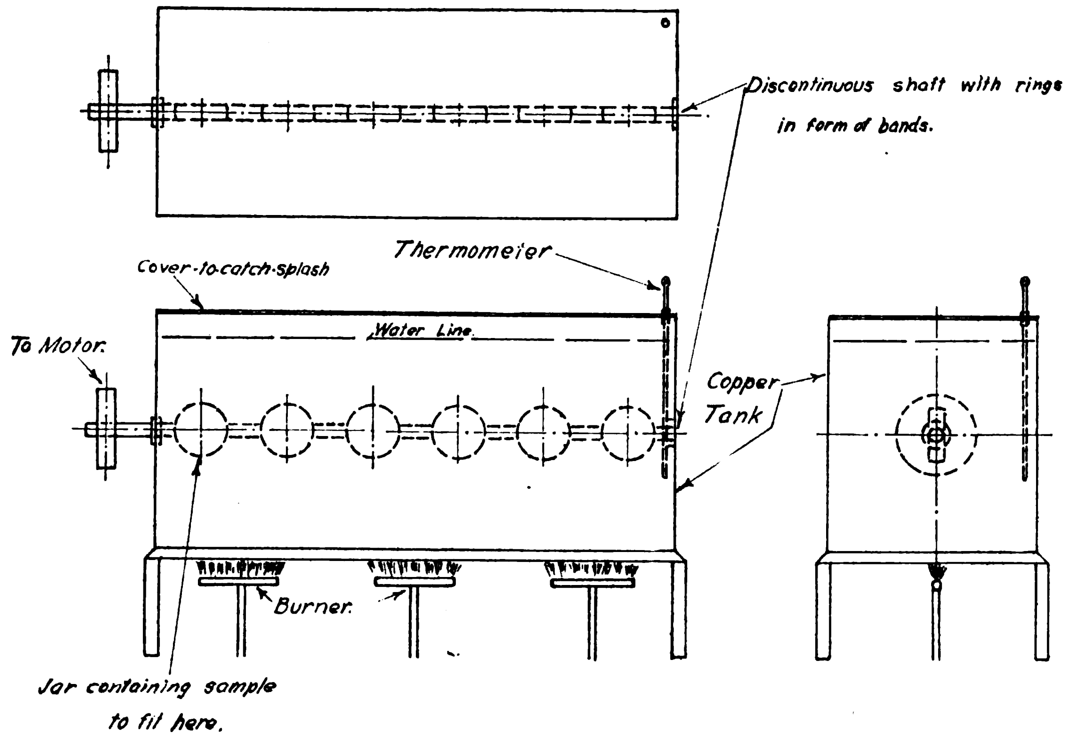
* This J., July, 1917, page 279.



Method to Fasten Jars in Ring Bands.





APPARATUS FOR MAKING UNIFORM DYEINGS ON LEATHER SAMPLES AT UNIFORM TEMPERATURE.

REPORT OF COMMITTEE ON SEWERAGE AND SEWAGE DISPOSAL.*

Sanitary Engineering Section, American Public Health Association.

The Committee on Sewerage and Sewage Disposal presented a report at the Annual Meeting of the Sanitary Engineering Section of the American Public Health Association held in Cincinnati on October 26, 1916, suggesting definitions for the terms used in sewerage and sewage disposal practice.

This was intended as a progress report and a full discussion of the definitions was invited. A number of members of the Sanitary Engineering Section forwarded written discussions, and all endorsed the purpose of the committee to clearly define the terms used in sewerage and sewage disposal practice.

The committee has amended a number of the definitions contained in the report presented at the Cincinnati meeting in accordance with the weight which they thought should be given to the criticisms and suggestions received, and has prepared a revised report.

It is hoped that the definitions now presented may be generally acceptable to those engaged or interested in work of sewerage and sewage disposal, and that they will be helpful to the engineering profession.

We recommend that in reports, contracts and agreements prepared by engineers and health officers the terms defined in this report be used and be given the meanings designated herein.

DEFINITIONS OF TERMS USED IN SEWERAGE AND SEWAGE DISPOSAL PRACTICE.

SEWERAGE AND DRAINAGE.

1. SEWAGE

Sewage is a combination of the liquid wastes conducted away from residences, business buildings and institutions, together with those from industrial establishments; and with such ground, surface and storm water as may be present.

(*a*) *Domestic Sewage* is that from residences, business buildings or institutions.

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* *American Journal of Public Health*, Vol. VII, No. 10, 1917.

[1](*b*) *Industrial Wastes* are the liquid wastes resulting from the processes employed in industrial establishments.

2. DRAINAGE

(*a*) *Surface Water* is that portion of the precipitation which runs off over the surface of the ground.

(*b*) *Storm Water* is that portion of the precipitation which runs off over the surface during a storm and for such a short period following a storm as the flow exceeds the normal or ordinary run-off.

(*c*) *Ground Water* is that which is standing in, or passing through, the ground.

3. SEWER

A Sewer is a conduit for carrying off sewage.

(*a*) *A Common Sewer* is a sewer in which all abuttors have equal rights of entrance and use.

(*b*) *A House Connection* is a pipe leading from a building to a common sewer.

(*c*) *A Lateral Sewer* is a sewer which does not receive the sewage from any other common sewer.

[2](*d*) *A Sub-main or Branch Sewer* is a sewer into which the sewage from two or more lateral sewers is discharged.

(*e*) *A Main or Trunk Sewer* is a sewer into which the sewage from two or more sub-main sewers is discharged.

(*f*) *An Outfall Sewer* is a sewer extending from the lower end of the collecting system to the point of final discharge into a body of water, or to a sewage treatment plant.

[3](*g*) *A Separate*[2] *Sewer* is a sewer intended to receive domestic sewage and industrial wastes without the admixture of surface or storm water.

(*h*) *A Combined Sewer* is a sewer intended to receive domestic sewage, industrial wastes and surface and storm water.

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[1] In the opinion of the committee, the term "Industrial Wastes" is preferable to "Trade Wastes."

[2] The committee is of the opinion that preference should be given to the term "Sub-main Sewer" rather than to "Branch Sewer."

[3] In the opinion of the committee the use of the term "Separate Sewer" is preferable to "Sanitary Sewer," which latter term should be discontinued.

(*i*) *An Intercepting Sewer* is a sewer generally laid transversely to the general sewer system to intercept all the sewage collected by the sewers of a separate system or the dry weather flow of sewage and such additional surface and storm water as may be determined from a combined system.

(*j*) *A Relief Sewer* is a sewer designed to carry a portion of the flow from a district already provided with sewers of insufficient capacity, and thus prevent overtaxing the latter.

(*k*) *A Storm Water Overflow Sewer* is a sewer designed to carry the excess over a certain volume of combined sewage from a main or intercepting sewer to an independent outlet.

4. DRAIN

A Drain is a conduit for carrying off storm water, surface water, sub-soil or ground water.

(*a*) *A Storm Drain* is a conduit for carrying off surface and storm water.

(*b*) *A Land Drain* is a conduit for carrying off sub-soil or ground water, and for draining land.

5. SEWER SYSTEM

A Sewer System is the collecting system of sewers and appurtenances, together with such small pumping stations as may be required to lift the sewage from low-level districts.

(*a*) *A Combined System* is a system of combined sewers.

(*b*) *A Separate System* is a system of separate sewers.

6. SEWERAGE WORKS

Sewerage Works comprise the sewer system, main pumping stations, treatment works, means of disposal of effluent and sludge, and all other works necessary to complete the collection, treatment and disposal of the sewage.

7. SEWER APPURTENANCES[4]

(*a*) *A Manhole* is a shaft, or chamber, leading from the surface of the ground to the sewer, large enough to enable a man to gain access to the latter.

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[4] **Drain-structures similar to those defined under sewer, sewer-system, sewerage works, and sewer appurtenances are to have like names and definitions.**

(*b*) *A Lamphole* is a small vertical pipe or shaft leading from the surface of the ground to the sewer, for admitting a lantern or reflected light for purposes of inspection.

(*c*) *A Wellhole or Drop Manhole* is a vertical shaft in which sewage is allowed to fall from one sewer to another at a lower level.

(*d*) *An Inlet* is a connection between the surface of the ground and a combined sewer or drain for the admission of surface or storm water.

(*e*) *A Catch Basin* is a chamber inserted in an inlet to prevent the admission of grit and other coarse material into the sewer or conduit.

(*f*) *A Flush Tank* is a tank in which water or sewage is accumulated to be quickly discharged later, for the purpose of flushing the sewer.

(*g*) *A Regulator* is a device for controlling the quantity of sewage admitted to an intercepting sewer.

(*h*) *An Outlet* is the end of a sewer or drain from which its contents are finally discharged.

(*i*) *A Storm Overflow* is a weir, orifice or other device for permitting the discharge from a combined sewer of that portion of the storm flow in excess of that which the sewer is designed to carry.

SEWAGE DISPOSAL.

8. GENERAL TERMS

(*a*) *Sewage Disposal* is a generic term applied to the act of disposing of sewage by any method.

[5](*b*) *Sewage Treatment* is the process to which sewage is subjected in order to partially remove its impurities or so change them as to render the effluent fit for final discharge.

(*c*) *Contamination* is the introduction into a water of bacteria or other substances which tend to render it unsuitable for domestic use.

(*d*) *Pollution* is the introduction into a water of substances of such character and in such quantity that they tend to render the body of water or river objectionable in appearance, or to cause it to give off objectionable odors.

[5] The term "Sewage Purification" should be abandoned.

(*e*) *Influent* is sewage, or partially treated sewage, flowing into any sewage treatment device.

(*f*) *Effluent* is partially or completely treated sewage flowing out of any sewage treatment device.

(*g*) *Putrescibility* is the susceptibility of sewage, effluent, or wet sludge, to putrefaction under the conditions to which it is subjected.

(*h*) *Stability* is the capability of sewage or effluent to resist putrefaction under the conditions to which it is subjected.

(*i*) *Relative Stability* is the ratio of available oxygen to the oxygen required to prevent putrefaction, expressed in per cent.

(*j*) *Suspended Solids* are those which are removed from sewage or effluent by standard laboratory methods of filtration.

(*k*) *Settling Solids* are those suspended matters which will subside in quiescent sewage in two hours.

(*l*) *Clarification* is a relative term denoting the partial removal of suspended and colloidal matter by straining, sedimentation, or by coagulation and sedimentation.

(*m*) *Colloidal Matter* (conveniently defined) is the suspended matter which is so finely divided that it will not subside in two hours, yet will not pass through a parchment membrane in the ordinary process of dialysis.

9. SCREENING

Screens. A screen is a device containing openings of proper size to retain a part of the suspended matter of sewage.

(*a*) *A Coarse Screen* is one having openings in excess of one inch in least dimension.

(*b*) *A Fine Screen* is one having openings of one-fourth inch, or less, in least dimension.

(*c*) *A Medium Screen* is one having openings intermediate between a coarse screen and a fine screen.

(*d*) *A Bar Screen* is one composed of parallel bars or rods.

(*e*) *A Mesh Screen* is one composed of a fabric, usually of wire.

(*f*) *A Grating* consists of two sets of parallel bars in the same plane, the sets intersecting at right angles.

(*g*) *A Band Screen* is one consisting of an endless band or belt of wire mesh or other screening material which passes over upper and lower rollers.

(*h*) *A Wing Screen* is one having radial or curved vanes, usually composed of uniformly spaced bars, which rotate on a horizontal axis.

(*i*) *A Drum Screen* is one in the form of a cylinder or cone, consisting of perforated plates or a wire mesh which rotates on an approximately horizontal axis.

(*j*) *A Disc Screen* consists of a rotating circular perforated disc, with or without a concentric truncated cone of similar material.

(*k*) *A Cage Screen* consists of a cage, usually with sides of parallel bars or rods, so arranged that it may be lowered into the sewage and raised therefrom for cleaning.

10. TANK TREATMENT

Tank Treatment is the detention of sewage or sewage sludge in tanks, either quiescent or with continuous flow.

(*a*) *A Grit Chamber* is a chamber or enlarged channel in which the cross-section is so designed that the velocity is such that only heavy solids, such as grit and sand, are deposited, while the lighter organic solids are carried forward in suspension.

(*b*) *A Sedimentation Tank* is a tank for the partial removal of suspended matter either by quiescent settlement or by continuous flow at such a velocity and time of retention as to allow deposition of suspended matter.

(*c*) *A Dortmund Tank* is a vertical sedimentation tank, usually cylindrical above and with a conical or hopper-shaped bottom, into which the sewage or partially treated sewage is introduced near the center and after rising through the tank passes out at the surface —the sludge being drawn off, without emptying the tank, before it becomes septic.

(*d*) *A Hydrolytic Tank* is a sedimentation tank in which by biological processes a portion of the suspended matter is converted into liquid and gaseous form.

(*e*) *A Septic Tank* is a horizontal, continuous-flow, one-story hydrolytic tank in which the suspended matter is retained until anaërobic decomposition is to a considerable extent effected.

(*f*) *A Travis Tank* is a two-story hydrolytic tank consisting of an upper, or sedimentation chamber, with steeply sloping bottom, terminating in one or more slots through which the solids may slide as deposited into the lower or sludge digestion chamber, through which a predetermined portion of the sewage is allowed to pass for the purpose of seeding and maintaining bacterial life in the sludge and carrying away decomposition products, thus inducing digestion of the sludge attended by its reduction in volume.

(*g*) *An Imhoff Tank* is a two-story hydrolytic tank, consisting of an upper, or sedimentation chamber, with steeply sloping bottom, terminating in one or more slots through which the solids may slide as deposited into the lower or sludge digestion chamber—these slots being trapped so as to prevent the rise of gas and solids from the lower chamber—the lower chamber being provided with vents for the escape of the gases, the tank being so constructed as to facilitate the passage of the sewage quickly through the upper chamber and prevent the flow of sewage through the digestion chamber, and intended to be so operated that the sludge may be thoroughly decomposed, rendered practically free from offensive odor and so filled with gas that it can be readily drawn off and dried.

(*h*) *Activated Sludge Process* is the agitation of a mixture of sewage with about 15 per cent. or more of its volume of biologically active liquid sludge in the presence of ample atmospheric oxygen, for a sufficient period of time at least to coagulate a large proportion of the colloidal substances, followed by sedimentation adequate for the subsidence of the sludge flocculi; the activated sludge having been previously produced by aëration of successive portions of sewage and maintained in its active condition by adequate aëration by itself or in contact with sewage.

(*i*) *Chemical Precipitation* is the addition to, and thorough mixing with, the sewage of such chemicals as will, by reaction with each other or with the ingredients of the sewage, produce a flocculent precipitant; and subsequent sedimentation.

11. SLUDGE DISPOSAL

Sludge is the suspended solids of the sewage deposited in tanks or intercepted at the surface of filters, mixed with more or less water.

(*a*) *Sludge Digestion* is the biological process by which organic matter in sludge is gasified, liquefied, mineralized, or converted into stable organic matter.

(*b*) *Separate Sludge Digestion* is the digestion of sludge in tanks entirely independent from the tanks in which it is produced.

(*c*) *A Sludge Drying Bed* is a natural or artificial layer of porous material upon which sludge is dried by drainage and evaporation.

(*d*) *Sludge Concentration* is the process of reducing the volume of sludge, and increasing its proportion of solids by allowing it to stand in a suitable tank until the solids settle down, and drawing off the relatively clean water at the top.

(*e*) *Sludge Drying* is the process of drying sludge by drainage and evaporation.

(*f*) *Sludge Dewatering* is the process of removing a portion of the water contained in the sludge by draining, pressing, centrifuging, or by other natural or mechanical processes.

(*g*) *Sludge Pressing* is the process of dewatering by subjection to pressure, the solids being retained by a cloth fabric which permits the water to pass through it.

(*h*) *Sludge Cake* is the mass of dewatered sludge resulting from sludge pressing.

(*i*) *Commercially Dry Sludge* is sludge containing not more than ten per cent. of water.

12. MISCELLANEOUS

(*a*) *Scum* is a mass of sewage solids, buoyed up in part by entrained gas or grease, and which, consequently, floats at the surface of the sewage.

(*b*) *Screenings* constitute the material removed from sewage by screens.

(*c*) *Grit* is the heavy mineral matter deposited from sewage.

(*d*) *Sleek* is the oily film of microscopic thickness present on the surface of waters about and often extending a considerable distance from sewer outlets.

13. SEWAGE OXIDATION

Sewage Oxidation is the process whereby through the agency of living organisms in the presence of air, the organic matter is converted to a more stable condition or into mineral matter.

(*a*) *Irrigation* is the process of sewage treatment in which the sewage is applied to land for the primary purpose of purifying the sewage and the secondary purposes of supplying water and fertilizer to crops.

(*b*) *Surface Irrigation* is the process in which sewage is applied to and distributed over the surface of cropped ground.

(*c*) *Sub-surface Irrigation* is the process in which sewage is distributed beneath the surface of the ground by means of open-jointed pipes.

(*d*) *An Intermittent Filter* is a natural or artificial bed of sand or other fine-grained material to which sewage is intermittently applied in doses, and which by its capillarity holds the sewage for a time sufficiently long, in the presence of air, to effect by biological processes a high degree of purification.

(*e*) *A Contact Bed* is a water-tight basin filled with coarse material, such as broken stone, in contact with which the sewage is for a time held by control of the underdrains—the cycle of operation involving periods of filling, standing full, emptying and resting empty; so regulated as to secure such contact with the bacterial films adhering to the surface of the coarse material, and such aëration of the bacterial surfaces as may be required to oxidize the sewage.

(*f*) *A Slate Bed* is a water-tight tank filled with slabs of slate or other similar material, laid horizontally and spaced an inch or more apart vertically, equipped so that it may be filled with sewage, allowed to stand full for a definite period of time, drained and allowed to stand empty for a time, for the purpose of oxidizing the organic matter deposited upon and adhering to the slates.

[6](*g*) *A Trickling Filter* is an artificial bed of course material, such as crushed stone or clinkers, over which the sewage is distributed as a spray from fixed nozzles or as a film from moving distributors, through which it trickles to the underdrain system, coming in contact with the bacterial films adhering to the surface of the stones, and in which such aëration of the bacterial surfaces as may be required to oxidize the sewage is afforded.

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[6] The committee is of the opinion that the term " Trickling Filter " is preferable to the term " Sprinkling Filter " or " Percolating Filter," which are frequently used as synonymous terms.

(*h*) *A Dosing Apparatus* is the apparatus used for regulating the application of sewage to filters or for applying the required quantity of chemicals to sewage.

(*i*) *A Dosing Tank* is a tank into which raw or partially treated sewage is introduced and held until the desired quantity has been accumulated, and then discharged at such a rate as is necessary for the distribution essential to the subsequent treatment.

(*j*) *A Sprinkler Nozzle* is a nozzle used for applying sewage in the form of a spray to trickling filters.

(*k*) *A Distributor* is a movable perforated pipe, channel or water wheel which distributes sewage upon the surface of a trickling filter. There are two types of distributors—the rotary and the traveling; the rotary moves about a central axis with delivery to a circular filter; the traveling moves back and forth the length of a rectangular filter.

14. DISINFECTION

Disinfection is the destruction, by the agency of some chemical of a large percentage of the bacteria in sewage or contaminated water, so as to materially reduce the danger of infection.

15. STERILIZATION

Sterilization is the destruction, by the agency of some chemical, of all the bacteria in sewage or contaminated water, including their spores.

Respectfully submitted,

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HARRISON P. EDDY,
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COMMITTEE ON SEWERAGE AND SEWAGE DISPOSAL: Mr. Kenneth Allen, Municipal Bldg., New York City; Mr. Frank A. Barbour, Boston, Mass.; Mr. Harrison P. Eddy, Boston, Mass.; Mr. Langdon Pearse, Chicago, Ill.; Mr. George S. Webster (Chairman), Philadelphia, Pa.

THE ABSORPTION OF BASIC CHROME SALTS BY SKIN.*

By H. R. Procter and R. W. Griffith

Mr. Griffith sent the manuscript of this paper, which appeared in the *J. S. C. I.*, volume 19, 1900, suggesting that in view of the recent articles on chrome liquors and chrome tannage which have appeared in the JOURNAL it would be of interest and value to reprint part of it.—[EDITOR.]

Although the absorption of chrome salts by skin, and their tanning effect, has so long been known, considerable uncertainty exists as to the constitution of the basic salt absorbed; and the object of the experiments we are about to describe was to determine whether the absorbed salt possessed the same degree of basicity as that contained in the bath, or whether it was absorbed in a more or less acid condition. This point is not only interesting from a theoretical point of view, but is of considerable practicable importance, since, in order to strengthen a partially exhausted chrome bath for further use, it is necessary to restore it to the same degree of basicity as it has at first, and no easy means of determining this are at present known. It was further desired to ascertain how the absorption of the chrome salt was affected by the addition of common salt to the bath, which in practice is found to produce a softer, if perhaps a thinner leather.

These problems, most of which also arise with regard to alum tannage, have occupied the attention of several chemists. Berzelius (Lehrbuch, 9, 372) expressed the opinion that in alum tanning a basic salt was absorbed, but Knapp " Natur und Wesen der Gerbersi," 1858) showed that in solutions of alum and aluminium chloride that residual solutions had the same composition as those before use—a conclusion which does not wholly correspond to the work of later investigators. The problem is by no means an easy one, since no practical method exists of measuring the acidity of the basic salts except that of determining the whole of the acids and bases present, and in all technical cases it is complicated by the presence of sodium and potassium salts of the same acids. Where salt is used the additional difficulty of the presence of chlorine in an unknown state of combination occurs, for, though no complete reaction takes place, theory shows that an equilibrium must be formed in which all the acids

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* *J. S. C. I.*, March 31, 1900.

and bases present take part; and, as aluminium and chromium chlorides are freely absorbed by the skin, the salts fixed probably consist of a mixtures of chlorides and sulphates. Owing to neglect of this point, an elaborate research of Reimer (*Ding. Polyt. Jour.* 205) failed to give any decisive result; and the following experiments have been made principally to clear up the points yet doubtful.

Our experiments were carried out with pieces of "sheep grain" (i. e., the outer side of a split sheepskin), which had been delimed by a solution of boric acid and phenol, and afterwards well washed in several changes of water. The following was the method adopted in the first series of experiments. In each of two flasks were placed 10 grams of chrome alum dissolved in water up to 80 cubic centimeters, and to this 3 grams of crystallized sodium carbonate, dissolved to 20 cubic centimeters, were gradually added. To one of these were further added 20 cubic centimeters of a solution containing 7 grams of common salt. Pieces of wet squeezed pelt, weighing 50 grams each, were introduced into large stoppered bottles with 200 cubic centimeters of water, which were placed in the rotating frame of a Kent's "Speedwell churn," which is found very convenient for such experiments; and to each of them, one of the chrome solutions was added in quantities of 30 cubic centimeters at a time, at intervals of half an hour. When about half the chrome solutions had been added, the pelt was allowed to remain at rest in the solutions over night, and the operation continued in the morning till the pelt showed a uniform color throughout. Twenty hours were allowed for this tannage, in order as far as possible to reach a condition of equilibrium. After wringing the leather till nearly dry, a portion was taken from each piece and reserved for analysis. The remaining portions of the leather were then washed, and placed in separate bottles, each containing 1.5 grams of borax in sufficient water to cover the leather, and were again placed in the churn frame, and rotated for half an hour, when the leathers were again wrung out, and dried for analysis. The volumes of the residual chrome liquors, which we may dstinguish as "no salt chrome liquor" and "salt chrome liquor" were at this state 356 cubic centimeters and 352 cubic centimeters respectively. We now placed in these liquors fresh pieces of sequezed wet pelt as before, that in the "no salt liquor" weighing 35 grams and that in the salt liquor 33 grams. These were now churned in exactly the same manner as the previous pieces, the length of the tannage being 22 hours in each case. The leathers were wrung out of the solutions as before, and set aside for analysis without further treatment, being labelled "2nd tannage no salt" and "2nd tannage salt," respectively. This was similarly repeated to a third and fourth tannage. In each case the fourth tannage was very imperfectly tanned, and the liquor was nearly exhausted.

We now proceeded to the analysis of the leathers, and residual liquors. As the ignited ash of chrome leathers is insoluble in acids, it was necessary to bring the chromium into solution by fusion with soda and oxidation to chromate, which was subsequently acidified with hydrochloric acid, and the chromic acid estimated volumetrically with potassium iodide and thiosulphate —a method which previous work had shown to be very exact. The sulphuric acid was also estimated in a portion of the same solution. Where salt had been used, the chlorides were estimated in a separate portion of the leather. Unfortunately the necessity of fusion with soda rendered it impossible to estimate sodium and potassium in the ash, and as portions of the SO_4 (and Cl) were present in combination with these bases, fresh experiments were undertaken to determine their amounts.

It became evident from the results of these new experiments that the precautions taken in the first series were not sufficient to ensure the absolute uniformity of the different portions of the same tannage of leather taken for the different determinations, and that other sources of error existed which were afterwards eliminated, and it would be idle therefore to give numerical results or to employ them as the base of elaborate calculations; but it was quite clear, as was to be expected, that with progressive exhaustion of the liquors, the percentage of chromium taken up by the leather was correspondingly lessened, falling from 2.9 to 1.4 per cent. in the salt tannage, and from 3.7 to 1.0 per cent. in the non-salt, reckoned on the weight of the leather dried at 100°, the later tannages being distinctly undertanned. In fact, it may be taken that about 3 per cent. of Cr is necessary to produce a fully tanned leather. Comparing the two sets of tannages, it appears that salt does not facilitate the absorption of Cr, the amount taken up by the pelt being less, and the exhaustion of the bath less rapid and complete in its presence than without it. This is not necessarily a disadvantage in practice, and may partly account for the fact that leathers tanned with addition of salt are softer and thinner than in its absence. A somewhat similar action appears to be produced by salt in vegetable tannages.

The SO_4 found in the leather remained approximately constant throughout the experiments, amounting to about 2.6 of the dry leather weight on the average, and rather rising than diminishing as the bath became exhausted. About 1 per cent. of this, however, consisted in soluble alkaline sulphates easily removable by washing, and only mechanically retained by the leather; and we found later that a portion had also been driven off in ignition.

A second set of experiments was therefore undertaken in which these salts were removed by washing, and returned to the residual liquors before analysis, so as to determine the salts actually fixed by the leather, and the changes in constitution of the tanning liquors. The tanning solution for each experiment was made with 100 cubic centimeters of 10 per cent. chrome alum solution, to which was added 25 cubic centimeters of a normal sodium carbonate solution containing 1.32 grams Na_2CO_3.

For each tannage 100 grams of wet sheep grain were used in 200 cubic centimeters of water, and to one 25 cubic centimeters of a 20 per cent. solution of common salt was added, and the chrome solutions were introduced in successive portions as the tannage proceeded, as in the first experiments. The length of the tannage was 19 hours, at the conclusion of which the leathers were well squeezed and washed in successive portions of distilled water, which were added to the residual liquors till each was made to one liter. The leathers were air-dried and weighed, and portions were then weighed out for analysis and treatment with borax, while the residual liquors were also submitted to analysis. Portions of the leather samples were ignited at a low temperature to avoid loss of sulphuric acid and chlorine, but it was found that with the utmost care considerable amounts were expelled, and fresh analyses were therefore made in which the leather was moistened with Na_2CO_3 solution before ignition. This was effective in preventing loss of SO_4 and Cl, but introduced another difficulty. It is known that purified pelt contains a portion of organic sulphur, the amount being given by Stohmann and Langbein as 0.3 per cent.; and this on fusion with Na_2CO_3 and the resulting chromate, was also oxidized into H_2SO_4. Nothing remained therefore but to determine and allow for the SO_4 so formed. The ash in each case was fused, as before, with sodium carbonate in excess, till the whole was oxidized to sodium chromate and soluble in water. The chromic and sulphuric acids and the chlorine were determined by the same methods as before, in aliquot parts of the resulting solutions.

The residual tanning solutions were similarly analyzed, except that for determination of chromium a portion of the solution was oxidized with permanganate and described by one of us,* so that in all cases the chromium might be determined by the same standard thiosulphate. In most cases several determinations were made and the average taken.

A test analysis made with skin and a known quantity of chrome alum gave almost exactly the theoretical value.

Table I gives the result of these analyses. It was attempted to determine the SO_4 formed by oxidation of the pelt by ignition and fusion of a weighed portion with sodium carbonate and potassium bichromate, and a result of 0.124 grams per 100 grams of wet pelt was obtained; but as want of material prevented the analysis being made on the same skin as that used for the tanning experiments, and the results of repeated analysis of both skin and liquors showed an equal excess of SO_4 in both cases over that present in the original liquors, which could not be accounted for by the reagents used, it was thought best to assume that the excess was due to sulphur in the original pelt, the amount required (0.186 gram) agreeing very clearly with Stohmann and Langbein's value, which would yield about 0.180 gram SO_4 on the weight of pelt employed. The differences of the chromium and chlorine from that originally present may be taken as experimental errors, as in both cases the actual quantities determined were only small fractions of the whole quantities employed, and in a material like leather it is impossible to secure absolute uniformity of the samples analyzed.

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* *J. S. C. I.*, 1897, page 414.

TABLE I.—TOTAL QUANTITIES USED AND FOUND.

	No salt tannage		Salt tannage		
	Cr	SO_4	Cr	SO_4	Cl
Residual liquor	0.369	3.032	0.420	3.162	2.910
Fixed in leather	0.725	0.994	0.625	0.864	0.150
	1.094	4.026	1.045	4.026	3.060
Difference	0.054	—	0.005	—	0.010
Less amount of SO_4, original in raw pelt	—	0.186	—	0.186	—
Theoretical constitution of unused liquor	1.040	3.840	1.040	3.840	3.050

Table II gives the percentage composition of leathers obtained. It will be noted that in this, as in the previous experiments, a somewhat larger amount of chromium is fixed in the "no salt" leather than in the salt leather, while no great difference is to be observed in the total acid fixed.

TABLE II.—PERCENTAGE COMPOSITION OF LEATHERS.

	No salt leather 20.07 grams dried at 100° C.			Salt leather 20.74 grams dried at 100° C.		
	Washed	Extracted by borax	Left in leather	Washed	Extracted by borax	Left in leather
Cr	3.6	—	3.6	3.0	—	3.0
SO_4	5.0	3.0	2.0	4.2	2.5	1.7
Leather fiber by deduction	91.4	—	—	92.1	—	—
Cl	—	—	—	0.7	0.5	0.2
	100.0			100.0		

In the salt tannage it is clear that a small part of the SO_4 has been replaced by Cl.

In both cases a portion of this acid is removed by the borax treatment, but it may be noted that if a more alkaline substance than borax is used, or even if it is used in such excess as to remove the whole of the acid, the quality of the leather is destroyed, and although no Cr is removed, it returns to an undertanned and horny condition. One of the most important points which it is desirable to settle is the question of the degree of the basicity of the salts fixed by the leather and remaining in the residual liquor.

This is calculated in Table III, in which the proportionate number of molecules of SO_4 and Cl_2 combined with Cr_2 is given in each case.

TABLE III.—RELATION OF Cr_2 TO ACIDS FIXED IN LEATHER AND IN RESIDUAL LIQUORS.

Unused liquor	$Cr_2(SO_4)_{1\cdot 8}$
No salt leather	$Cr_2(SO_4)_{1\cdot 21}$
Residual, no salt liquor	$Cr_2(SO_4)_{2\cdot 6}$
Salt leather	$Cr_2(SO_4)_{1\cdot 2}(Cl_2)_{0\cdot 5}$
Residual salt liquor	$Cr_2(SO_4Cl_2)_{2\cdot 3}$

Of course the formulae given in Table III are not intended to express the actual constitution of the salt, but only the relative number of molecules of Cr_2, of SO_4, and of Cl_2 present. Naturally these proportions are usually fractional, as the basic salts may be regarded as mixtures containing various proportions of normal salts and oxides and hydrates.

The numbers are obtained from the proportion:—

$$\frac{\text{Weight of } Cr_2}{104} : \frac{\text{Weight of } SO_4}{96} :: 1 : X$$

and similarly with regard to Cl.

Taking first the simpler case of "No Salt" leather. The composition of the Cr salt in the original liquor is obtained by deducting the SO_4 present not only in the chrome alum as K_2SO_4, but also as Na_2SO_4 formed with the Na_2CO_3. In this case we find that the chrome salt is as Cr_2 is to $(SO_4)_{1\cdot 8}$ in place of $Cr_2(SO_4)3$, as it exists in the chrome alum. Turning to the unboraxed leather, we find that the proportion is $Cr_2(SO_4)_{1\cdot 2}$ making it clear that a somewhat more basic salt has been fixed than that present in the original bath. Correspondingly we find that after deducting the alkaline sulphates from the residual liquor, the chrome salt remaining has become distinctly more acid, being $Cr_2(SO_4)_{2\cdot 6}$. Turning to the salt tannage, very similar results may be observed: the basicity of the original liquor is the same of course as in the former case, though it is quite probable that in the acid constituent of the salt, Cl_2 has been partly substituted for SO_4.

In the residual liquor the proportion of Cr to SO_4 molecules is as 2 to 2.6, and we have no means of determining directly what proportion there is between the Cl_2 and SO_4, since alkaline salts of both radicles are present in the solution.

Turning, however, to the leather, we find that it contains in combination with Cr_2, 1.2 molecules of SO_4 and 0.5 molecule of

Cl_2, showing, therefore, a greater total acidity than the "No Salt" leather, though the SO_4 alone is really somewhat lower. This, of course, should involve a lower acidity in the liquors, and the fact is that a part of the SO_4 which has been estimated as representing the acidity in combination with chromium in the liquor, has really been employed in liberating Cl from the salt and exists as Na_2SO_4. Deducting the amount of this as calculated from the Cl in the leather, and amounting to 0.3 molecule per Cr_2 in the liquor, we have left an actual acidity of 2.3 acid molecules for Cr_2, which is thus materially less than in the case of the "No Salt" liquor in which the acidity is as $Cr_2 : (SO_4)_{2.6}$. It is therefore evident that used liquors require not merely strengthening for use, but also some addition of either chromic hydrate or an alkali to increase the basicity of the liquor.

If Na_2CO_3 were used for this purpose Na_2SO_4 would, of course, accumulate in the liquors and our experience is not enough to say whether this would prove injurious.

Should this be the case the use of barium or calcium carbonates or hydrates may be suggested as a way out of the difficulty.

Our results differ with regard to the fixation of a more basic salt than that in the solution from those of Messrs. Krutwig and Dalimier (Rev. Univ. des Mines, 48 (3), 23, abstracted in this Journal, Vol. 19, page 58). They, however, operated with normal salts, $Cr_2(SO_4)_3$, and it is very possible that the basic salt in the liquor tends to revert to that form, allowing the dissolved oxide to be more freely taken up by the skin. Normal salts are, however, incapable (at least without the addition of salt) of making a satisfactory commercial leather.

It is probable that the basicity of the salts absorbed is influenced both by the constitution of that present in the original bath and by its concentration, since untanned skin has a very marked absorptive power for acids, and it is quite possible that with different conditions in these respects the relation between the Cr and the acid absorbed might be altogether reversed. We think, however, that it may be taken that our conclusions hold good under the conditions prevailing in practical tannage. After the skin has been washed from the chrome bath it is completely converted into leather, but it has been found that its durability and permanency are much increased by removing a still further portion of the acid contained in it by alkaline treatment. Borax is the agent most generally used for this purpose in about ½ percent. solution; though other alkaline compounds, such as suspended chalk or sodium bicarbonate solutions may be substituted.

Portions of the leathers produced, equal to about 12 grams, if dried at 100° C., were therefore treated each in 500 cubic centimeters of water with 2 grams borax. No chrome was dissolved out, but considerable quantities of SO_4, and in the case of "Salt" leather of Cl, were withdrawn. Columns 2, 3 5, and 6 of Table II show the amount of composition of the leathers.

It may be noted that the proportion of acids to Cr in the boraxed leathers are much reduced, the salts remaining in the leather being very basic, the relation being $Cr_2(SO_4)_{0\cdot 6}$ in the "No Salt" tannage, and $Cr_2(SO_4)_{0\cdot 6}(Cl)_{0\cdot 1}$ in the case of the salt leather.

Since doing most of our analytical work, our attention has been drawn to an article by Paul von Schroeder on the estimation of Cr in chrome-tanned leather, published in the Deutsche Gerber Zeit. 42, 153-156. He incinerates about 3 grams of the leather, and then oxidizes the ash in the wet way with nitric acid and potassium chlorate. He subsequently evaporates frequently with concentrated hydrochloric acid to drive off the nitrous and chlorine fumes, the chromic acid becoming again reduced. In order to estimate volumetrically with KI and sodium thiosulphate, he subsequently oxidizes with sodium peroxide, removing traces of hydrogen peroxide left by evaporation with a few drops of alcohol.

The results of this method, when very carefully carried out, are no doubt accurate, but the process is altogether unnecessarily complex, since mere fusion of the ash with dry Na_2CO_3 in an open crucible for a few hours will produce complete oxidation, and leave the chromic acid ready for immediate titration.

This can be easily carried out with one of the excellent Teclu burners, and is the method by which most of our analyses have been performed, and which by working on known quantities we have proved to give accurate results. But we have since found that by employing a mixture of two parts of dry Na_2CO_3 to one part calcined magnesia (light), with which the ash is thoroughly pulverized before fusion, we can obtain a thoroughly oxidized fuse from the ash of 3 grams of leather within 20 minutes. It is necessary to dissolve the fuse in a little acid, as a small quantity of the chromic acid remains in combination with the magnesia.

ABSTRACTS.

Bookbinding Leather Decay. ALFRED SEYMOUR JONES. *The Leather World* 1917, p. 506.

The author's article is inspired by a contribution to the *Leather World* by Mr. W. R. Taylor of the Winnipeg Branch of the International Brotherhood of Bookbinders.

Mr. Taylor showed that acid-free varieties of leather are not free from decay and attributes the main cause of decay to the action of light on the leathers. He does not differentiate the tannages that are not free from decay.

The author shows that by articles published by himself and others in the Journal of the Society of Arts July 5, 1901 and in the Library Association Record December 15, 1906, the deleterious effect of light was shown.

In addition he states that the tannage was also important in this connection. For example all the catechol tannins particularly turwar (cassia) bark are affected.

The action of light, especially direct sunlight, is very detrimental to leather, varying in degree according to the tannin employed in tanning. Any librarian can meet this difficulty, provided he will act upon the advice given in the Report to glaze the library windows with suitable tinted glass or glasses. He can select his glass or glasses for correct tints according to the following test. Let him send to the glass-makers for pieces of glass, each one and a half inches by two inches, representing all the colors they produce. Number each piece with a reference number in black ink. Arrange all the glasses, side by side, like a chess board, in a photo printing frame, in which a sheet of plain glass has been inserted as a bedplate, superimpose a sheet of ordinary silver print photographic paper, and close up the frame. Expose to direct sunlight (or daylight). The results will show clearly the types of glass most suitable.

From time immemorial it has been known how serious are the results, due to action of sunlight, to fabrics, paintings, books, etc. In days of old, monks protected their books from direct sunlight, not only with the intention of preserving the bindings, but also to preserve the handwriting and paintings, which would have perished under the action of direct sunlight. As will be seen from the Report, no bookbindings are safe—no matter what the tannage may be—from light-action; and the best which humans can devise is to restrict that activity so far as it is practicable. When rare bindings and manuscriptsare to be preserved, they are always encased in a "box bindings" lined with velvet. In public libraries, the exclusion of direct injurious light rays is the only possible remedy. This is of urgent importance in those countries where the light rays are particularly active, and the tannage of leather is too often of the wrong character, having been prepared too often from pickled stock.

Capybara Skins. CONSUL HOMER BRETT, La Guaira, Venezuela, in *Commerce Reports*. In the valleys of the Orinoco River and its tributaries are found millions of "chiguires." This animal, more properly called the capybara, is the largest living rodent, and is common throughout South America from Venezuela to central Argentina. It is sometimes called the "carpincho" as well as the "chiguire." It is aquatic, inhabiting the marshy banks of brackish streams, and is notorious for the great damage that it does to neighboring sugar plantations. When full grown the animal is about 4 feet long and has a girth of 3 feet, weighing nearly 100 pounds. The skin is thick, and is covered with a rough, brown coat of short coarse hair. The animal has a heavy, flat head, and very short tail.

The chiguires have been officially pronounced undesirable animals, and the Government of Venezuela advocates their extermination. No use for their skins, however, has ever been found. A firm at San Fernando de Apure, Venezuela, exporters of hides and skins, offers to send samples of these chiguire pelts to any firm of specialists in the tanning business which would like to attempt to find a use and a market for them. This firm would also like to find a market for alligator and jaguar skins, and to form new connections with importers of cattle hides and deerskins.

[The name of the firm mentioned may be obtained from the Bureau of Foreign and Domestic Commerce, its district or co-operative offices. Refer to file No. 91032.]

Estimation of Sodium Sulphide. *Leather World.* A method for the estimation of sodium sulphide in sulphide dyebaths has recently been published by H. Swann (*Jour. Soc. Dy. Cols.*, 1917, p. 146). It no doubt could be applied to the estimation of sodium sulphide in lime liquors, etc. The details given as to dilution apply to liquors containing about 10 ounces per gallon of $Na_2S.9H_2O$.

Fifty cubic centimeters of the liquor are diluted to 250 cubic centimeters, and 20 cubic centimeters of this measured into a 150 cubic centimeter flask; 10 cubic centimeters to 20 cubic centimeters of 25 per cent. ammonium chloride solution containing 5 per cent. ammonia are added, and the liquid distilled into a known volume of decinormal iodine solution made acid with acetic acid. After boiling for five minutes the excess of iodine is titrated back with decinormal sodium thiosulphate solution in the usual way. Each cubic centimeter N/10 iodine solution used equals 0.012 gram $Na_2S.9H_2O$.

Nitro-Cellulose For Leather. *Leather World,* abstracted from the *Oil and Color Trades Journal.* "Cellulose ester lacquers and the like for leather can be prepared from cellulose scrap by dissolving in amyl acetate, amyl formate, amyl-and propy-alcohol, ether-alcohol, acetone, chlorinated hydrocarbons (tetrachlorethane), and diluents such as light benzine, benzol, toluol, methyl alcohol, oil of turpentine, etc. An opaque lacquer is obtained by using a solvent that is of high boiling point, or not quite anhydrous. Oils, such as castor oil and linseed oil, are sometimes employed to give increased flexibility, and resins to impart body and lustre. The coloring matters may consist of pigments or dyestuffs that are soluble in alcohol, though the former are liable to render the lacquer brittle by catalytic oxidation of the oil. The use of ultra-marine and certain color lacks that are sensitive to free acids should be avoided."

The use of nitro-cellulose for finishing leather deserves more attention than has yet been given, especially at the present moment, when foreign competition in patent leathers is practically absent.

A New Antiseptic. *Leather World.* Considering the importance of the subject of disinfection, the introduction of a new antiseptic should be of interest to leather manufacturers. Some details concerning the new substance, known as "mercurophen," are given in an abstract in *J. S. C. I.*, 1917, p. 733. The chemical name for the substance is oxymercuri-o-nitrophenoxide, and it contains about 53 per cent. of mercury. It is red in color, and freely soluble in water. Some comparative tests made with various organisms show that its antiseptic value is considerably more than mercuric chloride. Under stated conditions it destroyed *Staph, aureus* in a dilution of one in ten million (fifty times more active than mercuric chloride). Tested against *B. typhosus* it showed 10,000 times the power of phenol (carbolic acid), while the hands may be disinfected by washing in a solution of 1 in 10,000 to 1 in 40,000.

Such a powerful antiseptic as this might possibly be of service in the disinfection of hides and skins.

PATENTS.

Leather Dressing Machine. U. S. Patent 1,241,363. OTTO F. FEIX, Gloversville, N. Y.

Dissolving Insolubles in Quebracho Liquors. U. S. Patent 1,241,950. HANS FRANKE, Wilsdorf, Austria. Process consists of heating crude quebracho liquors, while air is excluded, with an alkaline earth compound that makes insoluble compounds with a suitable acid and afterwards treating with a calculated amount of this acid and separating the liquor from the insoluble residue.

Belt Dressing. U. S. Patent 1,242,424. PAUL H. CRAWFORD, Divisadero, Salvador. Consists of linseed oil, rosin and finely ground aluminum.

Multistretchable Leather. U. S. Patent 1,242,622. EMIL WEINHEIM, New York, N. Y. Consists in giving a body fabric of knitted yarn a coating and filling of leatherized dope of the oxidizable oil type.

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PROPOSED PROVISIONAL METHOD.

The result of the vote on the Proposed Provisional Method for the Determination of Total Magnesium as $MgSO_4$, $7H_2O$ (Epsom salts) in leather ash was as follows:

Yes	16
No	13

This did not carry as it did not have two-thirds of the total vote.

THE ESTIMATION OF SULPHIDE IN LIME LIQUORS, PART II.*

By Hugh Garner Bennett, M.Sc.

In a further paper by McCandlish and Wilson on this subject (The Determination of Alkaline Sulphides, Part III, *J. A. L. C. A.*, p. 598, 1916; *Collegium* (London) p. 10, 1917), these authors attempt to defend their statement that there is no "practical advantage" in adding ammonia as well as ammonium chloride to the N/10 zinc sulphate solution.

It was surprising that these authors made this statement, and more surprising that they defend it, for they also first indicated the practical "disadvantages" of *not* adding the ammonia. In their first paper (*J. A. L. C. A.*, p. 30, 1913), referring to the reagent which contained ammonium chloride only, they say:

> "it is not sufficiently alkaline to prevent a loss of hydrogen sulphide, formed by the hydrolysis of sodium sulphide in aqueous solution, and it does not contain sufficient ammonia to prevent the precipitation of zinc hydrate in lime solutions."

In their second and third papers also, these authors admit that the "disadvantage" of zinc hydrate percipitation is overcome by the addition of ammonia. Now, the disadvantage mentioned

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**J. S. L. T. C.*, July, 1917.

above, due to loss of hydrogen sulphide specifically refers only to aqueous solutions of sulphide. These authors admit also [(Part III), *J. A. L. C. A.*, p. 598, 1916], that with aqueous solutions

> "the presence of ammonia is of advantage in preventing the hydrolysis of the sulphide with the formation of hydrogen sulphide."

It is for the estimation of sulphide *"in lime solutions"* that the addition of ammonia "has no practical advantage." The italics are due to McCandlish and Wilson (Part III, *J. A. L. C. A.*, p. 598, 1916). And—(p. 600),

> "where the conditions are such as to bring the alkalinity of the liquor very near to the neutral point the presence of ammonia will be of value in preventing hydrolysis of the sulphide with consequent loss of hydrogen sulphide."

It is clear that in denying the advantage of adding ammonia in the case of lime liquors, they consider such liquors sufficiently removed from the dangerous "neutral point," and that they consider the alkalinity of limes great enough to prevent the hydrolysis of sulphide and escape of hydrogen sulphide.

Now the writer begs to suggest that McCandlish and Wilson are mistaken here, and that this mistake explains the experimental results given in their last paper (*J. A. L. C. A.*, p. 599, 1916, *Collegium* (London) p. 11, 1917). They titrate 50 cc. lime-sulphide solutions requiring 1 cc. to 9 cc. of N/10 zinc reagent, and find that the reagent containing ammonium chloride only, gives lower titrations than when ammonia has been added also (25 cc. per liter). They explain these results as *"due no doubt"* (1) to the suppression of the zinc ion, but the writer is of the opinion that the escape of hydrogen sulphide during titration is the principal reason for the observed difference. Now "the titrations are easy to perform, so that anyone interested can easily satisfy himself as to the point under discussion."

In the first place, to illustrate the admitted danger of escape of hydrogen sulphide when working with aqueous solutions of sulphide, the following experiments were made. A solution of sodium sulphide of approximately decinormal strength was titrated with the zinc-ammonium chloride reagent containing no ammonia, and 25 cc. sulphide solution required in one experiment 18.7 cc. N/10 zinc reagent and in another 23.5 cc. of the same reagent. Titration results lying anywhere between these two could be obtained with ease, the determining factor being the vigor of mixing during the titration. No two titrations yielded the same result, and in all cases the odor of escaping hydrogen sulphide was very noticeable.

In the next place we have to consider how far this danger may be ignored in the case of sulphide lime liquors saturated with lime. Such a liquor was prepared and titrated with N/10 zinc sulphate containing 50 grams ammonium chloride and 25 cc. concentrated ammonia per liter. Fifty cc. of the settled lime liquor required 11.1 cc. N/10 reagent; duplicate titrations gave concordant results, and no escape of hydrogen sulphide could be detected.

The same liquor was similarly titrated with a N/10 reagent containing the ammonium chloride but no ammonia. Fifty cc. settled lime liquor was used as before. The titration results lay between 10.0 cc. and 11.0 cc., and the odor of hydrogen sulphide was always very evident, especially during the middle of the titration. The maximum result was obtained by adding 10.5 cc. of N/10 reagent at once, mixing very gently indeed, and then finishing the titration with very gentle mixing. There is little wonder therefore, that McCandlish and Wilson observed similar difference in results in titrating 50 cc. lime sulphide solutions which required from 1 to 9 cc. of N/10 zinc reagent, McCandlish and Wilson refrain from giving their actual experimental results, but if the titrations are performed in an approximately uniform manner, the results of the two reagents will be nearer the less sulphide there is in the solutions. Less hydrogen sulphide escapes, when there is less to escape.

Now a volumetric process estimating a substance which is obviously escaping into the air during the process, does not seem satisfactory, and when the titration results are discordant up to 10 per cent. of the total titration, the process may be dismissed without much hesitation. McCandlish and Wilson quibble because the writer described such a process as "utterly unworkable." Possibly this was a descent into rhetoric, but it should not be necessary to have to explain that the meaning of the phrase was not that titrations could not be made, but that the results of such titrations had no reliable significance.

The reagent containing ammonium chloride only gives a process "unworkable" in the above sense, because the alkalinity of sulphide limes saturated with lime is insufficient to ensure that sulphides will not hydrolize and hydrogen sulphide escape. One cause of this is found in the addition of ammonium chloride with the reagent during titration, which salt reduces the concentration of the hydroxyl ion and which may also by double decomposition yield the easily hydrolizable ammonium sulphide in the liquor being titrated. This danger has been previously pointed out by the writer (*Collegium* (London), p. 313, 1915). As the titration proceeds, more and more ammonium chloride is added and this danger increases also. When ammonia is present in the reagent, however, the alkalinity of the liquor increases proportionately with the ammonium chloride added. Yet another reason why this reagent gives an "unworkable" method, and hydrogen sulphide escapes, is that when saturated with lime these liquors do not contain so much calcium hydrate in solution as saturated lime water alone. The stronger limes are in sulphide the weaker they are in lime. Hence in lime liquors stronger in sulphide, the tendency of hydrogen sulphide to escape is greater not only because there is more to escape, but also because the alkalinity restraining it is less. Lime liquors with increasing strength in sulphide gradually approximate to aqueous solutions of sulphide, in which McCandlish and Wilson are in agreement that hydrogen sulphide would escape. Even with sulphide limes of which 50 cc. require 1 to 9 cc. N/10 zinc reagent, precisely as suggested by McCandlish and Wilson, these factors are at work.

The only other experiments recorded by McCandlish and Wilson in their third paper are with reagents consisting of N/10 zinc sulphate only and of N/10 zinc sulphate containing 40 cc. per liter of concentrated ammonia. Again, that with no ammonia gave the lower results, and again the escape of hydrogen sulphide affords an explanation. The precise cause is, however, slightly different, *viz.*, the reagent with zinc sulphate only, gives a considerable precipitation of zinc hydrate, and liquor being titrated is rendered practically neutral thereby.

The solution containing 40 cc. concentrated ammonia per liter could not be made by the writer. The first precipitate of hydrate was nearly redissolved, but not quite. On dilution to mark it was reprecipitated. This fact needs mention because no others than McCandlish and Wilson have ever specified the amount of ammonia which alone will redissolve the zinc hydrate first precipitated.

It is particularly curious that McCandlish and Wilson should have overlooked or ignored the escape of hydrogen sulphide as a possible explanation of their recent experimental work, for in their 1913 paper they recorded experiments with lime-sulphide solutions in which hydrogen sulphide was observed to escape during titration. The experiments of their third paper have been discussed at length because they are the only experiments recorded in that paper. They are recorded as crucial experiments, which professedly give experimental support to and confirmation of their theoretical reasoning. If, as the author thinks, they are mistaken in the explanation of their experiments, they are equally mistaken in thinking that they have adduced experimental confirmation of their theoretical reasoning. That reasoning is as pretty as it is sound, and thanks are due to these authors for their painstaking clearness, but under the conditions of experiment mutually accepted as typical, (*viz.*, 50 cc. sulphide lime = 1 to 9 cc. N/10 zinc), they have produced no experimental evidence that the suppression of the zinc ion has any serious practical significance.

The addition of ammonia to the N/10 zinc sulphate, 5 per cent. ammonium chloride reagent, has the following practical advantages for estimating sulphide in lime liquors: it prevents practically serious errors due to the precipitation of zinc hydrate and also serious errors and discordance due to the hydrolysis of the sulphide and escape of hydrogen sulphide; while it is true that it also introduces another error due to the suppression of the zinc ion, the writer still maintains that it is possible to employ such a quantity of ammonia in the reagent, and that for lime liquors of any usual strength in sulphide the error is practically negligible. That quantity of ammonia should be sufficient to keep zinc hydrate and hydrogen sulphide in solution, and yet be the minimum amount necessary for these purposes, when titrating a definite volume of lime liquor of any approximate strength in sulphide.

It was from this point of view that the writer suggested that for ordinary sulphide limes the reagent might contain 25 cc. concentrated ammonia per liter. If any less ammonia be employed, zinc hydrate is precipitated by the dilution of the reagent during titration. If only a little ammonia be used (*e.g.* 10 cc. per liter), it is impossible to make the solution, as zinc hydrate is not redissolved in the reagent itself. Moreover, for quantities of ammonia not much less than 25 cc. it is possible to notice a distinct odor of hydrogen sulphide during titration, and if the amount be any less than 20 cc. per liter the results begin to be discordant owing to the escape of hydrogen sulphide. Thus a minimum of 25 cc. concentrated ammonia per liter is necessary to retain hydrogen sulphide and zinc hydrate in solution. On the other hand any amounts of ammonia in excess of this, produce an increasing error due to the suppression of the zinc ion. These points are illustrated by the following experimental results, obtained by reagents N/10 to zinc sulphate and containing 5 per cent. ammonium chloride, but with quantities of concentrated ammonia varying as shown in the table. The experiments were all made on the same fresh sulphide lime liquor.

cc. conc. ammonia per liter of N/10 reagent	cc. N/10 reagent required per 50 cc. lime liquor	Notes
0	6.0 to 6.4	—hydrogen sulphide escaping.
10	—	—reagent impossible.
15	6.9 to 7.1	—hydrogen sulphide escaping.
20	7.2	
25	6.2	
30	6.4	

It will be noticed that no ammonia and 25 cc. ammonia give (as McCandlish and Wilson say), results not far apart, but the former is by a compensation of errors. When no ammonia is used, the amount of hydrogen sulphide escaping is indefinite and the amount of zinc hydrate precipitated is also indefinite, owing to the varying ammonia content of used lime liquors. The use of 25 cc. ammonia per liter would be justified on the ground of concordance alone.

If McCandlish and Wilson are still inclined to maintain that the addition of ammonia has no practical advantage when estimating sulphides in lime liquors, if they still think its use introduces an error or errors equal to or greater than those it has been shown to eliminate, then it is legitimate to ask that they demonstrate their case by experimental data rather than by the ionic theory. In particular let them state the amount of error when estimating sulphide in a lime liquor containing 0.1 per cent. of sodium sulphide crystals, and also in a liquor containing 0.2 per cent. sulphide crystals. Theoretically, 50 cc. lime liquor are equivalent to 4.15 cc. and 8.3 cc. of N/10 zinc reagent respectively, both cases being therefore within the limits suggested by these authors and accepted as typical of many lime yards.

There is one last point in the third paper of McCandlish and Wilson which calls for comment. They say (p. 600)

> "The discussion of the various zinc sulphate, ammonia, and ammonium chloride solutions, contained in our first paper, was not intended to convey the impression of our favoring any one of these solutions."

That may be, but in point of fact these authors gave one solution a very strong recommendation indeed in their first paper. They definitely referred to a solution with which there was no error due to precipitation of zinc hydrate and a minimum error due to the removal of zinc ions. They equally definitely state also that "this solution gives correct results with aqueous solutions of sulphide," (*J. A. L. C. A.*, p. 32, 1913). Now such a solution is almost all that can be hoped for. They have published three papers on this subject without saying how this solution is made up, and in particular how much ammonia is used. Until they do so, and until they support by experimental evidence the value of this solution, and show also the extent of error in using the solution favored by the writer, it would appear that further discussion is barren.

THE ESTIMATION OF SULPHIDE IN LIME LIQUORS,— A REPLY.

By Douglas McCandlish and John Arthur Wilson.

This last paper of Bennett's[1] evidently calls for further reply. His contentions appear divisible into four parts as follows:

1. Unless as much as 25 cc. concentrated ammonia per liter of reagent be used, H_2S will escape during the titration, causing low and variable results.
2. This amount of ammonia is sufficient to prevent escape of H_2S.
3. This amount of ammonia is sufficient to prevent precipitation of zinc hydroxide without causing appreciable error due to retention of zinc ammonium ions in solution.
4. A N/10 zinc sulphate solution containing 40 cc. concentrated ammonia per liter could not be made.

The first three points can be treated by a repetition of Bennett's experiments varying the concentration of ammonia in the reagent. Using the same pure lime-sulphide solution we obtained the following results:

Reagent number	cc. conc. ammonia in N/10 reagent containing 50 gm. NH_4Cl per liter	cc. N/10 reagent required per 50 cc. lime liquor
1	0	5.85
2	15	5.9
3	20	5.9
4	25	6.0
5	30	6.0

The concentrated ammonia used contained 15.5-gram molecules NH_3 per liter.

Numerous titrations were made with each reagent and the end-point finally determined by filtering the titrated solution, adding 0.5 cc. of a 0.2 per cent. solution of sodium nitro prusside to 15 cc. of the filtrate and noting the presence or absence of a purple color. In this way concordant results were obtained with all of the reagents when care was taken to see that the filtrate was free from any suspended zinc sulphide. No odor of H_2S was noticeable with any reagent during titration, but all gave a slight discoloration to moist lead acetate paper held in the neck of the flask.

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[1] This JOURNAL, page 626.

When reagent No. 1 was added slowly and with vigorous shaking of the liquor, only one drop of reagent less was required than when nearly all of the reagent was added at once. With lime liquors containing as much as 0.5 per cent. of sodium sulphide crystals, there is a very appreciable evolution of H_2S when titrated with any of the reagents. The foregoing should be a sufficient reply to Bennett's first two points.

For 50 cc. of one lime liquor, reagent No. 1 gave a titration of 4.65 cc. and reagent No. 5 gave 4.7 cc. and no evolution of H_2S could be detected. But if 4.7 cc. of reagent No. 1 is added to 50 cc. saturated lime water a distinct precipitate of zinc hydrate is formed, while with 4.7 cc. reagent No. 5, the precipitate at first formed is redissolved. Why, then, do we not get a higher result with reagent No. 1? The answer is to be found in the reasoning given in our last paper[1] in which it is shown that the addition of ammonia will not lessen the error due to the alkalinity of the liquor, even though it does prevent actual precipitation.

A deci-normal zinc sulphate solution containing 40 cc. concentrated ammonia per liter may be readily made by dissolving the zinc sulphate in one quarter of the total volume of water required, adding all of the ammonia quickly and diluting to the correct volume with water. If the ammonia is added very slowly, the reagent cannot be made. On the other hand, the solution is unstable and there will be a precipitate formed on standing for a considerable time. However, the reagent was stable long enough to make the titrations mentioned in our earlier papers. If the zinc sulphate solution is made one-twentieth normal, the reagent will be permanent because the solubility of zinc hydroxide in ammonia of this strength is not exceeded.

[1] This JOURNAL, XI, page 598 (1916).

LEATHER BELTING IN THE TEXTILE INDUSTRY.*

DISCUSSION OF PURCHASING AND MAINTENANCE OF BELT EQUIPMENT.

By Louis W. Arny.†

The textile industry was one of the first patrons of the leather belting industry. The wants of textile mills, as large consumers of leather belting, have received careful attention from the leather belting manufacturers, and they gradually have developed the production of lines that are specially adapted for the requirements of the textile industry. These requirements are different in some particulars from those of other lines of manufacture. On textile machinery the load is usually steady, and power must be supplied to maintain constant and uniform speeds.

The power loads on the belts of some classes of textile machinery are heavy as compared with some of those of miscellaneous manufacture, but the pulleys are usually of large diameters, and the belt speeds within the proper range for efficient work. So that, though belts are often steadily overloaded, or at least are given a heavier load than is customary with belts of their width, because of the uniformity of this load, and the favorable belt speeds and favorable pully diameters, good belts are enabled to render most satisfactory service. The pulley diameters, too, are favorable to the use of the heavier grades of single leather belting, and this is, perhaps, a factor in securing the long life which characterizes them, and which is so essential in producing a small cost per horse-power per annum.

This question of the weight of single leather belts is not well understood in its relation to transmission. In many cases it is quite possible that better transmission results may be secured from thinner belts, especially where the pulley diameters are not favorable, but it is quite certain that the thickness of the belt is a material factor in its long life. Some scientific study is now being given this subject, and the relation of thickness and weight of belt to load transmitted, and to length of life, soon will be better understood than it is at present.

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* *Textile World Journal*, Sept. 1, 1917.

† Secretary, The *Leather Belting Exchange*, Philadelphia, Pa.

It is certainly true that the comparatively large pulleys generally in use in the textile trade are much more favorable to the use of heavy single leather belts than are the excessively small pulleys which are found so frequently in other classes of machinery. Though textile belts have in their favor the avoidance of the excessive belt speeds at which some other lines of machinery operate, it is certainly a fact that a thick single belt will withstand the ordinary wear of travel around pulleys for a longer time than will a thin one.

In this connection, the wonderful longevity of the leather belt, under reasonable or favorable conditions, should be noted. Leather is one of the most remarkable articles in the whole range of production. It is not affected by time, only slightly and remediably by air and water; it does not oxidize, corrode, or ferment, and with any ordinary attention a leather belt is more of a permanent investment than an item of expense. Just how long a leather belt will last must depend entirely on the conditions under which it runs.

There is a record of one leather belt which has traveled some thirteen million miles in forty years, and is still in daily use, with every prospect of a continuance of the performance of its duty for many years to come. There is, therefore, but little real wear on a leather belt in its travel around the pulleys under favorable conditions—that is, in the transmission of power within its capacity. Where a belt is subject to a large temporary overload at times, so that it slips on the pulley, there is a friction between the belt and the pulley which must produce wear, but in the absence of this condition the daily travel of the belt of hundreds of miles seems to produce no unfavorable effect upon it.

The greatest enemy of the leather belt in its attainment of old age seems to be the accidental or intentional application of injurious greases, either in the form of machinery oil dripping on the belt, or in the form of some unwise belt dressing. Leather is not injuriously affected by pure greases, but those which contain acids in various forms, and in sufficient quantities, necessarily destroy the strength of the fiber. For though practically indestructible under ordinary conditions, leather is susceptible to the action of certain acids.

The leather belt is not only remarkable in its length of life, but it is a material which is particularly well adapted for transmission purposes; a well-tanned and well-curried piece of belting leather soon adjusts itself to the pulley in such a manner as to transmit its power practically without slippage. It has been determined scientifically that the slippage of a leather belt, on a well-devised drive where the proper tension is maintained, is very small. Under such a load as fairly can be considered reasonable for a belt of given width, this slippage will not amount to more than 2 per cent., and in most cases it can be reduced much under 1½ per cent.

There are other materials which are stronger than leather, though any good leather is amply strong enough for any belting requirements, but there is none which has its peculiar surface adhesion to the pulley or the elasticity of the leather belt, or its capacity of carrying temporarily such a large overload. The ordinary tables for the calculation for horse-power transmission by belts have been figured on a very liberal basis for the leather belt, and investigations which have been made show conclusively that a well-made leather belt will readily withstand a temporary overload of as much as 100 per cent. over the figures usually used in determining its capacity. This is a factor of less importance in the textile industry than in others where machines and belts are subject to unusual and spasmodic overloads. The capacity for overload, however, is one of great importance and adds much to the life of the belt.

The textile industry generally has not given enough attention to the tensions under which its belts operate. It has been demonstrated that the best result in belt transmission can be secured by determining the most suitable tension at which belts of a given class shall operate, and in maintaining that tension in all the belts of that class. Fred W. Taylor applied this plan to machine shop practice and it has been eminently successful. It should be more generally applied to textile machinery. The greatest possible output, and the best quality of production from any one machine, can be secured only by having that machine run as nearly continuously as possible and by having its speed maintained at a standard.

Leather belts stretch and their capacity for stretch is one of their merits. Because of this the belt increases in length, and with the increase in length the tension decreases. With the decrease in tension there is a diminution of power transmitted, and if this reduced quantity of power transmitted is not sufficient to maintain the machine at its specified rate of speed, a loss in quantity of product, and oftentimes in quality of product, must result. This can be remedied by systematic care of the belts. They should be kept at a uniform tension so that there will be no diminution of the power transmitted, of the speed of the machine, and of its output. This involves some care and trouble, and possibly some expense, just as do all other good things, but Taylor has proven the wisdom of the expenditure in machine shop practice, and it must be equally wise and profitable as applied to textile machinery. The old method of placing a belt upon the pulleys, and permitting it to run as long as it will before giving it any attention, may be a simpler one and at first sight seems a cheaper one. But it is possible to systematize this work in such a manner as to get the results without any large burden of care or expense, and the results are profitable.

The multiplication of the same machine in textile mills renders this very desirable and makes it comparatively easy of application. By the maintenance of a suitable tension on leather belts, properly proportioned to their load, the loss of power and of production may be reduced to a negligible figure, the efficiency of the leather belt under proper tension being somewhere between 98 per cent. and 99 per cent.

Buyers of belting for textile mills should take some care to buy a good grade of belting. It is customary with new mills in the purchase of their equipment to receive bids from a large number of sellers, and unfortunately it usually is customary for them to buy from the lowest bidder. The lowest bidder, in a close competitive article like leather belting, is often the man least able to supply the best goods because of the smaller price he receives, and many textile mills have thus been led into the equipment of their plants with an inferior quality of belting. The purchase of goods from the lowest bidder may be justified in an article of which the buyer is an expert, but the average textile buyer really knows little about leather belting. It is an article which must be bought on confidence in the maker, and hence should be of a recognized brand of established merit, secured from a house with a reputation.

A proper purchase of a leather belting equipment should be expected to last, in whole or part, for a great many years; probably for a longer time than the purchaser himself can hope to be with it, and there should be no possible sacrifice of quality for the sake of the saving of a few dollars in original cost.

Good belting will do so much better work during its lifetime, that any difference in first cost may be made or lost during a very small part of the time the belt is in use.

The best results, then, in the purchase of leather belting are to be obtained by the purchase of recognized brands of excellence rather than by dependence on the judgment of the buyer as to the quality of goods. There is a sufficient number of these brands of excellence, made in many different parts of the country, to afford that keen competition which maintains qualities and reduces prices, and there is not much danger that the buyer shall pay for his equipment more than its proper value.

The purchase of a proper quality of leather belting and its careful maintenance undoubtedly would produce better belt transmission results in the textile industry than usually are secured, and a careful consideration of methods by which these results may be attained is well worth while.

NOTES ON DELIMING.*

By J. R. Blockey, M. Sc.

A liquor which has been used for deliming should not be allowed to become alkaline. If an acid deliming liquor has become alkaline, it shows that all the acid has been neutralized and that some of the free lime has dissolved or diffused out of the goods to be delimed. This can only happen when the goods have been left in the deliming liquor for a long time, or when the amount of acid added to the liquor has been too little. If the amount of acid added to the deliming liquor is sufficient to

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**Shoe & Leather Reporter*, Oct. 25, 1917, and Nov. 1, 1917.

neutralize the whole of the lime contained in the skins then the deliming liquor cannot become alkaline, but in most cases, the amount of acid used is not sufficient for this purpose. In most cases of deliming it is not desired to neutralize the whole of the lime; it is generally only desired either to remove the surface lime or to remove only so much lime that the middle portion of the goods still remains alkaline. In these cases therefore, the amount of acid which is added to the deliming bath is not sufficient to neutralize the whole of the lime contained in the goods, and in these cases it is possible for the liquor to become alkaline. As an illustration, the case may be taken where, say, only half the amount of acid required to neutralize the whole of the lime, has been added. When the goods are placed in this liquor the acid first of all neutralizes the lime on the surface of the goods, and then gradually neutralizes the lime further in towards the middle of the skins. The acid gradually diffuses into the skins and the lime gradually diffuses to the surface of the skins. At a certain point, when half the lime has been neutralized, the whole of the acid will have been neutralized, but the reactions do not come to an end at this point. The lime still left in the skins continues to diffuse out of them so the liquor instead of being acid actually becomes alkaline.

It might be asked at this stage: what is the harm of allowing the liquor to become alkaline? It is undesirable in two ways. In the first place and the most important, is the fact that when the surrounding liquor is alkaline it is a sign that the pelt is alkaline, and as a consequence, that the beneficial action of the deliming process is largely lost. Consider for a moment the changes in the pelt which have just been outlined, and as a help in this direction the usual test which is applied to measure the progress of the deliming process, may be borne in mind.

This test consists in the application to a cut section of the hide or skin, of an alcoholic solution of phenolphthalein. In the presence of free lime this solution will be turned crimson, while in the presence of acid the solution remains colorless. If therefore this solution be applied to a cut section of a fully limed skin, the whole section will be colored crimson. On the other hand, if the solution be applied to a fully delimed skin the whole section will remain colorless. Similarly, if applied to a cut section of a skin which has been partially delimed, that is, which has been delimed on the outsides but which still contains free lime in the middle of the skin, there will be a crimson streak in the middle, with colorless outsides. This is an extremely useful test for measuring the progress and extent of the deliming process.

Consider how this would apply in the case under discussion, that is where the amount of acid is only sufficient to remove about half of the free lime. At the beginning of the process, a cut section will appear crimson throughout, and if the solution be applied to the surface of the skin it also will be turned crimson. Suppose that the solution is applied at short intervals to freshly cut sections. In a very short time the surface no longer is colored crimson, showing that the lime on the surface has been neutralized. The cut section will also show the depth of penetration of the acid. The crimson streak will gradually get narrower up to a certain point. When almost the whole of the acid has been neutralized the crimson streak will not get any smaller. (If there were sufficient acid present to neutralize the whole of the lime the crimson streak would of course become smaller and smaller until it completely vanished.) When all the acid has been neutralized, the lime which is still free, will begin to diffuse outwards again. This will have the curious effect of making the crimson streak become broader and broader until the whole section will be colored crimson. The outside portions which have once been freed from lime again become alkaline. It may seem strange that the crimson streak should increase since there cannot be an increase in the amount of lime. The phenolphthalein solution is however, colored by a trace of free lime and as there is sufficient free lime left in the middle of the skin to diffuse to the outside of the skin, the whole section will again become crimson. The phenolphthalein solution, in other words shows the presence of free lime rather than the amount, and in this way may be very deceptive. For example, if the test were made at the end of the process above outlined, that is when the acid has been neutralized and when the remaining free lime has been allowed to diffuse throughout the skin, the whole section would be crimson just the same as though the goods had not been delimed at all. In other words, a partially delimed skin would present the same appearance as a no-delimed skin. With this reservation, the phenolphthalein test is very useful. The most use can be made of it by applying it at intervals during the process rather than only at the end.

To come back to the disadvantage of allowing the deliming liquor to become alkaline; when the section shows crimson again, free lime will then begin to diffuse out again into the liquor which will therefore become alkaline.

This can only occur when the amount of acid added is not enough to neutralize the whole of the lime and also only when the goods are kept in the liquor for a long time, that is for a time sufficiently long for the free lime to diffuse out of the goods again. If this has been allowed to take place, it follows that the whole section of the skin must be alkaline. If the deliming bath be alkaline, the whole of the pelt must be alkaline, and when this is the case the beneficial effect of the deliming process is lost. In order to make use of the good effect which an acid deliming process has on pelt, the surface of the pelt must be freed from lime. In most processes of deliming a complete removal of the lime is not aimed at, the beneficial effects on the color and feel of the grain are produced even when only the surface is delimed. In these cases the amount of acid added to the deliming liquor is not enough to neutralize the whole of the lime, so that in all these cases it is possible for the lime to diffuse to the outsides again and so undo the good done by the acid.

The way to obviate this is not to have the goods in the liquor sufficiently long for the lime to diffuse out again. This can best be done by applying the solution of phenolphthalein at short intervals both to the liquor and to freshly cut sections of the skins. The goods can then be removed from the liquor before the liquor becomes alkaline and the best time to remove the goods from the liquor will be when the crimson streak is at its narrowest limit. When regular lots of skins are being delimed it will only be necessary to apply the test occasionally. If the test be carried out thoroughly once then this can be taken as a guide for succeeding lots. If it is found that by the method at present in use the liquor does become alkaline then there are two alternatives, either to give more acid or a shorter time. In many cases it would not be convenient to give any shorter time. For instance in the deliming of sole butts, these are often placed in the deliming liquor during the day and left in overnight. In this case it would not be very convenient to shorten the time. In all cases therefore where it is not wise to shorten the length of time the goods are left in deliming liquor, the other alternative should be adopted, that is, more acid should be added. In the above case, that of sole leather butts, the deliming is carried out by suspension, but in the case of lighter classes of goods the deliming may be carried out in the paddle and in this case the length of time may be conveniently cut down.

One of the most important factors governing the nature of the deliming process but which is often not taken into account is the ratio of the volume of the liquor to the amount of goods to be delimed. This is important in most processes in the tannery but in none is it more important than is deliming. Consider two cases, where the volume of liquor is twice the amount in one case it is in the other, the weight of goods being the same. As concrete figures take *A* 1000 pounds weight of pelt in 1000 gallons in one case and *B* 1000 pounds of pelt in 2000 gallons in the other case. If the same amount of acid be added in both cases to delime the 1000 pounds of pelt, the pelt in *A* will be much more quickly delimed than in *B*. This gives another alternative to those already mentioned for overcoming the difficulty of the deliming bath becoming alkaline. That is, instead of shortening the length of time or increasing the amount of acid, the bulk of liquor may be increased, or in other words, the amount of goods placed in the deliming vessel may be reduced.

This question of the ratio of weight of goods to volume of liquor is also important in another way. Since the object of deliming is to remove lime and since a given weight of acid will always neutralize the same weight of lime, it is always the plan or should be, to calculate the amount of acid to be added to the deliming bath, upon the weight of goods to be delimed instead of upon the volume of the deliming liquor. It follows, therefore, that if the ratio of weight of goods to volume of liquor is higher in one case than another that the strength or concentration of acid in the deliming bath will also be higher. For instance in the cases above cited, where 1000 pounds of pelt are delimed in 1000 gallons in one case and in 2000 gallons in another, if the amount of acid added is the same in both cases, then the concentration will be double in one what it is in the other. Where the goods are closely crowded together, that is, where the ratio of goods to liquor is high, it may happen that the strength of liquor is excessive. This is particularly important when the acid used for deliming is a strong acid such as sulphuric, hydrochloric or formic. In these cases the deliming bath may be so strong that other effects besides those of removal of lime, are produced.

As an extreme case, consider that of sulphuric acid, used for deliming stout goods, where the ratio of weight of goods to volume of liquor is high, or in other words where the goods are crowded in the deliming bath. If sufficient acid be added to the liquor, at the beginning, to neutralize the whole of the lime the swelling action of the acid may come into play as well as the deliming action. The visible effect will be a very marked; instead of the opaque appearance produced by the deliming action, the outside of the goods will appear more or less transparent and swollen. In the ordinary deliming action of acids one of the effects is to produce a whitening appearance on the grain of the pelt. A limed skin is usually swollen and turgid and also slightly transparent. In the deliming the skin becomes fallen, flaccid and more opaque than before, a condition which is sometimes described as "leathery." If a neutral skin be placed in a weak solution of an acid, particularly a strong acid such as sulphuric, it swells, becomes hard or turgid and fairly transparent. The appearance is in fact that of fully limed pelt, but exaggerated. The same thing happens in such a case as that outlined, in the deliming of goods using sulphuric acid when the goods are crowded. The sulphuric acid not only neutralizes the lime but also exerts its swelling influence. This arises owing to the rapidity of the action of the acid. The outsides of the skin become delimed, but before the insides have time to be delimed the outsides begin to be swollen by the acid. In the correct process the lime should be so gradually neutralized that at no time is there sufficient acid in the pelt to swell it.

This trouble is of course most likely to occur with acids which have strong swelling properties such as sulphuric acid and cannot occur with such an acid as boracic which has practically no swelling action even when used in excess. This is partly responsible for the popularity of boracic acid as a deliming agent since it is more or less fool proof.

Even with strong acids such as formic or sulphuric acid it is only likely to occur when the goods to be limed are crowded together. When goods are too crowded the surface swelling may occur even when the amount of acid added is insufficient to neutralize the whole of the lime.

Many tanners fight shy of strong acids for deliming, but with the precautions which should have suggested themselves in the previous condition they may be made to act quite well. (The main reason for using such an acid as sulphuric is of course the cost, deliming with sulphuric acid being easily the cheapest method. In normal times the cost of deliming with sulphuric acid is only one-tenth of that of boracic or formic and only one-twentieth of that of lactic acid.)

If it is desired to use sulphuric acid for deliming, the most obvious precaution is to use as large a volume of liquor as possible so that the concentration of the acid should be as low as possible, but perhaps the best precaution is to add the acid in instalments,—say in three portions, the second portion being added before the liquor becomes alkaline and similarly with the third. In any case the total quantity of acid added should be less than is needed to neutralize the whole of the lime. With these precautions it is quite safe to use sulphuric acid for deliming.

One thing which may have frightened tanners in the use of sulphuric acid for deliming apart from the question of swelling, is the effect of free mineral acid in the finished leather. It is widely known for instance that even a trace of free mineral acid (*e. g.* sulphuric) in tanned leather will cause such leather slowly to deteriorate by rotting. The use of sulphuric acid in any stage of the process has therefore been banned in cases where the leather is to be preserved indefinitely, *e. g.* bookbinding leather.

This fear is justified when the acid is used after tanning, for instance for bleaching, cleaning or dyeing, but it is not justified when used for deliming as the following condition should show. There are two reasons why free sulphuric acid will not be found in the finished leather if it has only been used for deliming. In the first place it has already been pointed out, that always less acid is added to the deliming bath than is required to neutralize the whole of the lime so that pelt delimed with any acid should contain no free acid. In the second place, even if free acid were present in the delimed pelt it would be removed during the processes of tanning. Vegetable tan liquors always contain excess of weak organic acids such as acetic and lactic as well as the so-called tannic acids. These weak acids will during the long tanning process, replace any traces of free sulphuric acid which may be present in the pelt, so that the final leather will contain no trace of free mineral acid.

THE UTILIZATION OF CONDEMNED ARMY BOOTS.*

By M. C. Lamb.

In times of peace condemned army boots were sold to contractors, who cleared all items of condemned clothing from the various barracks and camps. When war broke out and the army grew rapidly, it was soon found that the standards of condemnation varied considerably, and an organization was therefore set up to deal with old boots. By this means no boots are prematurely condemned, and all boots that are fit for further military wear are repaired for that purpose. The remaining boots are sorted into two grades, one of which is considered to be suitable for civilian wear after repair, and the other, although occasionally purchased by clog-makers, is generally speaking of no further use as footwear.

With an army of such magnitude, although every step has been taken to secure economy in footwear, there must be an increasing quantity of boots unfit for further wear. The successful utilization of this waste leather presents a very interesting problem. The director of army contracts, who is responsible for the disposal of army boots, has taken a great interest in this matter, and is of opinion that a solution can be found to the problem of discovering profitable utilization.

The author has been permitted by the director of army contracts to publish the results of the investigations of himself and others, including a special Committee of the British Association, in this field of operations, with a view to stimulating the interest of manufacturers in this waste material.

* *J. S. C. I.*, Sept. 29, 1917.

The average composition of this discarded footwear is as follows:—The total weight per pair varies from 3½ to 4 pounds, consisting of approximately 11 ounces of leather uppers, and 45 ounces of sole, or say 20 per cent. uppers and 80 per cent. sole. The leather employed in the soling of army boots is practically all vegetable tanned. The leather used in the manufacture of the uppers is of vegetable origin, to the extent of about 80 per cent. of the total quantity of boots contracted for, the remaining 20 per cent. being chrome tanned. The metal used in making of the boots is approximately 19 per cent. calculated on the total weight of the boot, and consists of 18.9 per cent. of iron, and 0.1 per cent. of brass; the latter is used chiefly in the eyelets.

Waste Boot Leather for Road Making. A promising way of utilizing this waste leather is in the making of roads. In the early part of 1910, a patent was taken out by Mr. S. Brough, of Handsworth, for a road-making material which was subsequently known as "Broughite," in which scrap leather was incorporated with slag, granite, or limestone in conjunction with asphalt and bitumen. The claim made for this material was that a road was obtained which possessed the hardness and rigidity of the ordinary tar macadam road, and at the same time reduced attrition and dust and was more resilient than the ordinary road, possessing an amount of "cushion" without liability of cracking on the surface.

The author was entrusted with the investigation into the merits of this method of road-making, and found that while all the reports which had been obtained upon the experimental roads which had been treated with this product, were of a laudatory character and in all cases where the experiment had been tried it had been found successful, no further progress had been made chiefly owing to the fact that the patentee had died. The Roads Board are now interesting themselves in this matter with a view to the use of leather from discarded army boots as an ingredient in the process.

The quantity of leather used in compounding the macadam ranges from 5 per cent. when the roadway is to be subjected to very heavy traffic, to 10 per cent. when only light traffic has to be experienced. Assuming that the average amount of leather to be employed for the purpose is 7½ per cent. of the road covering material, it will require 158 tons 8 hundredweight per mile of roadway 8 yards wide. One ton of the tarred material is required for covering 6 square yards making an application 4 inches thick. Taking the average number of pairs of boots per ton at about 560 pairs, some 89,000 pairs of the worn-out product would be utilized in making each mile of the special roadway.

The method employed is simply to mix the scrap leather with the mixture of asphalt, bitumen, limestone, etc., lay the surface of the road with this composition, and afterwards give a top facing of slag, granite, or limestone.

Under the supervision of the assistant surveyor for Birmingham, Mr. H. H. Richardson, when district surveyor for Handsworth, several pieces of roadway were laid. These experiments have indicated the advisability of the leather being in comparatively small pieces. The author has suggested that in the initial experiments now being carried out under the roads board the soles of the boots only should be used, a more profitable use for the uppers having been found. The soles should be cut into strips about one inch wide and the heels used intact, the strips from the soles being subsequently cross cut into pieces about 1 inch square. It is proposed, as above stated, to utilize the leather macadam mixture as a bottom dressing in making the roadway, as if used near the surface there is likely to be some difficulty owing to the fact that it would probably be too costly to remove the nails and the iron heel and toe plates before use.

The original experimental road made with "Broughite"—though laid as far back as 1910 and subsequently repaired with ordinary macadam, still retains to a considerable degree its original virtues of resilience and noiselessness under ordinary traffic conditions. It is a cheap and excellent substitute for wood paving, as in addition to possessing greater wearing qualities, and being equally silent, it costs much less than wood, and no more than bituminous macadam.

The experimental roadways provide excellent foothold for horses, as has been testified by the officer commanding the Military Riding School at Regent's Park Barracks where an original broughite roadway was laid in 1911; such a roadway also affords a good grip for rubber tires.

Animal Charcoal. Of the numerous investigations made by the author, the one which from the standpoint of commercial applicability is the most promising, is the use of the waste product in the manufacture of animal charcoal.

Animal charcoal is now almost exclusively prepared from bones as a raw product, and is in considerable demand for use in the manufacture of munitions and as a decolorizing agent for use in clarifying and decolorizing sugar, oils and fats, gelatin, etc.

On submitting the leather to dry distillation the yield of crude charcoal obtained, in repeated experiments on a fairly large scale, was found to be in the neighborhood of 35 per cent. of the total waste leather used. The resulting charcoal was boiled with dilute hydrochloric acid, treated with dilute caustic soda solution, and finally washed and dried, the result being a yield of comparatively pure charcoal equivalent in weight to about 25 per cent. of the total weight of leather distilled. The carbon so produced has been tested for its decolorizing powers on sugar syrup and gelatin, with very satisfactory results; and the product, so far as could be ascertained from the small scale experiment, was in every way quite equal to any of the ordinary commercial products made from bones.

Ammonium Sulphate. The distillation products were collected in sulphuric acid and resulted in a yield of 23 per cent.—25 per cent. of crude ammonium sulphate. The maximum amount available from leather is about 28 per cent. of the weight of material used.

Grease and Fatty Matters. On analysis the leather of the uppers was found to contain on an average 15 per cent. of extractable grease and fatty matter, consisting chiefly of wool stearine, cod oil, sulphonated oil, mineral oil, tallow, and paraffin wax. The fatty mixture as extracted from a number of representative samples of the leather was in the form of a moderately hard grease, of melting point 37°—39° C. This product was quite suitable for use in the currying of leather or for other purposes for which a low grade of grease is desired.

The present commercial price of charcoal prepared for decolorizing purposes is in the neighborhood of £40 per ton, crude ammonium sulphate for manurial purposes £16 per ton, and solid greases from £50 to £80 per ton. The value of the yield of products may therefore be taken as follows:

1 Ton boots=560 pairs	Per cent. lb.	Per ton	Approx. value		
		£	£	s.	d.
Metal........................	19.0=425	5	0	19	0
Grease and fatty matter (uppers)	15.0= 67	50	1	10	0
Purified charcoal...............	25.0=560	40	10	0	0
Crude ammonium sulphate.....	23.0=515	18	4	2	9
		Total......	£16	11	9

It would appear from the above figures that there is a good margin for profit in the employment of this raw material, which will be available in very large quantities, and as the process of conversion is very easy, requiring very simple apparatus, the matter should be of interest to practical charcoal burners and others, particularly in view of the fact that the raw material ordinarily employed is scarce in quantity, and not so commercially remunerative in the result; in addition, there is a considerable demand and extremely short supply of charcoal for commercial purposes at the present.

Manure. Leather waste is sometimes employed as a manure. The manurial value of leather, owing to its extremely slow decomposition, is small unless supplied in the form of dried or finely ground powder to the soil. It should be added that chrome leather, which will not decompose under ordinary conditions, is in consequence of no use as manure. It has also been noted that chrome tanned material is harmful to plant life.

Some of the specially compounded manurial products on the market possess a small quantity of leather as an ingredient, but this has usually been treated in some way to render it more suitable for the purpose.

The fusing of the waste leather with nitre cake after removal of the iron and brass rivets or eyelets, etc., was tried, fusing one part of the leather waste with two parts of the nitre cake. The result was a dry block of manure which could be easily powdered, and which on analysis gave the following results:—Ammonia 0.58 per cent. (equivalent to ammonium sulphate 2.2 per cent). Total ammonia 1.8 per cent. (equivalent to ammonium sulphate 6.98 per cent). This experiment was not very successful owing to the low manurial value of the resulting product, and the presence of large quantities of sodium salts.

Leather carbonized by aid of sulphuric acid is sometimes used as an ingredient in "patent" manures, and as the raw material now under discussion is cheaper than ordinary scrap leather, discarded army boots might very well be used for this purpose.

Leather-board. The manufacture of leather-board has been the subject matter for a considerable number of patents, but as far as the author is aware, the manufacture of this article has not met with any considerable amount of commercial success, no doubt due to the fact that formerly the price of leather of inferior grade was not sufficiently high to enable leather-board to compete with it successfully. At the present time, the manufacture of leather-board for use in insoles of boots, and soles of slippers, etc., employing this cheap discarded army footwear for the purpose of pulping, appears to be more attractive than in less strenuous times.

The following suggestions have also been made:

Clogs. Uppers of the old boots in a fair condition can be cut from the soles and nailed round wooden soles to make clogs.

Washers. The uppers of chrome tanned leather could be used for making washers for screw-down water taps. Experiment has shown that they possess considerable durability.

Mats. Waste leather can be used for making door-mats on the principle of chain belting.

Leather-pulp. Pulping the leather for leather-board or paper is probably practicable but its competitor for this purpose would be the quantity of waste scraps, cuttings, and machine turnings of new leather which is more suitable to work up. The relative prices of the two materials would decide whether this would be a sound commercial proposition.

Leather Powder. Leather powder for casehardening could be obtained from vegetable tanned leather by treatment with wet steam.

Cyanides. The possibility of making cyanides has been discussed.

Glue and Size. Glue of an inferior quality could be made, the chief difficulty lying in the presence of an admixture of chrome and vegetable tanned leathers. It is possible to separate these by treatment with wet steam, and there are two processes (one of which is already patented) for obtaining glue material from chrome leather. One of these consists in treatment with sodium peroxide, and the other treatment with a solution of Rochelle salt or a salt of some other hydroxy-acid. At present, the price of tartrates is a serious consideration, but they can be recovered almost quantitatively in the process.

The author desires to express his indebtedness to Mr. A. Harvey for his assistance in carrying out many experiments, and to Mr. A. Bradley for his kindness in making several tests of the prepared charcoal in decolorizing sugar syrups.

DISCUSSION.

MR. ROBERT STEWART said that many years ago—as far back as the early eighties—he had used several hundreds of tons per annum of leather waste in the manufacture of prussiate of potash by the old pot process. The works in which he had been interested was situated in Leeds, where, at one time, the prussiate industry had been one of some magnitude. The locality was a particularly favorable one for the prussiate manufacture, inasmuch as there was always a plentiful supply of "animal matter" from the woollen mills in the neighborhood, and leather waste from the tanneries and boot factories; there had been also a ready market for the finished prussiate, as it had been in those days extensively used in Yorkshire dye houses. There had been two or three good-sized prussiate factories at Manchester, but the most important one of all was just outside Glasgow, owned by the Hurlet and Campsie Alum Company. The trade had been heavily hit by German competition, although there had always been a decided preference in favor of English or Scotch prussiate, but the *coup de grace* had been given to the industry by the growing use of aniline dyes and the continual development of methods for the obtainment of prussiate of potash and soda from gas residuals. Doubtless there would later on have been a partial resuscitation of the defunct pot process to meet the demand for cyanide for gold extraction but for the discovery of more direct methods of producing cyanides. There was a considerable amount of "prussiate char" produced as a by-product, but, at the time of which he spoke, it had been difficult to get more than a few shillings per ton for it. Some few years after the closing down of the last prussiate works in the United Kingdom, this char had been worth £20 per ton, several important applications, such as the bleaching of ozokerite and paraffin wax, having been found for it. To-day, as Mr. Lamb had mentioned, its value would be about £140 per ton. "Prussiate char," after having been freed from certain impurities, was said to have ten to twenty times the decolorizing power of other forms of animal charcoal. He was under the impression that some of the decolorizing charcoal met with in trade, and which he believed came from Germany, was actually made by the prussiate process, the ferrocyanide in this case being the by-product. Mr. Lamb had made some reference to the production of cyanogen compounds being one possible way of utilizing leather waste, and he thought this suggestion was deserving of consideration in view of the present value of animal char. Except for the latter circumstance the fusion process of manufacturing prussiate of potash could not possibly compete with modern methods, such as the fixation of atmospheric nitrogen, and of course, unless or until potash was once more obtainable at something like pre-war prices it could not stand at all, even with animal char at £140 per ton. Given potash at £15 to £20 per ton, however, there was no doubt that the old pot or fusion process would be profitable. Much of the leather waste dealt with in Mr. Lamb's paper would consist of "uppers." Now while sole leather parings gave a very fair yield of prussiate the waste from upper leather gave very poor results. That was found to be due to the quantity of grease it contained, although why the actual nitrogen content was not recovered in the finished product had not been solved. The upper-leather waste was, therefore, first boiled to extract the grease, which on cooling rose to the top of the vat; the boiled leather was submitted to hydraulic pressure to squeeze out the adhering grease; the pressed cake on cooling became quite friable, in which condition it could be very easily ground in an ordinary disintegrator to a very fine powder which might be applied as a fertilizer. The pressed cakes were quite as valuable as the sole-leather for prussiate making.

The grease obtained, amounting to 18—20 per cent. of the weight of the original leather, found an application in currying and soap making. The prejudicial effect of grease on the yield of cyanogen was very marked in all kinds of animal matter—such as woollen—used in prussiate making. It was a well-established fact that animal charcoal produced in contact with fused alkalie possessed a higher value as a decolorizer than the char obtained by the destructive distillation of animal matter *per se,* but he was not aware whether soda was as effective as potash. This was a matter well worth investigation, for, obviously, it would be far simpler to install a plant for producing animal char by the fusion of sodium carbonate and leather waste, than to rehabilitate the now obsolete pot process of manufacturing prussiate of potash. One process for utilizing leather waste mentioned by Mr. Lamb consisted in treating the waste with sulphuric acid; this recalled some work he (the speaker) had been engaged in eight or ten years ago. Leather waste was macerated in strong sulphuric acid whereby it was quickly reduced to a pulpy mass; the strongly acid mass was mixed with ground mineral phosphate, the aim being to produce a nitrogenous superphosphate. The patent, however, had never got beyond the provisional stage as it was found that the finished product contained much less nitrogen than the quantity calculated from the nitrogen content of the leather used.

ONE BATH CHROME LIQUORS.*

By Lloyd Balderston.

For several types of leather the one-bath process of chrome tannage seems to be well established, though the two-bath method may be better for some purposes. The recipes published in Europe a few years ago for one-bath liquors almost always used chrome alum as the starting point, and process of manufacture in that case is very simple. With the materials available in the United States, however, they are not so easy to make as the two-bath liquors, and many tanners buy them ready made in concentrated form.

Chrome alum is in some sense a by-product in Germany, where bichromate of potash is used as an oxidizing agent in dye-manufacture. The reduced material, if not already in the form of the well-known purple crystals called chrome alum, is easily converted into this form. Chrome alum is a double sulphate of potassium and chromium, whose formula is commonly written $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$. The crystals are of the same form as those of ordinary alum, (in which aluminum is present instead of chromium), and they contain the same large amount of water of crystallization. Chrome alum is a convenient form in which to market the chromium, because the crystals do not easily change in the air. At no time in recent years has this substance been an economical starting point for chrome liquors in this country, because potassium compounds are always relatively expensive here.

To make a liquor with chrome alum, it is only necessary to dissolve it and add enough sal soda to produce the desired basicity. For most purposes a satisfactory proportion is 1 pound of sal soda crystals to 4 pounds of chrome alum. A liquor so made when reduced so as to contain 1 per cent. of chrome (Cr_2O_3) has about 1.2 per cent. of potassium sulphate and about 0.8 per cent. of sodium sulphate.

In the United States, the common source of chrome for tanning is sodium bichromate. This salt tends to absorb water when exposed to the air, and for this reason potassium bichromate, which does not attract water, has been preferred for most pur-

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Shoe and Leather Reporter, Oct. 18, 1917.

poses to which the bichromates are applied. The sodium salt crystallizes with two molecules of water, while the other is anhydrous. The higher atomic weight of potassium just about makes up for this difference, so that the proportion of chrome, (Cr_2O_3), in the two is almost the same, about 51 per cent.

The sodium salt can now be made cheaply by the electrolytic process, and when it is furnished in small well-dried crystals in tight barrels, it keeps well and can be handled conveniently, if the quantity used is large enough not to keep packages open long before they are used up. An advantage of sodium bichromate over the potassium salt is its greater solubility in water. Both of these materials are poisonous, and great care must be taken not to inhale dust from them nor to let the solution come in contact with the skin to any considerable extent.

In order to make one-bath liquors, the bichromate must be "reduced," that is, a part of the oxygen must be taken away from the chromium. In the bichromate there are three times as many parts of oxygen as of chromium, and half of this must be removed in order to make a compound which can tan. If sulphuric acid is added to a solution of a bichromate it combines with the sodium or potassium, forming a sulphate, and the chromic acid is "liberated," as the chemist says. If now such a substance as sugar or glycerine is added to the solution, the oxygen which was in combination with the chromium, forming CrO_3, commonly called chromic acid, attacks the sugar or glycerine and literally burns it up, half of the oxygen being taken away from the chromium. The solution boils violently, so that the sugar must be added slowly. The Cr_2O_3 which results from the reduction unites with a part of the sulphuric acid to form "basic chromium sulphate" which is the active tanning agent. The basicity of the liquor may be varied within wide limits by varying the quantity of sulphuric acid used.

The same reaction may be carried out with hydrochloric ("muriatic") acid, but at the high temperature of the process a part of the acid is liable to be decomposed, and poisonous chlorine fumes given off. There is a slight difference in color between chloride and sulphate leather, the latter being regarded as preferable.

Formic acid may also be used in the making of these liquors instead of sulphuric or hydrochloric. The leather produced resembles sulphate in appearance. This process has been patented, but so far as the writer is aware has not been used in practice. Formic acid is too expensive at present to be economical. It is supposed that leather made with a liquor free from mineral acid will last longer, because in the case of sulphate leather, for instance, slow decomposition may in the course of years liberate sulphuric acid and so rot the leather.

The most economical method of making stock liquor from bichromate is to reduce it by means of sulphur dioxide gas. This method was described some years ago in the *Shoe and Leather Reporter,* and at least one of the liquors on the market appears to be made in that way. If a good sulphur burner is used so that no sublimed sulphur passes over into the solution, the process is very simple and satisfactory. It takes more time than the sugar and sulphuric acid method, but much less labor. When once started it proceeds without supervision until nearly complete, when tests must be made to determine just when all the bichromate is reduced.

The bichromate is dissolved in any convenient quantity of water (four times as much water as bichromate is a good proportion), and a current of gas from the sulphur burner is passed through until reduction is complete. The end of the reaction may be determined by placing a drop of the liquor in a little water and adding starch paste and potassium iodide. A blue color shows unreduced bichromate.

Among the earlier ready prepared chrome liquors on the market was one in liquid form having about 10 per cent. of Cr_2O_3 and 24 per cent. of sodium and potassium sulphates. This is such a liquor as might be made by adding soda to a solution of chrome alum.

A stock liquor made from sodium bichromate, if concentrated much beyond 10 per cent. chrome, say to 15 per cent. will deposit crystals of sodium sulphate on cooling. This is perhaps the reason why one of the most widely used of these preparations is furnished in solid form, containing about 25 per cent. of chrome. It is troublesome to dissolve, and the liquors made from it are liable to be cloudy, apparently because some of the chrome compound is rendered insoluble by drying.

If the stock liquor is made in high concentration, say 22 per cent. Cr_2O_3, it does not deposit crystals on cooling, but makes a viscous liquid, of a consistency not unlike liquid chestnut extract. This seems to be due to lack of water free to enter into crystals of sodium sulphate. Such a stock liquor dissolves easily, and makes clear liquors if its basicity is correct.

The basicity of liquors made with sulphur dioxide is fairly constant if the process is carried out uniformly, but if the rate of passæ of the gas varies very much, there will be noticeable differences in the basicity of different batches. In general character these liquors are practically identical with those made with sulphuric acid and sugar.

One-bath liquors are not usually regarded as poisonous, and one may put his hands in them freely without injury. Some of the tannery workers, however, whose hands are in the liquor much of the time, are liable to skin eruptions on the hands and arms. This may be avoided by keeping the hands greased with vaseline.

ABSTRACTS.

Nitrates in Sewage. E. B. PHELPS AND H. L. SHOUB. *J. S. C. I.*, abstracted *J. Ind. Eng. Chem.*, 1917-19, pp. 767-770. Twenty-five cc. of the sample is boiled for about half a minute with 0.5 cc. of a solution of sodium hydroxide and sodium chloride (5 grams NaOH and 1.5 grams NaCl in 100 cc.), and the liquid cooled and made up to its original volume or weight. Of the supernatant liquid above the precipitated iron or manganese, from 1 to 10 cc. (according to the proportion of nitrate present) is evaporated and the residue mixed with 0.2 cc. of a solution of 0.4 gram of *o*-tolidine in 100 cc. of N/1 hydrochloric acid, and then treated with 0.5 cc. of strong sulphuric acid, which is poured down the side of the vessel so that the liquids do not mix. After 5 minutes the sides of the basin are moistened with the liquid, and, after another half minute the liquid is diluted with about 5 cc. of water, transferred to a colorimetric tube and made up to 10 cc. and the color compared within 5 minutes with those given by standard nitrate solutions under the same conditions. Permanent standards may be prepared by diluting N/40 potassium bichromate solution to match solutions containing from 0.5 to 10.5 parts of nitric nitrogen per million after treatment with the reagent.

Good Meat Wasted on Hides. *Weekly News Letter. U. S. Dept. of Agri.*, Oct. 10, 1917. According to reports received by the meat-marketing specialists of the Bureau of Markets, United States Department of Agriculture, a Washington, (D. C.), dealer states that nine steer hides purchased by him carried seventy-nine pounds of waste meat. A Detroit dealer reports that an average of 6 pounds of waste meat was found on forty cow and steer hides received at his plant, and that in 10 days his men scraped 2,177 pounds of waste meat from hides, or enough to supply low-grade meat to about 5,000 people for one day. Faulty butchering, in addition to causing a loss of the food value of the meat which is wasted, results in a considerable loss of edible fats which remain on the hides.

South Africa's Wattle-Bark Trade. *Commerce Reports* from Handelsberichten, The Hague, Netherlands, Aug. 2, 1917. Wattle bark is a product of the "black wattle," one of the acacias known to botanists as *Acacia molissima,* which is said to have been imported about 35 years ago from Australia into Natal, where it is now cultivated very extensively, chiefly for the excellent tanning material it furnishes in its bark. In 1914 the area of the black-wattle plantations was about 200,000 acres. The fall in the price of the product, which resulted from the lack of shipping soon after the outbreak of the war, induced many planters to utilize their lands in other ways, and the area of the plantations was reduced.

Wattle bark contains a high percentage of tannin, and its use has increased considerably in recent years. The tanning material is easily obtained and gives both weight and strength to leather, so that it can be used not only for sole leather, but also for harness and upper leather. The following table shows the area planted in South Africa, the exports, and the average value per ton during the last 10 years:

		Exports		Average value per ton
Year	Acreage planted	Long tons	Value	
1907	48,640	24,320	$ 678,332	$27.89
1908	49,698	24,849	654,846	26.35
1909	71,542	35,771	947,488	26.46
1910	82,688	41,344	1,067,871	25.83
1911	99,290	49,645	1,409,124	28.38
1912	105,542	52,771	1,377,268	26.10
1913	200,000	65,053	1,505,350	23.14
1914	200,000	58,132	1,393,761	23.98
1915	190,000	40,027	950,155	23.74
1916	......	50,867	1,240,296	24.38

It is expected that the cultivation of the black wattle will increase greatly in the near future, as there is a scarcity of tanning materials in the United Kingdom.

South Africa itself consumes but a small quantity of the product. Prior to the war the United Kingdom was the best market for wattle bark, followed by Hamburg, Australia, Russia, Belgium, and New Zealand. Hamburg usually re-exported large quantities to the Netherlands. Exportation was hampered greatly by the outbreak of the war; only 58,000 tons of the bark were exported from South Africa in 1914, although it had been expected that the amount would reach 75,000 tons. Germany and other foreign markets having been closed by the war, the United States stepped in and began purchasing large quantities, and the exports to Australia also increased. During the past year considerable quantities were shipped to Russia, *via* Vladivostok.

Before the war the freight rate for bark had been $7.30 a ton, but rose to $12.65 soon after the outbreak of hostilities, and in the past year as much as $29.20 had to be paid. Freight was also charged by space, amounting to $14 per 40 cubic feet.

South Africa's first shipment of the extract prepared from wattle bark was made in April of the past year. It was the product of the Natal Tanning Extract Co. (Ltd.) at Pietermaritzburg, and the whole quantity, 982,454 pounds, valued at $70,340, went to London. The extract is cast in forms while still liquid and solidifies into hard blocks. It is shipped in sacks. The freight rate for the extract by the Union Castle Co. to London now is $23.48 per ton of 2,240 pounds, plus 20 per cent.

The prices of the bark in South Africa have fluctuated between $21.90 and $26.75 per ton, *f. o. b.* port of shipment. The prices in the British market formerly were $58.40 to $65.70 per ton of cut bark, *c. i. f.*, and $65.70 to $71.80 for ground bark. Owing to the scarcity of tanning materials, the prices increased rapidly during the first months of the current year; on March 31, 1917, cut bark was quoted at $73 to $75.40 and ground bark at $82.75 to $83.95 per ton. The market price for cut bark in bags at Durban is now $23.70 to $24.35 per long ton, *f. a. q.* [fair average quality]. The extract was quoted in February at $170.35 to $184.95 per ton.

Stellite as a Substitute for Platinum, by ELWOOD HAYNES. From *J. Ind. & Eng. Chem.*, Vol. 9, No. 10. The malleable alloys called stellite consist almost entirely of cobalt and chromium in varying proportions. These alloys are all very hard. They resist organic acids, caustic alkalies, nitric acid and all chemical compounds with the exception of hydrochloric, sulphuric or hydrofluoric acids which attack them only very slowly. They are practically immune to acid vapors. They are practically unbreakable, the tensile strength exceeding 100,000 pounds. They can be subjected to temperatures up to 1200° C. without material damage. They retain their weight, stability and smooth surface, indefinitely under all sorts of use.

Vegetable-Wax Industry of Japan. *Commerce Reports.* An industry of Japan which has made remarkable progress in recent years is that concerned with the extraction of vegetable wax, which is coming into greater demand on foreign markets. The output has been gradually increasing, and now stands in the neighborhood of 1,700,000 yen, or about $850,000 per year. The work of extraction is being organized on a larger scale.

The principal regions of production are in the Island of Kyushu, especially around the city of Fukuoka, which accounts for nearly half of the total output. The product is used abroad principally in the manufacture of polishes, pomade and soaps, and in dressing leather.

Most of this vegetable wax is derived from the fruit kernels of a tree peculiar to Japan, which begins to fruit at about 15 years, and sometimes bears heavily when it is over 100 years old. It reaches a height of 20 to 25 feet, and produces from 30 to 150 pounds of nuts annually. The best wax is made from nuts that have been kept over the winter, and generally speaking, the quality of the product improves with the age of the nut. The wax is extracted by crushing and steaming the nuts, and then subjecting the mass to pressure. A second wax is secured by repressing. One workman can handle about 150 pounds of raw mass in a day, and this produces about 16 pounds of wax.

The crude wax, which solidifies at 50°, is cast into round moulds of a little more than a pound each. It is next refined, the process used being a traditional one and peculiar to Japan. It is mixed with wood or charcoal, ash and water, thoroughly boiled, and dropped into cold water, so as to form what are called wax flowers. These are taken out and exposed to the sun for about 20 days, when the process of boiling, making the flowers, and sunning is repeated. The wax is then boiled a third time, and the best quality taken off the top while it is in a molten condition. Recently improved methods have begun to come into use, and the crude wax is treated with an alkaline solution.

The most important foreign consumers of this product are the United States, Great Britain, France, and Hongkong, followed by various other countries of the Orient and Europe.

The Journal of the

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INDEX TO VOLUME XII, 1917

Numbers refer to pages. (A) indicates an abstract. (P) a patent.
Patents relating to leather-working machinery are not indexed.

INDEX TO AUTHORS' NAMES

SUBJECT INDEX

ARTICLES FROM OTHER JOURNALS

(Page numbers without titles denote abstracts.)