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ORIGINAL PAPERS.

THE CHEMICAL EXAMINATION OF ASPHALTIC MATERIAL.

By S. W. Parr, Brainerd Mears and D. L. Weatherhead.

Received August 2, 1909.

The asphalt products of the United States have increased in value from six hundred and seventy-five thousand dollars in 1898 to nearly three million dollars in 1907, and the accompanying increase in the use of material by municipalities, together with the fact that the substances are mixtures and offer temptation for adulteration, has led to frequent demands for ratings and analyses. On attempting to comply with these requests, we have encountered serious obstacles. Most of the specifications for contracts and methods of analysis have been worked out and depend upon the presence of Trinidad asphalt in the product, and seem to be unsuited for the mixtures prepared in the middle and western part of the United States. These very frequently contain gilsonite tempered with petroleum residues of either an asphaltic or paraffine base, or both, and, while often not complying strictly with the specifications, are undoubtedly good mixtures for the purposes for which they are prepared.

Setting aside the physical tests, which are of great importance and which must be made in judging any asphaltic mixture, and turning our attention to those methods which are based on extractions with organic solvents and which are intended to give light on the quantity and properties of the chemical constituents, we find the methods in use most unsatisfactory. They are time-consuming, expensive and, owing to the changing specific gravity of the solvents used, do not furnish the concordant results desired. It accordingly seemed necessary, despite the numerous efforts of other investigators, to improve, if possible, the method of attack at this point.

In 1907, Mr. W. H. Leverette, working in this laboratory, started on a plan of analysis differing from the older methods of extraction, the principle being to dissolve the bitumen as completely as possible and successively precipitate out the significant portions with partial solvents. It is along this line of procedure that the following investigations have been carried on.

EXPERIMENTAL.

With a view of obtaining the most complete solvents, experiments were carried out on a sample of practically ash-free gilsonite with chloroform, carbon disulphide, carbon tetrachloride, hot turpentine, benzol and toluol. From these, carbon disulphide was selected as the most suitable. After considerable experimentation, the method resolved itself into the following procedure: Half-gram samples of the powdered gilsonite are placed in separatory funnels of about two hundred and twenty-five cubic centimeters capacity and dissolved in five cubic centimeters of carbon disulphide. When complete solution has taken place, one hundred cubic centimeters of hexane (sp. gr. 0.6516) are added which precipitates a substance termed Precipitate No. 1, and which corresponds

to the "Asphaltene" of the usual methods. After standing two hours the mixture is filtered on a specially prepared Gooch crucible,[1] which is dried in an air bath to constant weight at 105° C. This procedure was permissible as experimentation showed that no oxidation of the precipitate took place. The precipitate calculated in percentage of the sample was termed Precipitate No. 1.

Experiments carried on with freezing mixtures and also tests to determine the effect of boiling on the hexane mixture were found unsatisfactory, as precipitation seemed incomplete and variable under these conditions. Shaking and standing longer than two hours before filtering were shown to have little beneficial action.

In obtaining Precipitate No. 2, the filtrate from the preceding determination is evaporated to dryness in a separatory funnel on a water bath, the hexane recovered by condensation, and the residue taken up with ten cubic centimeters of the same. This hexane solution was then allowed to flow slowly into three hundred cubic centimeters of methyl alcohol, with constant stirring. Other solvents, such as a mixture of acetone and methyl alcohol, were tried, but methyl alcohol proved the most satisfactory. When the precipitation is complete the mixture is filtered on one of the specially prepared Gooch crucibles referred to above and dried at 105° C. As some of the precipitate adheres to the beaker, it is dissolved in five to ten cubic centimeters of hexane or toluene, transferred to a small glass dish, dried at 105° C. and weighed, the gain in weight of the crucible and the dish together representing the second precipitate.

Precipitate No. 3 was obtained by evaporating the methyl alcohol from the second determination and weighing the residue in a glass dish.

With a view of ascertaining the value of asphalt products and also to afford a means of comparison with other methods of analysis, the following substances were analyzed: Refined gilsonite; a petroleum residue called "Sarco Petrolene;" a mixture of equal weights of the same; a mixture of three parts "Sarco Petrolene" and one of the gilsonite; a mixture of two parts "Sarco Petrolene" by weight and one of gilsonite; a light cementing pitch; a mixture of equal parts of this pitch, "Sarco Petrolene" and gilsonite; a sample of Trinidad Lake Asphalt cement and a pure coal-tar pitch.

The material obtained as Precipitate No. 1 from each substance analyzed, excepting the coal-tar pitch, had the same physical properties. With this exception, they were all solid at 105° C. and could be easily powdered when dry. The precipitate from the coal-tar was more or less gummy at room temperatures and readily melted at 105° C. Precipitate No. 2, in the case of gilsonite, was sticky and soft at 105° C. From the other asphaltic samples it was sticky at room temperature and flowed at 105° C. In the case of the coal-tar there was no precipitate for No. 2. Precipitate No. 3 had the appearance of machine oil, but was more viscous.

The following tabular results of analysis were obtained:

TABLE I.—GILSONITE.

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
1	48.17	39.21[1]	10.09	97.47[1]
2	47.64	42.62	9.14	99.40
3	45.64	43.67	11.30	100.61
4	47.18	42.92	9.88	99.98
Average	47.16	43.07	10.10	99.99

TABLE II.—"SARCO PETROLENE."

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
1	3.07[1]	69.92	27.94	100.63
2	7.64	69.70	22.23	99.66
3	5.49	77.01	18.11	100.61
4	7.53	71.63	20.41	99.57
5	7.95	83.81	9.18[1]	100.44
6	4.90	75.44	19.04	99.38
7	7.50	82.32	9.65	99.47
8	6.93	72.15	20.51	99.59
Average	6.85	75.15	19.71	99.92

TABLE III.—MIXTURE 1.

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
1	27.48	52.16	20.48	100.12
2	27.29	53.03	19.64	99.96
3	29.20	50.20[1]	16.42	95.82[1]
4	29.48	54.83	16.92	101.23
5	29.40	56.03	14.88	100.31
6	29.38	50.86	19.52	99.76
Average	28.71	33.38	17.97	100.28 100.06

TABLE IV.—MIXTURE 2.

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
1	17.83	70.49[1]	12.29[1]	100.61
2	18.58	67.87	13.66	100.11
3	17.77	63.06	19.05	99.88
4	19.02[1]	59.37	22.15	100.54
5	18.71	65.59	16.86	100.16
6	18.52	66.39	14.36	99.27
7	18.28	56.92[1]	25.77[1]	100.97
Average	18.28	64.46	17.22	100.22 99.96

[1] *Jour. Ind. and Eng. Chem.*, by B. Mears, Vol. I, 477.

[1] Omitted from the average.

TABLE V.—MIXTURE 3.

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
1	20.03	...	...	..
2	20.92	64.45	14.21	99.58
3	20.24	64.30	16.01	100.55
4	21.85[1]	63.59	14.73	100.17
Average	20.40	64.11	14.98	100.10
				99.49

TABLE VI.—CEMENTING PITCH.

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
1	18.63	39.54	17.17	75.34
2	18.78	40.38	26.72	85.88
3	19.06	40.69	22.69	82.44
Average	18.82	40.20	22.19	81.22
				81.21

TABLE VII.—MIXTURE 4.

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
1	26.29	45.08	24.60	95.97
2	27.74	51.45	16.39	95.58
3	26.38	48.10	22.15	96.63
4	24.13	50.43	22.04	96.60
Average	26.13	48.76	21.30	96.19
				96.19

TABLE VIII.—MINERAL MATTER IN TRINIDAD LAKE ASPHALT CEMENT.

Sample.	Per cent. ash.
1	27.74
2	25.59
3	25.07
4	24.28
Average	25.69

TABLE IX.—TRINIDAD LAKE ASPHALT CEMENT.

Sample.	Insol. in CS_2. Per cent.	Non.-bit.[1] org. matter by diff. Per cent.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
1	29.89	4.20	16.96	39.44[1]	13.94[1]	100.23
2	28.82	3.13	18.99	33.19	18.67	99.67
3	23.94	..	18.81	36.82	20.56	100.13
4	27.21	1.52	16.04[1]	32.86	23.84	99.95
5	25.14	..	18.96	30.71	25.71	100.52
Average	27.00	..	18.43	33.39	22.20	100.10
						101.02

TABLE X.—TRINIDAD LAKE ASPHALT PRECIPITATES CALCULATED TO PERCENTAGES OF MATERIAL SOLUBLE IN CARBON DISULPHIDE.

Sample.	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
1	24.09	55.99[1]	19.79[1]	99.87
2	26.54	46.38	26.04	98.96
3	24.73	48.41	27.05	100.19
4	22.03	45.15	31.90	99.08
5	25.32	41.02[1]	34.94[1]	99.08
Average	24.54	46.64	28.33	99.75
				99.51

[1] Omitted from the average.

TABLE XI.—COAL TAR PITCH.

Ordinary coal tar direct from tar-well concentrated by heat to soft pitch.

Sample.	Insol. in CS_2.	Ppt. No. 1.	Ppt. No. 2.	Ppt. No. 3 by diff.
1	28.88	...	...	...
2	28.76	20.96	None	50.28
3	28.64	21.09	None	49.27

Precipitate No. 1 softens at 100° C. and melts at 105° C.

Gilsonite furnishes the highest percentage of Precipitate No. 1 and the lowest percentage of Precipitate No. 3 of any sample analyzed; while "Sarco Petrolene," an oil refinery residue used in tempering asphaltic material, gives the lowest percentage of Precipitate No. 1 and the highest of Precipitate No. 3. By taking the average of the percentages of the three precipitates obtained from gilsonite and the tempering oil we get, theoretically, the percentage composition of Mixture No. 1. A comparison of the percentage by analysis and the theoretical percentages is given below:

MIXTURE NO. 1.

	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
Theoretically	27.00	59.11	14.90	101.01
By analysis	28.71	53.38	17.97	100.06

Though the actual analysis does not exactly agree with the theoretical, yet the same general division of the constituent hydrocarbons of the bitumen is seen.

MIXTURE NO. 2.

	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
Theoretically	16.93	67.13	17.31	101.37
By analysis	18.28	64.46	17.22	99.98

Again a general likeness is seen, although an exact agreement was not found. The comparison in the case of Mixture No. 3 is more favorable.

MIXTURE NO. 3.

	Ppt. No. 1. Per cent.	Ppt. No. 2. Per cent.	Ppt. No. 3. Per cent.	Total. Per cent.
Theoretically	20.28	64.46	16.51	101.25
By analysis	20.40	64.11	14.98	99.49

In this case a better agreement is obtained and shows that if the percentage composition, according to this method of analysis, of the hard bitumen and the tempering oil were known the proportions used for tempering could be estimated with a fair degree of accuracy. It must be borne in mind, however, that in melting together these mixtures to make a homogeneous compound, volatile products were given off which probably contained some of the

lighter constituents and may account for some of the discrepancies in the comparison.

From the data obtained on Trinidad Lake asphalt it seems that this method applies to this natural bitumen as well as to the artificial asphalts. Moreover, a comparison of the results obtained for Mixture No. 4 with those for the Trinidad Lake asphalt shows a sufficiently close agreement to expect of them similar qualities. Determination was therefore made of their flowing and melting points with results as follows:

MELTING POINTS OF ASPHALTIC COMPOUNDS.

	Softens.	Flows.	Sp. gr.
Trinidad Lake asphalt	65°	83°	1.201
Mixture No. 4, compounded of gilsonite, oil residue, etc.	68	80	1.015

These results, it will be seen, are quite consistent with the analytical data and make it evident that if the intrinsic qualities of these substances differ, the indication for that fact must be sought in a further examination of the fractions thus obtained by precipitation.

In the sample of coal-tar, the case stands very differently in that there is no second precipitate and in its yielding a first precipitate of such different properties from that found in the true asphalts as to make its detection a simple matter.

Much additional work needs to be done in the matter of the further examination of the various fractions to differentiate still further their properties, if indeed there are differences as between the various types of asphaltic compounds.

The method of separation as it now stands is no doubt susceptible of further improvement, but in its present state its advantages over the usual dissolving-out process are very pronounced. The use of hexane has been adopted because it is more nearly a constant compound than the heavier distillates. The amount of Precipitate No. 1 bears a direct relation to the specific gravity of the precipitating solution, a higher quantity being recovered with hexane than with ligroin, or the heavier distillates. While these latter are much cheaper, they vary not only from one lot to another, but frequently in the mere matter of handling, a modification in density will take place. For this reason the hexane is more satisfactory.

We wish to express our appreciation for materials furnished us gratuitously by the Standard Asphalt and Rubber Company, Barber Asphalt Company, and Standard Oil Company.

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PAINT AND VARNISH COATINGS AS ACCELERATORS IN THE CORROSION OF METALS.

By WILLIAM H. WALKER AND WARREN K. LEWIS.

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The packing of strongly acid fruits in tin cans has always been attended with more or less difficulty. A new method which has recently been developed for the protection of the can from the action of the fruit juices, is to lacquer the inside of the can with a high-grade copal-linseed oil varnish. The results are excellent so far as the preservation of the fruit is concerned, but an entirely unexpected difficulty has been met; namely, that the cans sometimes corrode through within a short time (six weeks or two months) after packing. An investigation of the nature of the varnish coating and the cause of its accelerating action on the corrosion of iron and tin has been carried out in this laboratory and has led to some very interesting results, which are the subject-matter of this paper.

The cans, placed at our disposal, were lacquered while still in the sheet, on one side, by a process analogous to that used in lithography. The lacquer was baked at 140–150° C. and the cans made up in the ordinary way from these sheets, the lacquered surface being inside. The interior of new cans was of a light, golden yellow color, and the coating to the eye was perfect in appearance. Cans which had been packed with strawberries for six to eight weeks were, however, badly corroded

on the interior. The corrosion was concentrated, mainly at the soldered joints, at those points where the die had crimped the ends, and along straight parallel lines down the sides of the cans. The action was extremely serious, the attacked areas being deeply eaten away, in some points the metal being corroded through, with a resultant leak.

While it is true that certain very acid fruits attack an ordinary can to a certain extent, it is no less true that under ordinary conditions the total corrosion, despite the fact that the available corroding surface is greater, is decidedly less than is the case in a lacquered can. It is impossible, then, that this corrosion of the lacquered can is due entirely to the acid of the fruits. The only new factor introduced is the lacquer itself and it must be that the lacquer in some way causes or accelerates corrosion. According to the electrolytic theory of the corrosion of metals, the rate of reaction can be increased only in three ways, either (1) by decreasing the concentration of the metal ion in the electrolyte in contact with the surface, (2) by increasing the concentration of the hydrogen ion about the cathodic area, and in these two ways increasing the driving force of the reaction, or (3) by lessening the polarization of the deposited hydrogen by the use of some effective depolarizing agent. The only way in which the lacquer could alter the ionic concentration of the two metals, tin and iron, involved, would be by their absorption and consequent elimination from the solution. It is in the first place extremely improbable that the lacquer should do this to any appreciable extent and then again we know that since the rate of corrosion of both these metals in pure water is so extremely small, that this absorption, even though complete, would have but a slight effect on the rate of reaction. That the lacquer should increase the acidity of the electrolyte materially above that due to the acids of the fruit juices is equally improbable, and, consequently, we are driven to the conclusion that it must be as a depolarizer that the lacquer exerts its influence. This is made the more likely by the fact that depolarization is by far the most effective means of accelerating the corrosion of metals in general. It must be that the lacquer renders the corrosion of the cans possible by the absorption and removal of the depolarizing hydrogen from the cathodic surface.

All protective films made from so-called drying oils owe their properties to the unsaturated nature of those oils and their consequent ability to absorb oxygen, transforming themselves thereby into substances such as linoxylin and related compounds. As is well known, this absorption is a slow one and the unsaturated state disappears completely only after the lapse of a great length of time, unless accelerated by the use of catalyzers (artificial driers), or by the increase of the reaction velocity through the use of higher temperature. Thus it is not only possible but frequent that such films even in use are still partly unsaturated. It is equally well known that unsaturated carbon compounds in general possess not only a capacity for absorbing oxygen, but hydrogen as well, and the unsaturated state can be relieved equally well by reducing agents as by the use of oxidizing materials. We know, however, that such compounds are capable of absorbing hydrogen only in the nascent condition; it is then not surprising if a linoxylin film, which is as yet not completely saturated, will absorb the polarizing hydrogen deposited when a metal such as iron or tin is brought in contact with an electrolyte.

To investigate the accuracy of these deductions the following experiments were performed: A U-tube containing KCl solution with an agar plug at the bottom, from which air had been carefully expelled, had inserted into one arm a lacquered electrode and into the other, one of bare iron, the two being connected externally. While blanks showed no test for iron whatever, when one electrode was lacquered with an oil and varnish film, a strong test for iron was obtained in the other arm of the U-tube. The corrosion was greatest with a linoxylin film; copal-varnish, cellulose nitrate, shellac, and asphalt followed in order, while lacquer baked sufficiently long at 250 C., as well as paraffine, showed no corrosion whatever.

In order to make sure that the corrosion was not due to small amounts of air which it might have been possible to remove from the agar plug in the bottom of the U tube, or which might condense on the walls of the glass which could not be heated up after the setting of the agar, the experiment was repeated in an apparatus which precluded the possibility of such an error. In a Mason jar, thoroughly steamed out for forty-eight hours before use, were placed two concentric, porous, porcelain cups and the whole three-fourths filled with water, which was boiled down to about one-third the volume of the jar. The electrodes were inserted into the boiling solution and the cap, through which lead a tube delivering hydrogen, was screwed on while

steam was still escaping at full force from the jar. Numerous experiments have shown that under these conditions, with bare electrodes, sufficient iron to be detected with ferricyanide is never obtained. If, however, a lacquered electrode was inserted into the outside compartment and a bare iron electrode in metallic contact with it into the inner cup, the inner cup invariably showed a strong test for iron after from eighteen to twenty-four hours. No iron could be detected in either the jar or the larger cup.

If such films accelerate corrosion, it must be made possible only by the flow of an electric current, and this current must be carried either by the conductivity of the film as such, or by the solution penetrating through its pores to the metallic surface beneath. The conductivities of such films were tested by measuring the resistance of a circuit consisting of a metallic conductor leading to two electrodes immersed in a U tube, the resistance being measured before and after coating with the film in question. The electrodes employed were short iron wires and the electrolyte a strong solution of calcium chloride. The vessel was a small U tube. The resistance of the circuit with bare electrodes was approximately 30 ohms. Lacquered electrodes increased the resistance to some 270 ohms but in the course of a couple of hours this value had fallen to about 80 ohms. In the same time, shellac presented a resistance of 70 ohms, cellulose nitrate of 80, linoxylin of 65, asphalt of 43, while paraffine electrodes offered a resistance so great that it could not be measured with the apparatus at hand. In other words, paraffine was impervious to the solution employed. By the addition of paraffine to the lacquer, its resistance could be increased to from 1500–3000 ohms, but the lacquer had become so brittle thereby that the practical use of such a film would be out of the question.

To show that the corrosion of the iron occasioned by the lacquer film is accompanied by the flow of an electric current through the external circuit, the following experiment was tried: A U-tube, as previously described, with a KCl solution and an agar plug, carefully boiled out, the whole under an atmosphere of hydrogen, contained two iron electrodes, the one bare and the other covered with a linoxylin film. An electrometer was inserted into the external circuit and the current flow measured as shown in the table below. It was found undesirable to use a silver voltameter for the excessively small currents employed and resort was had to a modification of Ostwald's Bromide Voltameter, described elsewhere in the Journal of this Society. This voltameter was used for all measurements made, after the first, which was done with the silver nitrate instrument.

Deposit obtained from current due to depolarization by two different linoxylin films.

	Time in hrs.	Deposit of mgs. bromine.	Deposit mgs. per hrs.
Film No. 1	48	0.6	0.012
	76	1.0	0.013
Film No. 2	41	1.8	0.044
	89	4.1	0.046
	185	8.7	0.047

These figures prove beyond doubt that the corrosion of the iron on the unlacquered side is due to the flow of an electric current through the external circuit from the lacquered surface.

These experimental facts seem to allow of but one explanation, namely, that the films in question are porous in their nature, allowing the electrolyte to penetrate them to the surface of the metal beneath, that some of these films, due to their unsaturated state, are capable of absorbing nascent hydrogen and in this way acting as depolarizers, and that aside from this, all the porous films allow the penetration through them to the surface beneath of any depolarizer that may exist in the solution, thus rendering the coated surface cathodic and concentrating the solvent action at the exposed part of the metal.

The reason for the failure of the fruit cans mentioned at the beginning of this article is now easily understood. While the lacquer film applied to the uncut sheet was probably a perfect one, still in the process of making the can, this film was ruptured at many points. Thus the die stamping out the head of the can broke the film at the place where the tin was bent; the mandrel, on which the body of the can was formed, scratched the sides in long parallel lines upon the removal of the can; and the burning of the joints destroyed the lacquer in their immediate neighborhood. When the fruit was introduced into the can, the depolarizing action of the lacquer itself, coupled with that of the small amount of air left in the can in packing, threw the protected areas into the cathodic state, concentrating the solution of the metal at the exposed points, dissolving in this way both tin and iron, and maintaining this corrosion until both the air was consumed and the unsaturated state of the lacquer was completely relieved. Before this point was reached, however, the corrosion

had gone far enough to seriously damage the fruit and even in many cases to puncture the can. This action is entirely independent of any possible imperfections in the tin plate. The remedy would be to find a lacquer impervious to the solution, or if that prove impracticable to at least furnish one which will not act as a hydrogen depolarizer. A non-porous lacquer it has as yet proven impossible to find; a saturated one can be made by sufficiently baking any ordinary varnish, but there still remains work to be done to develop this into a satisfactory solution of the problem.

It is self-evident, however, that the importance of these phenomena is by no means limited to the problem of lacquering fruit cans. The majority of protective coatings for iron contain linseed oil or some one of the various substances found by our experiments to be either unsaturated, or porous, or both; and so soon as a piece of metal painted with these substances comes in contact with water after the abrasion of the paint film at any point, all the conditions for corrosion as above outlined are fulfilled, and we may be sure that corrosion at the exposed point will be accelerated by the presence of such films in its neighborhood. It is true that the porosity of these films is reduced to a minimum by the use of the best obtainable loading materials, such for instance as certain pigments of ordinary linseed paints, the bituminous bodies of asphalt or coal tar paints, etc., and that these paints offer in consequence a much greater electrical resistance to the flow of the current than otherwise. One must not forget, however, that the insertion of such a resistance to the current flow can only reduce the rate of the reaction, and in no way influence its tendency or driving force. The exposure of such films to the air for a long period of time finally entirely saturates them, but this again does not affect their porosity and consequently does not preclude the possibility of acceleration of corrosion at the exposed point due to the depolarizing action of air through the film. These facts make clear the reason for the rapid deterioration and pitting of the iron or steel surface at points laid bare by the breaking down of many paint films and show why it is so exceedingly important that a metal surface should be clean and bright before the application of a paint.

If a paint or lacquer film be intact, despite the fact of its porosity, corrosion does not seem to take place at once beneath its surface. Thus an iron can, carefully painted with a high-grade varnish and filled with cold 5 per cent. sulphuric acid, showed a test for iron with ferricyanide first after twenty-four hours. If heated on the water bath, however, a test could be obtained in slightly over one hour, but even then the action was not severe. It may perhaps be that the electrolyte does not find sufficient continuous surface beneath the film to allow of a ready separation into cathodic and anodic areas. At any rate, corrosion does not readily take place if the film be intact, but the surface below the film does easily become cathodic if an exposed area in the neighborhood can act as anode. This cathodic liberation of hydrogen loosens the film from the metal in some way not yet clearly understood and likewise softens it. The resistance of a film diminishes quite rapidly in this way and it soon becomes weak and rotten and easily removable from the iron. It is easy to see how, especially with rough usage, exposed points in a painted steel surface rapidly grow in size.

A few of the common commercial paints and paint-making materials were examined, using the following apparatus: A glass U-tube of 1′ tubing with 6′ arms and 8′ in length over all, contains 200 cc. of normal KCl. The electrodes are of commercial soft iron wire, 0.044′ diameter carefully cleaned with emery. The bare electrode is 25 cm. long and the lacquered one 100 cm. The electrode is coated by dipping in the paint to be examined, the excess removed by rapid twirling and then dried. The water about the *cathode* is kept saturated with oxygen by bubbling air through it. The depolarization current is measured by the use of the bromide voltameter already mentioned. The bromide deposited is proportional to the time, up to a point when the film gives way. This point of disintegration is different for different films and two quantities can in general be measured, (1) the initial rate of depolarization

Paint film.	Corrosion in mgs. Bromine per hour.
"Durable metal coating"	0.70
"Copal linseed oil lacquer"	0.76
"Cosmos" (coal tar)	0.34
Graphite	1.87
Carbon black	2.4
Lampblack	2.3
Zinc chromate	0.11[1]
Barytes	1.2
Zinc oxide	0.078[2]
Graphite (baked)	0.078
White lead	0.10[3]
Linoxylin	0.31
Paraffine	0.00

[1] Broke down in 36 hours, but not badly.
[2] Still perfect after 71 hours.
[3] Broke down in 30 hours.

and (2) the time of rupture. This second factor is somewhat difficult to obtain because our voltameter measures not current but total amount of electricity passed, and it is frequently, if not usually, impossible to tell at exactly what point the increase in current began. In the above table is the average of the data obtained.

It is evident that the electricity measured by the bromine deposited is the resultant of a number of factors acting at the same time. A comprehensive study of the relationship between such data and the value of various paints as a protective coating for iron is now in progress.

THE CARTER PROCESS OF WHITE LEAD MANUFACTURE.

By J. S. Staudt.

Received July 17, 1909.

This company has two plants in the United States: one in Chicago, Ill., and the other in Omaha, Neb. The former has a capacity of about 20,000 tons annually and the latter of about 10,000 tons annually.

All descriptions and illustrations as herein given refer to the Omaha plant.

The lead bars or pigs, weighing about 95 lbs. each, are drawn up a chain elevator at the rate of 500 pigs per day, to be melted in a cast iron trough about 8 feet long, 18 inches wide and 12 inches deep, placed upon the second floor of what is called the "blow room." The lead is melted by means of a coal fire placed immediately below the trough.

On the side of the trough opposite the elevator is an opening through which pass two concentric tubes. The inner tube, nozzle shaped, serves for the passage of molten lead, and the outer for the passage of superheated steam. The tubes lead or open into a large iron compartment, about 33 feet long and 10 feet high, with a maximum depth of about 10 feet, tapering toward the base. Superheated steam is here produced by the same source of heat used in melting the lead, and is thus made as needed. It is the action of this superheated steam, blown against the molten lead, blowing it against the walls of the compartment, that reduces it into a finely divided state, granular and blue in appearance, called "blue lead."

The blown lead is not supposed to be oxidized before being put into the corroding cylinders. It will, however, undergo a slight oxidation when subjected to the moist air and the gases of the plant. When heaped up it will rise in temperature and become partly oxidized. Trap doors at the bottom of the iron compartment serve as means for the removal of the blown lead. The blown lead is removed by means of iron trucks, mounted on cast iron wheels, each truck holding about 4,000 lbs. Each truck is hauled upon an elevator and raised to the third floor. The contents are then dumped through an opening leading into a "corroding cylinder," on the second floor beneath. All the "corroding cylinders" are filled in this way, each "blue cylinder" receiving about 4,000 lbs. of blown lead. In the "corroding room" there are 69 "blue cylinders," as they are called, and 58 "white cylinders." The cylinders are made of wooden

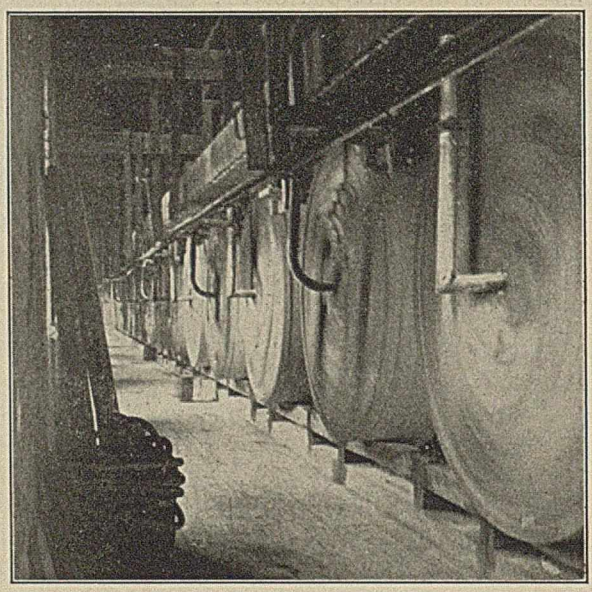

Fig. 1.—Corroding cylinders.

planks 2 inches thick, are 10 feet long and 8 feet in diameter. Lead is kept in the "blue cylinders" for 10 days, 16 lbs. of acetic acid being added for three days. For the remaining seven days it is sprinkled with cold water by means of a hose, inserted through an opening in the end of the cylinder. This is done twice a day, once in the morning and once in the evening. The carbon dioxide enters the cylinder through a 2-inch pipe inserted through an opening in the axis of one end of each cylinder. The cylinders revolve very slowly, making one revolution in nine minutes. The function of the cylinders is twofold: first, it serves as a grinder in so far as the particles rub against each other while the cylinder revolves.

second, it serves to expose more lead to the corroding influences of acetic acid and carbon dioxide gas.

The corrosion is only partially completed in the "blue cylinders." The product is taken from these

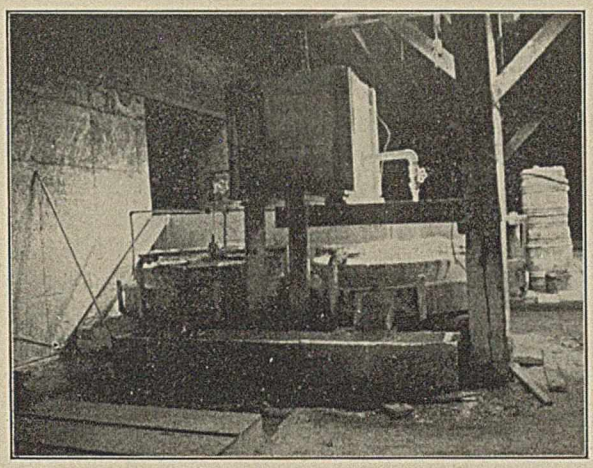

Fig. 2.—Classifiers.

cylinders by means of vertical chutes, leading to trucks on the ground floor. Loaded trucks are taken by means of an elevator to the tower, dumped into a large hopper, leading into a mill grinding it into a fine powder. From this mill it leads into a large vertical chute 4 feet by 4 feet to the ground floor. Trucks are hauled under the orifice of this chute, filled with the ground product, and elevated to the third floor to be dumped into the "white cylinders." There are 58 "white cylinders" having the same dimensions and period of revolution as the blue. The product is removed from these through wooden vertical chutes, leading to the ground floor below, loaded upon trucks, elevated to the third floor where it is dumped through an opening in the floor into a chute leading to a grinding mill below the floor.

The ground white lead is then washed with water, passed through the classifiers, four of which are in the corroding room south of the mill. The classifiers serve the purpose of separating the coarse particles from the fine. Abundant water is used here so as to cause it to flow and at the same time wash it. The finest separation from the classifiers goes over the "shakers" where it is still further separated. The "shakers" consist of a framework covered with silk of very fine mesh. This framework is moved back and forth in a horizontal direction by means of a piston. The liquid white lead is fed upon the sieve by means of openings in the bottom of a trough at the head of the sieve. An operator regulates the flow by taking out or inserting wooden pegs fitting these openings. The part that goes through the fine silken sieve passes by the action of gravity through pipes slightly inclined to the "settling tanks" on the ground floor. The coarse from the four classifiers above referred to as well as from the "shakers" passes through conduits leading into a main which in turn leads through an opening in the axis of the north end of a pebble mill, also on the ground floor. Only one pebble mill is used. It is about 10 feet long and 4 feet in diameter, partially filled with pebble stones from 3 inches to 4 inches in diameter. From the axis of the south end of the mill the ground material escapes, passes through an inclined conduit into an adjacent bin from which it is pumped through a 2-inch pipe up to the two "classifiers" on the third floor. Here it is again separated into coarse and fine, the fine flowing through wooden conduits to the "shakers." The coarse from this having gone over the classifiers and through the pebble mill now passes through a revolving screen (silken), located on the ground floor. This separates the tailings—consisting of particles of wood, coarse white lead and uncorroded lead—from the good product which drops into a large bin below the revolving screen.

The tailings are sold for what the lead is worth for the making of litharge and red lead.

The "settling tanks" are 13 in number, arranged in two rows running north and south on the ground floor.

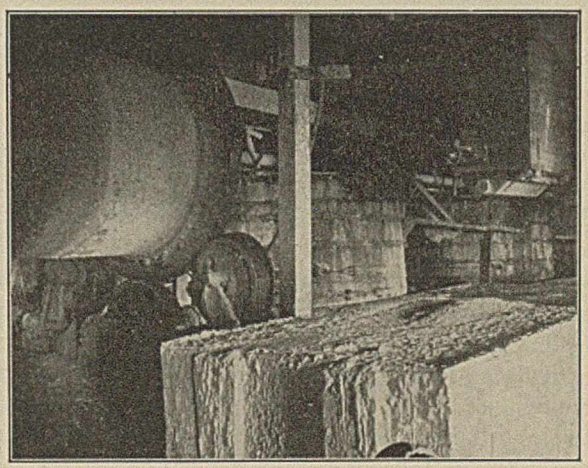

Fig. 3.—Pepper mill and settling tanks.

The tanks are about 11 feet in diameter, and about 5 feet high, tapering toward the top. These tanks are filled with the fine product from the "shakers" diluted with plenty of water. The product as

it comes from the "white cylinder" is partly basic lead carbonate and partly lead acetate. Acetic acid acting on the lead forms basic lead acetate in the presence of air. The carbon dioxide acting on the basic lead acetate forms lead carbonate

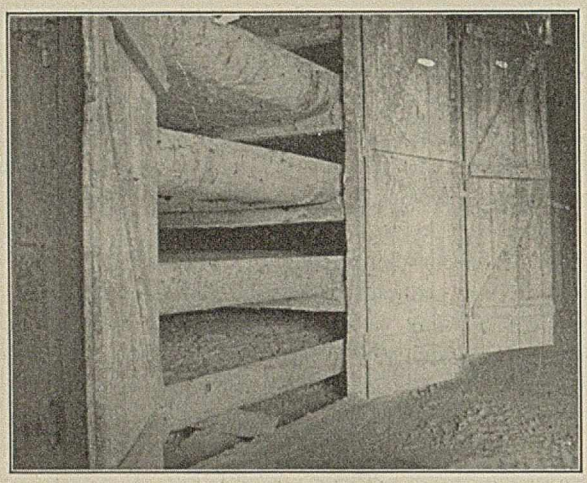

Fig. 4.—Drying pans.

and lead acetate. This is the product that goes into the settling tanks together with a large quantity of water. Two bucketfuls of soda solution are added to each tank. This solution is made by dissolving 150 lbs. of Na_2CO_3 in one barrel of water. The sodium carbonate acting on the lead acetate changes it into lead carbonate. The contents of the "settling tanks" are agitated by means of an agitator, consisting of a wooden plank extending down into the basin with a cross piece at the end. Each tank is provided with an agitator. They are attached to horizontal shafts above each row, extending the full length of the rows and rotated back and forth by means of a piston rod. The white lead is kept in these "settling tanks" for about fifteen hours, agitated part of the time and then settled. The solution is tested for acetate or free acetic acid by a 10 per cent. solution of potassium iodide. After the contents of the basins are thoroughly settled the water is removed from holes, fitted with wooden pegs extending down one side of the tank. By the removal of these pegs the water can be removed to any desired depth. Great care is taken that the excess of soda is washed out of the precipitate since it saponifies with the oil which is later added. Phenolphthalein solution is used to test for the carbonate. The water thus removed is passed through an 8-foot sewer pipe to a "settling basin" about 75 feet east of the building. It consists of a hole dug out of the ground 18 feet by 7 feet and 10 feet deep, lined with concrete. Here a further precipitation of white lead, held in suspension by the water, takes place. The settlings from this basin are removed about once every three months.

Pure white lead now constitutes the settlings from the "settling tanks" which are removed through openings in the sides of the basins near the bottom, emptying into deep and wide wooden flumes, immediately below the floor. These flumes are inclined so that the white lead slowly flows into a bin below the floor at the north end of the room.

From this bin it is pumped through a 3-inch lead pipe into the "dry room" on the third floor at the north end of the building.

The "dry room" consists of two bins 100 feet long, one on the east side and one on the west side. These bins are provided with iron pans lined with copper, extending through the full length of the bins. The east bin contains five pans and the west bin four. Each pan has a double bottom. Steam circulates through the hollow thus provided, furnishing heat by which the white lead is dried. It requires about five days for the white lead in each pan to dry, in which state it cracks and breaks up into blocks very similar to mud drying in the

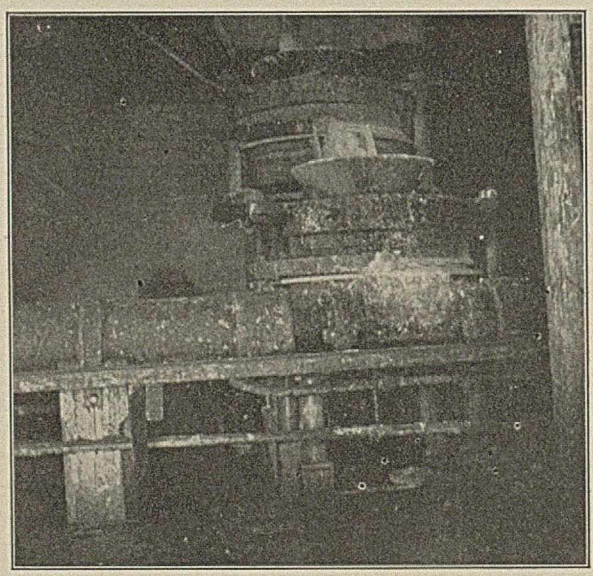

Fig. 5.—Mixer.

sun. When dry it is removed by means of a shovel, passed through chutes to the room below called the "mixing room." Two mixing machines are in this room, one at the north end and another at

the south end. In these machines about 32 lbs. of linseed oil are mixed with 500 lbs. of white lead. Two kinds of linseed oil are used—boiled and unboiled. Boiled oil serves as a bleaching agent. The ratio of boiled to unboiled oil is approximately 1 to 1. "Pulp lead," *i. e.*, white lead which has never been, dried is also mixed with oil at the rate of 11 lbs. oil to 100 lbs. white lead. Some is mixed with oil by taking it one-half pulp and one-half dried. It is preferred this way by a great many painters. Again: a great deal is shipped without being mixed with oil at all, either as pulp, dried, or a mixture of the two.

From each mixing machine the white lead is conveyed by means of screw conveyors placed horizontally near the floor. At various intervals there are pipes passing through the floor to hoppers leading into machines on the ground floor in which the mixing is completed. A great deal of heat is generated in these machines due to the saponifying action of the oil on the $Pb(OH)_2$. The machines are kept cool by cold water circulating through conduits encircling the machines.

With these machines the Carter Process of White Lead Manufacture ends. From the exits of these machines it is packed into kegs varying in capacity from 12½ to 500 lbs. The daily output of the Omaha plant is about 32,000 lbs.

[Contribution from the Department of Agricultural Chemistry of the University of Missouri.]

COMPOSITION OF THE FAT OF BEEF ANIMALS ON DIFFERENT PLANES OF NUTRITION.

(First Paper.)

By C. R. Moulton and P. F. Trowbridge.

The present paper is a study of the changes effected upon the fats of beef animals when subjected to different planes of nutrition. In connection with the work on the flesh of steers and the influence of feed, breed, and age on the development of the various parts of the steer's organism and on the chemical composition of the same, which work is being carried on at the Missouri Agricultural College Experiment Station, it has been thought advisable to investigate the factors affecting the composition of the fats. Only the effects of condition and of resorption, with a slight reference to age, are considered here.

HISTORICAL.

The interrelation of the water and fat content of the animal body has been pointed out by Carl Voit.[1] He says in substance: In the case of bad nourishment the whole body becomes watery; a well-nourished organism contains on the contrary more dry substance since in it there is more fatty tissue with less water content. The effect of partial starvation has been studied by S. Hatai.[2] He noted that partial starvation gave a high per cent. of water and a low per cent. of ether alcohol extract in the central nervous system of albino rats.

M. A. Muntz[3] in his work with fat beef animals has shown that with fat animals the fat is very poor in the amount of solid fats, olein predominating to a great extent. Thin animals have a higher melting point and lower liquid fatty acid content.

Concerning the effect of situation in the animal body Victor Subbotin,[4] working with dogs, and M. A. Muntz,[5] working with the fat of sheep, have shown that the subcutaneous fats have lower melting points, lower content of palmitin and stearin, and higher content of olein than have the internal fats. W. Lummert[6] and v. Raumer[7] substantiate these results. V. Henriques and C. Hansen[8] draw the following conclusions from their work on various animals. The farther from the surface the lower the iodine value of the fat. The interior of the body is warmer than the surface and it seems possible that the temperature at which the fat is stored up in the body has an effect on its chemical composition. O. Lemmerman and G. Linkh[9] make similar observations.

The greater part of the work concerning the effect of age has been with the fats of human beings. The results lead to the conclusion that the melting point and solid fatty acid content decrease with age. König and Schluckebier[10] as the result of their work with pigs come to an entirely opposite conclusion. They state that the melting point of the fats increases with the age of the animal while the iodine values fall.

In Lawes and Gilbert's classical work the weights of fatty tissue are recorded but no work was done upon the composition of the fats. There is a deficiency in the amount of available data concerning the fats of beef animals.

[1] Herman's *Handb. d. Physiol.*, **6**, 1–575 (1881).
[2] *Amer. Jour. Physiol.*, **18**, 309–320 (1907).
[3] *Comptes Rend. des Seances*, **90**, 1175 (1880).
[4] *Zeit. für Biologie*, **6**, 73–94 (1870).
[5] *Loc. cit.*
[6] *Pflueger Archiv*, **71**, 176–208 (1898).
[7] *Zeit. f. angew. Chemie*, **1897**, 210, 247.
[8] *Abstract, Jahresb. ü. Tierchemie*, **30**, 57 (1900).
[9] *Landw. Jahrb.*, **32**, 635–653 (1903).
[10] *Zeit. f. d. Unters. d. Nahr. und Genussm.*, **15**, 641.

EXPERIMENTAL.

The animals investigated were chiefly those used in the regular experiments of the Missouri Station.

Samples of fat from specific parts of the body of the steer were taken as the carcass hung in the cooler. All such samples were taken from the left side. The right half of the carcass was cut into the various wholesale cuts and a hand separation made of the lean, fat, and bone. After a thorough grinding and mixing samples were taken of the fats. In all cases a large enough sample was taken to allow for the determination of water, fat, nitrogen, ash, and phosphorus and to still leave a sufficiently large sample for rendering. The samples of fat were rendered on the hot water bath, squeezed through muslin, and then filtered through paper filters. The clear fats were collected in sample bottles and dried in a vacuum oven at 60° C. and a pressure of —60 cm. All of the samples were kept in cold storage at a temperature a little above freezing.

The fresh samples of fatty tissue—from two to four days old—were analyzed as follows:

Moisture Content.—The moisture content was determined by the Benedict vacuum method as further modified for use in this laboratory.[1]

Fat.—The thimbles from the above determination were placed in Soxhlet extractors and extracted for twenty-four hours with ether distilled from sodium. The ether remaining in the thimble was driven off at a temperature not to exceed 60° C. and the tubes were then dried in vacuum desiccators as per above. The loss in weight represented the fat content. The results were very satisfactory, the triplicates generally agreeing closely.

Protein.—Samples of from 3–5 grams were weighed out in triplicate into 9 cm. filter papers, rolled up in them, and transferred to 500 cc. Jena Kjeldahl flasks. They were then digested with sulphuric acid, using mercury and potassium sulphate. The ammonia was distilled off and determined in the usual manner, using tenth-normal hydrochloric acid and cochineal. The nitrogen found multiplied by the protein factor 6.25 gave the protein content.

METHODS OF INVESTIGATION FOR THE RENDERED FATS.

The rendered and filtered fats were kept in cold storage until they could be investigated. The tendency of the lower melting point fats to precipitate out the glycerides of the solid fatty acids on cooling was very noticeable. It was therefore necessary to melt the mass of rendered fat and mix it thoroughly. The containers were 50 cc. Erlenmeyer flasks stoppered with corks. It was thus easy to melt the sample by placing it in the air oven at 60° C. The sample was then mixed by rotating the flask and the portions for analysis were weighed out by difference while the fat was still melted. The last drop on the lip of the Erlenmeyer could be taken off by means of the cork stopper and returned to the flask. The fat was poured into the vessel used for analysis. The specific gravity, melting point, saponification value, and iodine value were determined. The methods employed were as follows:

Specific Gravity.—Sprengel tubes of 5–10 cc. capacity were made. Weighings were made of the empty tube, tube and water at 15° C., and tube and fat. The tubes were filled with fat at 100° C. and allowed to cool.

Melting Point.—This determination was carried out as per Wiley's official method as given in detail on page 133 of the Official and Provisional Methods of Analysis, Association of Official Agricultural Chemists, 1907. A flat disc of fat is placed in an alcohol water mixture and gradually heated. The temperature at which the fat rolls up into a sphere is taken as the melting point.

Saponification Value.—The saponification value was determined as given in detail on page 137 of the Official and Provisional Methods.

Iodine Value.—The iodine value was determined by the method of Wijs. The procedure was as outlined on page 136 of the Official Methods excepting that Wijs' solution was employed and the details slightly modified to agree with the accepted practice when using a Wijs solution.

CONDITION AND AGE OF STEERS AT TIME OF SLAUGHTERING.

Manner of Feeding.

Steer No. 18 was a grade shorthorn three and a half years old. He was a thin animal on maintenance, being fed 2.5 parts of grain (8 cracked corn to 1 linseed meal) to 1 part of hay. His carcass graded as a "cutter."

Steer No. 121 was a grade shorthorn three and a half years old. He was a fairly fat animal on full feed, being fed the same kind of feed as No. 18.

[1] P. F. Trowbridge, November, 1908, Proceedings of the Association of Official Agricultural Chemists (U. S. Dept. of Agriculture. Bureau of Chemistry—*Bulletin*, **122**), p. 215. L. F. Shackell, *American Journal of Physiology*, **24**, 325 (June, 1909).

He lacked sixty days of finish, but his carcass graded as number one.

Steer "Geordie" was a full blood Galloway two years old. He was a very fat show animal. His carcass was first-class beef but rather blubbery on the outside. He was fed grain 2 parts corn, 2 parts oats, 1 part bran, and 1 part alfalfa meal. He had alfalfa hay *ad libitum* and during the summer months he was on grass at night.

Steer No. 505 was a grade Hereford eleven months old. He was a fat animal on full feed, being fed 2 parts of grain (6 cracked corn, 3 whole oats, 1 linseed meal) to 1 part of hay. His carcass graded as good baby beef.

Steer No. 503 was a grade Hereford eleven months old. He was not full fed but was fed a good fair growing ration, the ratios of his feed being the same as for No. 505. His carcass graded as baby beef but a little thin and lacking finish. He was not as fat as No. 505.

The following steers belonged to the group known as "special maintenance." They were from the same sire and of the same herd of cattle, grade Herefords, and had run on grass until they were purchased for the experiment. They were then put on full feed until they were in prime condition. Their feed was 2.5 parts grain (8 corn to 1 linseed meal) to 1 part of hay. In February, 1908, steer No. 594 was killed as a check animal. The others were fed until September, 1908, when they were slaughtered.

Steer No. 594 showed shorthorn blood. He was a fat yearling (11 months) and he was in a nearly finished condition. His carcass was not as fat as No. 505 but fatter than No. 503. It graded as baby beef.

Steer No. 591 was on submaintenance from February to September, losing one-half pound a day. He was eighteen months old when killed. His carcass was very thin and graded as a "canner."

Steer No. 593 was on supermaintenance from February to September, gaining one-half pound a day. He was eighteen months old, and his carcass was in good condition grading as number two beef.

Steer No. 597 was on maintenance from February to September, neither gaining nor losing weight. He was eighteen months old, and his carcass graded as number three, being a little light for number two beef.

DISCUSSION OF DATA.

The results of the analyses are given in the following tables: Table I contains the moisture determinations in the adipose tissue, Table II the fat determinations, and Table III the protein determinations. The steers are arranged from left to right in the order of slaughtering and the fat samples in the order determined by the iodine values of steer No. 594.

TABLE I.—MOISTURE IN ADIPOSE TISSUE.

Per cent. of Total.

	Steer No. 18.	Steer No. 121.	Steer No. 505.	Steer No. 503.	Steer No. 594.	Steer No. 591.	Steer No. 597.	Steer No. 593.
Kidney fat	10.044	4.484	5.263	8.676	5.481	19.700	7.497	4.842
Offal fat	16.620	9.517	12.410	14.642	10.957	38.876	17.969	12.631
Circulatory system	.....	.....	33.230	36.244	.....	.....	.....	.....
Loin fat	.....	9.075	9.333	15.748	13.411	36.092	18.956	14.860
Head-tail fat	.....	.....	.....	.....	41.912	34.872	35.693	34.917
Inside chuck fat	25.055	11.213	9.814	21.140	14.414	47.324	20.737	15.503
Cod fat	.....	17.920	11.782	12.675	13.035	45.490	13.920	12.541
Chuck-neck fat	.....	.....	.....	.....	23.289	49.349	29.459	19.592
Rib fat	.....	10.677	10.913	23.294	14.273	40.465	21.859	19.434
Composite fat	.....	.....	.....	.....	20.047	42.366	25.492	19.989
Fat between hind legs	.....	7.204	.....	.....	.....	37.451	.....	.....
Flank fat	.....	.....	43.720	.....	19.567	47.229	22.236	18.762
Rump fat	.....	14.410	14.140	22.450	13.520	29.663	18.182	16.601
Round fat					20.754	44.868	26.640	20.927
Plate fat	.....	.....	see flank	.....	22.991	24.946	24.899	21.134
Shin-shank fat	.....	.....	.....	.....	see head-tail	51.579	40.190	41.150
Outside rump fat	14.315	10.870	13.350	16.814	13.451	.....	26.920	21.238
Outside rib fat	25.265	29.255	13.200	17.475	14.673	64.764	26.158	20.375
Same inner layer	.....	.....	6.957	.....	.....	.....	.....	.....
Outside chuck fat	23.280	.....	.....	.....	.....	.....	.....	.....
Brisket fat	.....	.....	.....	.....	.....	56.221	27.651	25.568
Marrow fat	.....	.....	.....	.....	.....	18.006	11.491	.....

An inspection of these three tables shows that the percentages of moisture, fat, and protein are dependent upon the degree of fatness or condition of the animal. The fatty tissue of the thin animal in each and every case contains more protein and more moisture and less fat than does the fatty tissue of the fat animal. The order of increasing per cent. of fat and decreasing per cent. of moisture

TABLE II.—FAT IN ADIPOSE TISSUE.

Per cent. of Total.

	Steer No. 18.	Steer No. 121.	Steer No. 505.	Steer No. 503.	Steer No. 594.	Steer No. 591.	Steer No. 597.	Steer No. 593.
Kidney fat	86.96	9.47	93.53	89.47	93.16	75.85	90.22	93.75
Offal fat	79.72	88.02	85.38	81.92	85.87	52.59	77.88	84.00
Circulatory system	.....	.....	59.06	54.91	.....	.....	.....	.....
Loin fat	.....	87.84	87.55	79.92	82.47	50.62	73.76	80.50
Head-tail fat	.....	.....	.....	.....	44.84	48.37	49.97	51.78
Inside chuck fat	68.80	86.84	88.21	73.80	81.56	36.46	71.74	79.28
Cod fat	.....	78.51	85.85	83.45	83.18	40.79	81.23	83.88
Chuck-neck fat	.....	.....	.....	.....	70.25	31.77	58.72	71.85
Rib fat	.....	86.04	85.39	66.94	80.82	34.83	70.19	70.97
Composite fat	.....	.....	.....	.....	72.90	37.69	62.82	73.10
Fat between hind legs	.....	90.64	.....	.....	.....	46.42	.....	.....
Flank fat	.....	.....	42.76	.....	72.58	25.05	68.20	72.73
Rump fat	.....	80.61	80.64	70.13	82.36	59.15	74.18	78.28
Round fat					71.01	39.64	63.61	69.09
Plate fat	.....	.....	see flank	.....	69.75	66.63	66.17	66.52
Shin-shank fat	.....	.....	.....	.....	see head-tail	25.64	44.31	40.47
Outside rump fat	80.63	86.56	83.64	78.37	83.48	.....	62.05	40.47
Outside rib fat	66.30	64.72	83.66	76.94	81.69	8.27	67.23	73.91
Same-inner layer	.....	.....	91.67	.....	.....	.....	.....	.....
Outside chuck fat	69.55	.....	.....	.....	.....	.....	.....	.....
Brisket fat	.....	.....	.....	.....	.....	25.80	65.40	68.66
Marrow fat	.....	.....	.....	.....	.....	79.57	87.30	.....

and protein is independent of age and is given in the following tabulation:

(1) Steer 591 very thin, graded as canner.
(2) Steer 503 fair condition, had never been fat.
(3) Steer 18 thin, graded as cutter.
(4) Steer 597 thin, graded as No. 3.
(5) Steer 594 rather fat baby beef.
(6) Steer 593 fairly fat No. 2 carcass.
(7) Steer 505 very fat baby beef.
(8) Steer 121 fairly fat No. 1 prime beef.

The packing houses grade their beef as follows: No. 1 is prime fat beef; No. 2 is a thinner carcass but very good; No. 3 is next in order; a cutter is poorer stuff than No. 3; and a canner is poorer than a cutter. Baby beef may vary in fatness either above or below No. 2, but it seldom is as fat as No. 1.

The internal fats contain less moisture and protein and more fat than do the skeletal samples and these again less moisture and protein and more fat than do the subdermal samples. In every case the kidney fat contains least moisture and protein and the offal fat ranks next. As an exception to this we may note that the inside chuck fat in the thinnest animals contains more moisture and protein than do some of the external samples. The marrow fat contains least protein, as is to be expected from the mealy consistency of marrow. The marrow fat of the thin animal 591 contains about 80 per cent. more moisture than does the marrow of the

TABLE III.—PROTEIN IN ADIPOSE TISSUE.

Per cent. of Total.

	Steer No. 18.	Steer No. 121.	Steer No. 505.	Steer No. 503.	Steer No. 594.	Steer No. 591.	Steer No. 597.	Steer No. 593.
Kidney fat	2.63	1.13	1.48	2.13	1.66	4.78	1.88	1.15
Offal fat	3.23	1.71	2.13	3.26	2.73	7.30	3.03	2.70
Circulatory system	....	....	8.03	7.81	....	.....	....	....
Loin fat	....	2.48	3.34	4.86	4.03	11.95	6.29	3.42
Head-tail fat	....	....	....	....	12.46	10.74	9.99	9.91
Inside chuck fat	5.95	1.95	2.27	5.09	3.71	10.78	5.71	3.94
Cod fat	....	2.91	2.87	4.88	3.95	10.70	3.87	3.47
Chuck-neck fat	....	....	.....	....	6.73	14.13	8.66	5.27
Rib fat	....	2.83	4.02	9.26	5.25	16.43	7.04	8.01
Composite fat	....	....	....	....	7.76	13.84	9.21	6.95
Fat between hind legs	....	1.92	....	....	....	11.51	....	....
Flank fat	....	....	13.81	....	6.77	27.57	8.74	8.86
Rump fat	....	3.86	2.82	7.58	4.52	12.05	5.87	4.79
Round fat					6.91	16.53	8.89	7.76
Plate fat	....	....	see flank	....	7.49	7.43	7.24	7.11
Shin-shank fat	....	....	....	....	see head-tail	19.76	15.23	17.44
Outside rump fat	4.89	2.48	2.76	5.14	4.94	.....	7.88	4.61
Outside rib fat	7.34	2.18	2.76	5.41	3.47	25.94	6.02	5.30
Same inner layer	....	....	1.54	....	....	.....	....	....
Outside chuck fat	6.48	....	....	....	....	.....	....	....
Brisket fat	....	....	....	....	....	14.53	5.83	5.80
Marrow fat	....	....	....	....	....	0.73	0.87	....

TABLE IV.—IODINE VALUES OF FATS.

	Steer No. 18. Thin, 3½ yrs.	Steer No 121. Fat, 3½ yrs.	Geordie, very fat, 2 yrs.	Steer No. 505. Very fat, full fed, 11 mo.	Steer No. 503. Fair, not full fed, 11 mo.	Steer No. 594. Fat, 11 mo., check animal.	Steer No. 591. Very thin, 18 mo.	Steer No. 597. Thin, 18 mo.	Steer No. 593. Fairly fat, 18 mo.
Kidney fat	33.41	40.84	32.90	34.95	29.50	33.25	33.54	32.44	34.10
Offal fat	33.97	38.39	.....	34.72	30.60	36.49	32.80	35.55	37.48
Circulatory system	.....	.....	.....	31.78	31.17	.....	.....	.....	.....
Loin fat	.....	43.64	.....	39.50	32.30	41.85	38.30	39.12	41.31
Head-tail fat	.....	.....	.....	.....	.....	.....	35.35	41.04	42.38
Inside chuck fat	45.88	46.90	.....	40.56	34.04	43.20	40.40	40.15	42.58
Cod fat	.....	46.67	.....	46.58	36.57	44.27	44.48	41.80	46.91
Chuck-neck fat	.....	.....	.....	.....	.....	44.75	39.93	42.44	45.05
Rib fat	.....	45.18	.....	44.61	36.32	45.02	36.58	42.25	47.14
Composite fat	.....	.....	.....	.....	.....	45.90	36.74	42.59	45.54
Fat between hind legs	.....	44.83	.....	.....	.....	.....	41.51	.....	.....
Flank fat	.....	.....	.....	45.32	.....	46.23	43.68	44.16	47.36
Rump fat	.....	46.32	.....	44.05	37.13	47.55	39.55	40.70	42.89
Round fat						49.25	44.53	45.07	48.32
Plate fat	.....	.....	.....	see flank	.....	49.44	47.11	47.46	48.53
Shin-shank fat	.....	.....	.....	.....	.....	.....	47.29	50.60	51.95
Outside rump fat	43.22	49.29	.....	51.07	43.29	50.11	.....	49.82	54.48
Outside rib fat	51.64	54.25	51.11	51.12	40.95	51.40	.....	.....	.....
Same-inner layer	.....	.....	49.35	45.95	.....	.....	.....	.....	.....
Outside chuck fat	46.68	.....	.....	.....	.....	.....	.....	.....	.....
Brisket fat	.....	.....	49.82	.....	.....	.....	53.49	55.57	59.75
Marrow fat	.....	.....	.....	.....	.....	.....	58.93	53.92	.....

fatter steer 597. The cod fat, on account of its situation in the scrotum and its being protected from the cold by the legs and body of the steer, acts more like an internal than like an external fat.

The physical and chemical constants of the rendered fats are given in Tables IV–VI. Table IV contains the iodine values, Table V the melting points, and Table VI the saponification values and the specific gravity of the fats of steer 594. The same order of steers and samples is adhered to.

By the study of Table IV it is clearly seen that the iodine values increase from inside to oustide while the melting points decrease in the same order. The cod fat again acts as inside fat. The order of increasing iodine values holds from inside to outside and is as follow: kidney, offal, circulatory, loin, head and tail, inside chuck, cod, chuck and neck, rib, composite, between hind legs, flank, rump, round, plate, shin and shank, outside rump, outside rib, marrow, and brisket. The values for the melting points (see Table V) do not decrease as uniformly, but they follow the same order in general. It appears that the rump fat might better take its position with the inside fats. This can be explained by the position of the cut. The rump lies on either side of the rectum near the tail. The high temperature maintained throughout the digestive tract extends to the end of the rectum. The fats closely surrounding this region would therefore be internal fats. The rump preponderates in this

TABLE V.—MELTING POINTS OF FATS.

	Steer No. 18.	Steer No. 121.	Geordie.	Steer No. 505.	Steer No. 503.	Steer No. 594.	Steer No. 591.	Steer No. 597.	Steer No. 593.
Kidney fat	47.40	45.05	46.30	46.30	47.88	48.10	47.00	48.10	47.30
Offal fat	48.58	45.20	.....	45.30	48.15	47.10	47.50	47.30	46.30
Circulatory system	.....	.....	.....	45.95	48.10	.....	.....	.....	.....
Loin fat	.....	41.95	.....	43.00	46.75	45.60	46.00	44.70	43.90
Head-tail fat	.....	.....	.....	.....	.....	.....	45.00	45.20	43.50
Inside chuck fat	41.75	40.50	.....	41.75	46.05	44.95	44.80	44.20	43.10
Cod fat	.....	39.85	.....	41.20	45.25	43.25	41.50	43.00	40.00
Chuck-neck fat	.....	.....	.....	.....	.....	43.80	44.70	43.00	41.50
Rib fat	.....	40.30	.....	39.80	46.55	43.10	46.10	43.60	41.00
Composite fat	.....	.....	.....	.....	.....	43.60	44.70	44.30	42.00
Fat between hind legs	.....	39.65	.....	.....	.....	.....	42.80	.....	.....
Flank fat	.....	.....	.....	44.90	.....	42.25	42.50	43.00	41.70
Rump fat	.....	39.60	.....	40.35	44.65	43.55	44.60	44.00	44.10
Round fat						41.30	42.40	41.70	41.30
Plate fat	.....	.....	.....	see flank	.....	42.40	42.70	42.00	40.70
Shin-shank fat	.....	.....	.....	.....	.....	.....	40.70	39.40	38.50
Outside rump fat	41.65	35.25	.....	36.60	42.60	39.90	.....	38.70	35.70
Outside rib fat	38.38	35.55	33.20	36.90	44.60	40.70	.....	38.30	34.80
Same-inner layer	.....	.....	35.35	38.70	.....	.....	.....	.....	.....
Outside chuck fat	38.95	.....	.....	.....	.....	.....	.....	.....	.....
Brisket fat	.....	.....	33.85	.....	.....	.....	35.50	35.10	32.10
Marrow fat	.....	.....	.....	.....	.....	.....	25.70	38.10	.....

sort of fat. The position of the head and tail sample among the internal fats is explained by the head fats alone. A larger part of the fat composing this sample is taken from within the jaws and the cavities of the cranium, such as the orbital cavities, and from the region of the tongue. It is thus mostly internal fat. The shin and shank on the contrary is entirely external fat, the fat being taken from between the hide and the bones. The chuck and neck and the rib samples contain in the one case considerable fat located within a heavily muscled region and along the neck and thoracic cavity and in the other case fat lying near the digestive organs. So their position near the head of the carcass cuts is explained. The loin contains a large piece of kidney fat and it would thus be placed first of the carcass cuts. It will be seen that the youngest and thinnest animal has the lowest iodine values and highest melting points and that these vary as the increasing age and fatness of the animal, the very fat three and a half years old steer being highest in iodine values and lowest in melting points.

The saponification values for but six steers have been determined, and these show little relation to the location. A tendency may be noted showing that the saponification values decrease as do the melting points and go inversely to the iodine values. The values for specific gravity of one animal, given in Table VI, show but slight variations. There can be noted a tendency to follow the iodine values.

Table VII contains the iodine values of the fats in each sample, the steers being arbitrarily arranged in an order dependent upon their age and fatness. The order is as follows: *First*, steer 503, an eleven months old animal in fair condition but never at any time fat. Its age gave it the grade of baby beef. *Second*, steer 591, an eighteen months, very thin animal which had however been fat. It graded as low as a canner. Its having once been fat as well as its greater age place it above steer 503. *Third*, steer 597, thin, 18 months old, had been fat and graded as number 3; being fatter than 591 it would rank above it. *Fourth*, steer 18, a thin, three and a half years old animal grading as a cutter. Its greater age assisted by its having once been fat place it above 597. *Fifth* and *sixth*, steer 505 and steer 594. These two steers were 11 months old and both fat. Although steer 505 was judged to be the fatter of the two it is placed fifth in order. It is, however, difficult to decide between

TABLE VI.—SAPONIFICATION VALUES OF FATS.

	Steer No. 18.	Steer No. 121.	Geordie.	Steer No. 505.	Steer No. 503.	Steer No. 594.	Specific gravity 100°/15° C. Steer No. 594.
Kidney fat	197.7	197.0	197.5	192.3	199.9	195.2	0.8604
Offal fat	198.8	195.8	.....	197.7	197.2	199.1	0.8568
Circulatory system	.....	.....	.....	201.7	196.1	.....	.....
Loin fat	.....	193.3	.....	200.4	189.4	196.2	0.8582
Head-tail fat	.....	.....	.....	.....	.....	.....	.....
Inside chuck fat	196.7	197.9	.....	199.3	197.5	195.5	0.8586
Cod fat	.....	199.5	.....	197.1	197.2	196.9	0.8589
Chuck-neck fat	.....	.....	.....	.....	.....	195.1	0.8602
Rib fat	.....	198.8	.....	200.4	185.2	197.9	0.8615
Composite fat	.....	.....	.....	.....	.....	197.0	0.8592
Fat between hind legs	.....	201.1	.....	.....	.....	.....	.....
Flank fat	.....	.....	.....	184.8	.....	194.0	0.8593
Rump fat	.....	194.30	.....	196.7	197.8	195.4	0.8591
Round fat						195.6	0.8606
Plate fat	.....	.....	.....	see flank	.....	196.0	0.8606
Shin-shank fat	.....	.....	.....	.....	.....	.....	.....
Outside rump fat	190.7	195.7	.....	196.0	183.1	196.6	0.8609
Outside rib fat	200.2	180.6	197.1	186.6	182.7	196.9	0.8605
Same-inner layer	.....	.....	202.3	199.2	.....	.....	.....
Outside chuck fat	199.1	.....	.....	.....	.....	.....	.....
Brisket fat	.....	.....	206.1	.....	.....	.....	.....
Marrow fat	.....	.....	.....	.....	.....	.....	.....

TABLE VII.—IODINE VALUES.

	Steer No. 503.	Steer No. 591.	Steer No. 597.	Steer No. 18.	Steer No. 505.	Steer No. 594.	Steer No. 593.	Steer No. 121.
Marrow fat	.....	58.93	53.92	.....	.....	.....	.....	.....
Brisket fat	.....	53.49	55.57	.....	.....	.....	59.75	.....
Shin-shank fat	.....	47.29	50.60	.....	.....	.....	51.95	.....
Outside rib fat	40.95	.....	.....	51.64	51.12	51.40	.....	54.25
Outside rump fat	43.29	.....	49.82	43.22	51.07	50.11	54.48	49.29
Plate fat	.....	47.11	47.46	.....	.....	49.44	48.53	.....
Round fat	.....	44.53	45.07	.....	.....	49.25	48.32	.....
Cod fat	36.57	44.48	41.80	.....	46.58	44.27	46.91	46.67
Flank fat	.....	43.68	44.16	.....	.....	46.23	47.36	.....
Chuck-neck fat	.....	39.93	42.44	.....	.....	44.75	45.05	.. ..
Rump fat	.....	39.55	40.70	.....	.....	47.55	42.89	.. ..
Composite fat	.....	36.74	42.59	.....	.....	45.90	45.54	.....
Rib fat	36.32	36.58	42.25	.....	44.61	45.02	47.14	45.18
Inside chuck fat	34.04	40.40	40.15	45.88	40.56	43.20	42.58	46.90
Head-tail fat	.....	35.35	41.04	.....	.....	.....	42.38	.....
Loin fat	32.30	38.30	39.12	.....	39.50	41.85	41.31	43.64
Offal fat	30.60	32.80	35.55	33.97	34.72	36.49	37.48	38.39
Kidney fat	29.50	33.54	32.44	33.41	34.95	33.25	34.10	40.84
Circulatory system	31.17	.....	.....	.....	31.78	.....	.....	.....

the two. *Seventh*, steer 593, eighteen months old, and pretty fat, graded as number two beef. His age places him above the eleven months animals as well as does his fatness, and this places him above all the steers excepting steer 121. *Eighth*, steer 121, three and a half years old and fat. Steer Geordie was not included since but four of his fats were investigated. Investigation of the values demonstrates the validity of the above grading.

A source of considerable complication in the grading of the samples of fat from outside to inside including the carcass cuts is this: that in all but the special samples the fat composing the sample is taken from three separate and opposing regions. The carcass cuts contain fat which is purely subdermal, fat which is entirely internal, and fat which is intramuscular and between internal and external. As examples, note the chuck and the round. The chuck has subdermal fat and frequently large rolls over the shoulder. Then there is the fat lining the thoracic cavity and the inside of the neck. There is also beneath the scapulo-humeral, or shoulder joint, a large pad of fat, which is probably a relic of its wild state and which was used to protect this joint and the muscles of the animal when jumping. The round has in addition to external fats a long ridge of fat running the greater part of the length of the femur. The loin has the external rolls of fats and the entirely different kidney fat. In order to remove these complications there are given in Table VIII the iodine values of the special samples only. The fat in any one sample is all of one kind. The steers are divided into two groups, the young steers (11 to 18 mo.) and the old steers (2 to 3½ years). This was done to avoid complications of age. The order for the young steers is as given just above. Geordie has been included among the old steers, and as he was but two years old though very fat he grades below the thin steer 18.

We may consequently state that the iodine values increase with both age and fatness. Since the relations between melting point and iodine value has been clearly demonstrated the melting point decreases with both age and fatness. As the animal increases in fatness the ratio of fat to water and protein increases. A fat animal placed upon a ration which is insufficient to support growth and maintenance will use his stored up fat for this purpose. He will take fat out of the fat cells and replace it with water. He will use up the lower melting point fats (olein) first and the fat that remains in the tissue will be of higher melting point (stearin). In confirmation of this, witness the increasing melting point and falling iodine value of the fat of the thin steer. The fatty tissue of the thin steer being soft and flabby is due to the great water content and not to a great olein content.

TABLE VIII.—IODINE VALUES OF SPECIAL SAMPLES.

	Steer No. 503.	Steer No. 591.	Steer No. 597.	Steer No. 505.	Steer No. 594.	Steer No. 593.	Steer Geordie.	Steer No. 18.	Steer No. 121.
Marrow fat	.....	58.93	53.92	.....	.....	.....	.....	.....	.....
Brisket fat	.....	53.49	55.57	.....	.....	59.75	49.82	.....	.....
Outside rump fat	43.29	.....	49.82	51.07	50.11	54.48	.....	43.22	49.29
Outside rib fat	40.95	.....	.....	51.12	51.40	.....	51.11	51.64	54.25
Same-inner layer	.....	.....	.....	45.95	.....	.....	49.35	.....	.....
Outside chuck fat	.....	.....	.....	.....	.....	.....	.....	46.68	.....
Cod fat	36.57	44.48	41.80	46.58	44.27	46.91	.....	.....	46.67
Fat between hind legs	.....	41.51	.....	.....	.....	.....	.....	.....	44.83
Inside chuck fat	34.04	40.40	40.15	40.56	43.20	42.58	.....	45.88	46.90
Offal fat	30.60	32.80	35.55	34.72	36.49	37.48	.....	33.97	38.39
Kidney fat	29.50	33.54	32.44	34.95	33.25	34.10	32.90	33.41	40.84
Circulatory system	31.17	.....	.....	31.78	.....	.....	.....	.....	.....

CONCLUSIONS.

In the fatty tissue of animals the amounts of fat and of moisture and protein are intimately connected, a high per cent. of fat being accompanied by a low per cent. of moisture and protein.

In the fatty tissue the per cent. of fat increases with the fatness of the animal while the moisture increases with the leanness. This is dependent upon condition irrespective of age.

The per cent. of fat in the fatty tissue of animals is dependent upon the location in the animal body. The per cent. of fat increases from outside to inside while the per cent. of moisture increases from inside to outside.

The iodine value of fat from the fatty tissue of an animal increases with the age of the animal while the melting point decreases.

The iodine value of fat from the fatty tissue of an animal increases with the fatness of the animal while the melting point decreases.

The iodine value of fat from the fatty tissue of animals increases from inside to outside of the animal body while the melting point decreases.

The iodine value and melting point are closely related, the one rising as the other falls.

The specific gravity seems to follow the iodine value while the saponification value varies as the melting point.

Credit is here given Mr. J. O. Halverson for the determination of part of the iodine and saponification values and melting points.

COLUMBIA, MISSOURI,
June, 1909.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW YORK AGRICULTURAL EXPERIMENT STATION.]

A VOLUMETRIC METHOD FOR THE DETERMINATION OF CASEIN IN MILK.[1]

By LUCIUS L. VAN SLYKE AND ALFRED W. BOSWORTH.

In 1892 there was worked out in the chemical laboratory of this station a method for the determination of casein in cow's milk.[2] This method, after careful trial by the Association of Official Agricultural chemists, was adopted as "official."[3] It was realized that the method was adapted only for use in well-equipped laboratories and in the hands of trained chemists. Unsuccessful efforts were made at different times to devise a simple, direct volumetric method, requiring less apparatus, time, manipulation and skill. Several attempts have been made by others to find such a method, among which we mention the following: (1) Estimation of casein, a preliminary study.[4] (2) Quantitative estimation of casein.[5] (3) A new method for the determination of casein.[6] These and other proposed methods are open to several practical objections.

In making a study of the accuracy of the results given by the method of Matthaiopoulos, it was found that a reconstruction of its details could easily be utilized in devising a method of equal accuracy but of much greater simplicity and rapidity.

The method which has been thus worked out is, in brief, as follows: A given amount of milk, diluted with water, is made neutral to phenolphthalein by addition of a solution of sodium hydroxid. The casein is then completely precipitated by addition of standardized acetic acid; the volume of the mixture is made up to 200 cc. by addition of water and then filtered. Into 100 cc. of the filtrate a standardized solution of sodium hydroxid is run until neutral to phenolphthalein. From the difference between the amount of acid and the amount of alkali used, a simple calculation enables one to determine the percentage of casein in the milk examined.

This method is based upon the following well-known facts: (1) Uncombined casein is insoluble in milk-serum, or water, or very dilute acids.[1] (2) It is acid in properties and combines with alkalis to form definite chemical compounds, which are neutral to phenolphthalein.

Of the total amount of acid used in the process of precipitating casein, a portion is taken to set casein free from combination, thus forming a soluble neutral salt and an insoluble compound (free casein) possessing the properties of an acid; and, on filtration, this amount of acid, as free casein, is removed from the mixture. The balance of the acid used in the process is accounted for in the filtrate on titration with alkali. Therefore, the difference between the total amount of acid used and that accounted for in the filtrate by titration with alkali represents the amount of acid corresponding to the casein present in the milk examined.

Since one gram of free casein neutralizes 8.8378 cc. of tenth-normal sodium hydroxide (or 1 cc. of tenth-normal sodium hydroxide equals 0.11315 gram of casein),[2] we have a definite basis for estimating the amount of casein in any given case, when we know the amount of alkali it neutralizes.

DESCRIPTION OF METHOD.

(1) *Measuring and Diluting Sample of Milk.*

The milk to be examined is well mixed and 20 cc. run into a 200 cc. flask, to which is added about 80 cc. of water.

(2) *Neutralizing the Milk.*

Add 1 cc. of phenolphthalein solution to the diluted milk and then run into it a solution of a sodium hydroxid until a faintly, but distinctly, pinkish shade of color remains through the mixture even after considerable agitation. Any marked excess of alkali should be avoided.

(a) *Preparation of a Color-standard.*—More uniform and satisfactory results can be obtained in this step of the process by preparing a color-standard for comparison. Our method of accomplishing this is as follows: about 20 cc. of

[1] Presented in abstract at the meeting of the American Chemical Society, Detroit, June, 1909.

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[1] L. L. Van Slyke and D. D. Van Slyke, *Am. Chem. J.*, **38**, 409.

[2] *Z. anal. Chem.*, **47**, 495.

fresh skim-milk and 80 cc. of water are put into a 200 cc. flask and a small amount of mercuric chlorid added. A few drops of ordinary carmine ink are considerably diluted with water and this is carefully added, a few drops at a time, to the diluted skim-milk until a faint but distinct pinkish coloration appears. This can be more readily and accurately perceived by placing beside the flask another flask half full of uncolored, diluted skim-milk. The coloration must be as slight as possible and yet be appreciably distinct when compared with uncolored milk. After the color-standard has been prepared, the flask is stoppered and kept in a dark place when not in use. With some carmine colors, the pinkish shade in the milk may deepen on standing, especially when exposed to light. If at any time this is observed, the proper shade can be reproduced by slight dilution with skim-milk. The object of using skim-milk in preparing a color-standard is to avoid the presence of fat, which, in case of whole milk, separates on standing, adheres to the sides of the flask and obscures the color.

(*b*) *Use of Color-standard.*—In neutralizing a sample of milk, the color-standard is placed beside the sample under examination for constant comparison after each addition of alkali. The flasks should be placed on a white surface and in a good light in order to render more sharp the observation of the coloration. In fresh milks, it is usually found that 3 or 4 cc. of tenth-normal alkali are sufficient to neutralize the milk. In cases where milk is not strictly fresh or where it has been kept for some time with mercuric chlorid, usually from 5 to 10 cc. may be required. After the milk begins to show signs of neutrality, the alkali is added a drop at a time, the flask being shaken and the color being observed after each addition.

(3) *Precipitation of Casein.*

(*a*) *Addition of Acid.*—Into the neutralized sample of diluted milk, which should be at a temperature of 18° C. to 24° C., one now runs tenth-normal acetic acid, adding the acid approximately in 5 cc. portions and agitating vigorously for a few seconds after each addition. It is usually safe to add about 25 cc. of acid before examining the milk to see if the casein is separating in the form of white flakes. After adding 25 cc. and shaking, the mixture is allowed to come to rest. If enough acid has been added, the casein separates promptly in large, white flakes, and, on standing a short time, the liquid above the settled casein appears clear and not at all milky. If the addition of 25 cc. of acid is insufficient to separate the casein properly, add 1 cc. more of acid and shake; continue the addition of acid, 1 cc. at a time, until the casein is observed to separate promptly and completely on standing at rest a short time. The number of cc. of acid used to affect precipitation is noted and this result is recorded as A.

(*b*) *Influence of Temperature.*—For convenience and uniformity of results, the temperature of the mixture at the time of the addition of acid may be between 18° and 24° C. Under these conditions, we have found that in most of the milks with which we have worked, 30 cc. of tenth-normal acetic acid gives satisfactory results. In some cases, especially with the milk of cows far along in lactation and high in casein (3.5 to 4 per cent.), we have had to use as high as 35 to 40 cc. of acid. We have seldom found any case in which 25 cc. of acid was excessive. The amount of acid may be 2 or 3 cc. in excess of that required to effect complete precipitation without seriously affecting the accuracy of the results, provided the temperature of the mixture is below 24°. At higher temperatures, good results are attainable, but care must be exercised not to use much excess of acid; and, of course, the higher the temperature, the less will be the amount of acid required for precipitation. Extra care must be used at higher temperatures in regard to the use of any marked excess of acid for the following reason: The higher the temperature, the more easily does casein dissolve in the presence of free acid,[1] the effect being to reduce the results of the determination in percentage of casein. In working at temperatures under 18°, the casein separates more slowly or requires more acid to separate promptly. In case of milk that is much below 18°, it is well to use for dilution water that is at a temperature of about 27°.

(4) *Filtration of Casein.*

After the casein is completely precipitated, water is added to the mixture up to the 200 cc. mark and the contents are vigorously shaken for 10 or 15 seconds, in order to make the distribution of acid through the mixture as uniform as possible. The contents of the flask are then poured upon a dry filter. It is well generally to allow the filtration to continue until practically all of the liquid has been filtered.

[1] *Am. Chem. J.*, **38**, 409.

(*a*) *Rapidity of Filtration.*—The usual time of filtration should not exceed 3 to 5 minutes, when precipitation is complete. The rapidity depends upon the temperature of precipitation and the completeness of the separation of casein. In general, the higher the temperature of the mixture when precipitated with acid, the more rapid should be the filtration, other conditions being uniform. In case of insufficient acid, the filtration is slower.

(*b*) *Appearance of Filtrate.*—The filtrate should be quite clear, though this is not always a sure indication that the right amount of acid has been added to effect complete precipitation and release casein entirely from its combination. Sometimes the filtrate may be clear when not quite enough acid has been added, in which case the percentage of casein found is apt to be low; under such circumstances, filtration is usually slow. In case of milk rich in fat, a slight turbidity may appear, due to fat-globules in the filtrate. The filtrate should be free from all signs of marked turbidity or anything like milkiness. If such a filtrate appears, a new sample of milk should be taken and the operation repeated from the beginning, more acid being used than before.

(5) *Titration with Alkali.*

After filtration is completed, one takes 100 cc. of the filtrate and runs into it tenth-normal solution of sodium hydroxide until the reaction is neutral to phenolphthalein. The number of cubic centimeters of alkali used is noted and this result is recorded as B. The exact neutral point is not perfectly sharp on account of the presence of phosphates, and the appearance of the end-reaction is not as pronounced as might be desired. However, with experience one should have no difficulty in getting within one drop of the correct amount of alkali. One should work to obtain the same shade and duration of color every time. In general, one takes for the end-reaction the appearance of a faint but distinct pink coloration, which remains clearly marked through the solution for half a minute or longer before beginning to fade. In the case of milks rich in phosphates, the solution usually grows quite turbid as the neutral point is approached, making it more necessary to use caution in observing the color of the end-point of the reaction.

If one desires to make a second titration of the same filtrate, one can use 50 cc. of the remaining portion, multiplying the result by 2 and recording this as B.

(6) *Calculation of Results.*

The calculation of the percentage of casein from (*a*) the amount of acid used (A) in precipitating the casein and (*b*) the amount of alkali used (B) in neutralizing 100 cc. of filtrate, is very simple. Divide A by 2, from the result subtract B and multiply the result by 1.0964; or expressed as a formula,

$$(A/2 - B) \times 1.0964 = \text{Per cent. of casein.}$$

By using 22 cc. of milk instead of 20 cc., the multiplication by the factor can be obviated, the formula then becoming simply $A/2 - B$, each cc. of tenth-normal solution being equivalent to 1 per cent. of casein.

(7) *Use of Preservatives.*

In making casein determinations by this method, it is desirable when possible to use milk comparatively fresh. Milk that is sufficiently acid to coagulate on boiling or that is well soured can not be used with satisfactory results. However, by adding to fresh milk powdered mercuric chloride in the approximate proportion of 1:1000 or 1500, and then keeping the mixture in a cool place, we have been able to obtain satisfactory results with milk that had been kept for two to three weeks. Milk thus treated should be shaken often enough to keep the fat well incorporated in the body of the milk.

RESULTS ILLUSTRATING USE OF METHOD.

The data below represent the results obtained by three different workers in comparison with the "official" method. The samples of milk used were obtained from individual cows. It will be observed that results usually come within 0.2 per cent. of those obtained by the official method.

PERCENTAGES OF CASEIN IN MILKS AS DETERMINED BY DIFFERENT WORKERS.

No. of sample.	Official method.	Volumetric method. 1.	2.	3.
1	3.09	3.00	2.95	3.10
2	3.36	3.40	3.45	3.45
3	3.21	3.30	3.40	3.30
4	3.16	3.20	3.20	3.10
5	2.95	2.90	2.90	2.80
6	3.11	3.05	3.10	3.15
7	2.66	3.00	3.00	3.05
8	3.34	3.20	3.00	3.10
9	3.62	3.55	3.60	3.55
10	3.20	3.30	3.20	3.10
11	3.22	3.20	3.00	3.10
12	2.68	2.85	2.75	2.80
13	2.92	3.00	2.90	2.90
14	2.79	2.85	2.80	2.95
15	2.84	2.85	2.80	2.70

It may be stated in this connection that the use of other acids (hydrochloric and sulphuric) and of

other alkalis (hydroxides of barium and calcium) was applied to the method but did not give satisfactory results. In the Matthaiopoulos method, sulphuric acid is used. The especial advantage of dilute acetic acid, as compared with the other acids tried, lies in its smaller dissolving and adsorbing properties for casein.[1]

By this method the percentage of casein can be determined in a sample of milk in 12 to 15 minutes, when one has at hand the solutions and apparatus needed. With proper conveniences a dozen determinations can be made in 45 to 60 minutes after one has acquired acquaintance with the operations of the method.

ON THE RELATION OF NATIVE LEGUMES TO THE SOIL NITROGEN OF NEBRASKA PRAIRIES.

By F. J. Alway and R. M. Pinckney.

Received August 4, 1909.

In a recent botanical study[2] Warren has called attention to the entire absence of published data on the relation between the native legumes and the amount of nitrogen in virgin prairie soils. He expresses the opinion that the amount of combined nitrogen added by rain and snow together with the amount of free nitrogen fixed by non-symbiotic bacteria "do not furnish a satisfactory explanation of the presence of such large quantities of nitrogen in the soil." His conclusions are based upon counts, made in 1908, of the leguminous plants on measured plots in prairie fields in different parts of Nebraska and adjoining states.

In the course of an investigation, the results of which are not yet published, we had in the preceding summer and autumn made a chemical study of the same question in the case of one of the prairie fields mentioned by Warren, from whom we have learned that his count was made on an adjoining but slightly lower portion of the gently sloping field. What data we have on the native leguminous plants, together with some of that on the soil, have been assembled for the present article. The removal of the junior author to the Montana Agricultural Experiment Station, a year ago, interrupted the continuation of the study.

The prairie referred to is in University Place, a suburb of Lincoln, and since 1889 has formed a part of the campus of the Nebraska Wesleyan University. Since that time the portion of it studied by both Warren and ourselves has been mown annually for hay; during the rest of the year it has been little visited except by children in search of wild flowers. Previous to 1889 it had formed part of a large pasture. This part of the field is typical of the virgin upland prairie of eastern Nebraska, as indicated by Warren's data obtained on July 2, 1908.

On July 12 and 13, 1907, we measured off a plot 50 ft. by 50 ft. and from this gathered all the leguminous plants, cutting them at the surface of the ground. The plants were exposed on the shelves of a storeroom until they were air-dry, and then weighed, ground and analyzed. From what we considered a representative square yard on this plot the non-leguminous plants were similarly gathered, dried, weighed and analyzed. We are indebted to Dr. F. D. Heald, both for assistance in the search for legumes and for the identification of the species. Soon after the plants had been gathered the prairie was mown for hay. There was so little aftergrowth of either legumes or grasses that it was not considered worth while to make a second collection. The growth of vegetation in 1907 may safely be considered representative of an average year.

Table I.

Legumes.	Yield of air-dry matter. On plot 50 ft. × 50 ft. Grams.	Yield of air-dry matter. On 1 acre. Pounds.	N in air-dry matter. Per cent.	Wt. of N per acre. Pounds.
1. Amorpha canescens.....	6,692	256.8	2.23	5.73
2. Kuhnistera candida.....	2,700	103.6	1.85	1.92
3. Astragalus crassicarpus.....	890	34.2	2.41	0.82
4. Psoralea argophylla.....	154	5.9	1.50	0.09
Non-leguminous plants.....	65,278	2,505.3	1.13	28.31
Total.....	75,714	2,905.8	....	36.87

The aerial portion of the leguminous plants collected contained 8.56 lbs. of nitrogen per acre. The aftergrowth of legumes and the leguminous plants which may have died and disappeared before the date of collection might increase the total annual production of nitrogen in the aerial parts to 10 lbs. per acre. It is not known what portion of the total nitrogen contained in leguminous plants is that which has been fixed by the symbiotic bacteria, and accordingly, we cannot estimate how much of the 10 lbs. per acre has been derived from the nitrogen compounds in the soil. What little data we have on the growth of alfalfa on Nebraska soils indicate that the nitrogen contained in the roots is about equal to that derived from the soil

[1] *Am. Chem. J.*, **38**, 409.

[2] "Notes on the Number and Distribution of Native Legumes in Nebraska and Kansas," *Circular* **31**, *Bur. of Plant Ind., U. S. D. A.* (June, 1909).

by the entire plant. If this holds true for the native legumes the amount of nitrogen fixed by the symbiotic bacteria would be about twice the amount added to the soil by rain and snow. Assuming that the non-symbiotic bacteria are able to fix one-half pound of nitrogen for every 100 lbs. of carbohydrate consumed, the carbohydrates contained in the non-leguminous plants, amounting to about 1600 lbs., would enable them to fix about 8 lbs. per acre each year. Thus the amounts of nitrogen added to the soil by the three agencies, *viz.*, the precipitation, the bacteria associated with legumes and the non-symbiotic bacteria, would bear approximately the ratio 1 : 2 : 2, provided that the whole of the aerial portion of the legumes was incorporated with the soil and that the whole of the carbohydrates of the aerial portion of the non-leguminous plants was oxidized by non-symbiotic nitrogen-fixing bacteria. Considering the incompleteness of any such disposition of the aerial portions of prairie vegetation it seems probable that the amounts of nitrogen added by the three agencies mentioned above are more nearly equal than is indicated by the above ratio.

The nitrogen content of the soil of the above described prairie is shown in the table above—Field A. Thirty-five samples to a depth of six inches were taken from different places in the field. The nitrogen content ranged from 0.250–0.317 per cent., with an average of 0.284 per cent. Fields B, E and F, also, are representative of the upland loess soils[1] of Eastern Nebraska. Fields G and H are representative of the heavier and lighter types, respectively, of tillable soil on the high plains of western Nebraska. Fields C and D are typical of the lowland loess soils[1] of eastern Nebraska which owe their depth of black soil to the deposit by summer floods of the surface soil eroded from the higher lands. The average of 29 samples from such deposits collected after a flood in 1908 showed 0.230 per cent. nitrogen. Field I is typical of an unusual accumulation of organic matter in western Nebraska, the wind playing the same part there that the water does in the eastern part of the state. The accumulation, however, had taken place on the lee side of a low ridge instead of in a valley. The common idea as to the great depth to which black soil extends on these prairies is erroneous and is due, largely, to exposures of such unusual accumulations of organic residues.

The upland prairies of eastern Nebraska contain in the first two feet of soil about 10,000 lbs. of nitrogen per acre. This amount is so small that its accumulation may be accounted for by any one of the three agencies mentioned, a fixation of nearly 100 lbs. of nitrogen per acre per annum having been observed at Rothamsted in the case of a piece of land "which for the last twenty-five years has been allowed to run wild and assume a natural prairie condition of self-sown weeds and grasses that are never taken away but left to rot where they die down."[2]

Evidently the nitrogen content of the upland prairie soils has long since reached equilibrium and an accumulation of nitrogen is to be expected only where the original amount has been reduced by erosion or by cultivation.

TABLE II.—DISTRIBUTION OF NITROGEN IN SOILS OF NEBRASKA PRAIRIES.

Field. Nearest town, approximate longitude.	A.	B. Lincoln, 96° 40′.	C.	D.	E. Elgin, 98° 7′.	F. Hastings, 98° 50′.	G. Imperial, 101° 40′.	H.	I. Madrid, 101° 35′.
First inch	0.346	0.465	0.416	.....	0.296	0.276	0.162	0.084	0.186
Second inch	0.315	0.312	0.344	.....	0.263	0.226	0.128	0.078	0.135
Third inch	0.279	0.265	0.271	.....	0.227	0.191	0.140	0.088	0.134
Fourth inch	0.262	0.234	0.230	.....	0.205	0.178	0.149	0.079	0.134
Fifth inch	0.247	0.230	0.209	.....	0.195	0.165	0.104	0.071	0.125
Sixth inch	0.234	0.214	0.198	.....	0.192	0.159	.....	0.067	0.110
Seventh inch	0.215	0.197	0.196	.....	0.177	0.153	.....	0.062	0.102
Eighth inch	0.201	0.190	0.190	.....	0.169	0.145	.....	0.060	0.096
Ninth inch	0.189	0.184	0.173	.....	0.155	0.149	.....	0.054	0.092
Tenth inch	0.181	0.177	0.165	.....	0.149	0.143	.....	0.053	0.102
Eleventh inch	0.176	0.165	0.158	.....	0.133	0.141	.....	0.057	0.086
Twelfth inch	0.173	0.165	0.153	.....	0.128	0.138	.....	0.065	0.089
First foot	0.240	.....	.....	0.265	0.201	0.170	0.127	0.068	0.117
Second foot	0.111	.....	.....	0.190	0.098	0.091	.....	0.043	0.077
Third foot	0.063	.....	.....	0.118	0.055	0.052	.....	0.035	0.038
Fourth foot	0.045	.....	.....	0.061	0.052	0.041	.....	0.027	0.019
Fifth foot	0.042	.....	.....	0.074	0.058	0 035	.....	0.025	.....
Sixth foot	0.042	.....	.....	0.061	0.053	0.029	.....	0.023	.....

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[1] *Marshall silt loam* according to the nomenclature of the Bureau of Soils, U. S. Dept. of Agr.

[1] *Wabash silt loam* according to Bureau of Soils, U. S. Dept. of Agr.

[2] A. D. Hall, Cantor Lectures on Artificial Fertilizers, p. 14 (1907).

SUGGESTED STANDARDS FOR MAPLE SUGAR AND SYRUP.

By H. W. Cowles, Jr.

Received August 14, 1909.

Maple sap, while being concentrated to a syrup, throws out a certain sediment, called "nitre," composed largely of salts of calcium, insoluble in water. When this "nitre" is removed by filtration or sedimentation the resulting syrup will always have an ash above 0.45 per cent., usually above 0.50 per cent. When this clarified syrup is further concentrated to a sugar, it will have an ash of about 0.65 per cent. on the water-free basis and thus conforms to the U. S. Standards. When this sugar is dissolved in the requisite amount of water it will again yield a syrup with 0.45 per cent. ash. Now, if the original maple sap is concentrated to a sugar without the removal of the "nitre," the sugar will have an ash well above the standard of 0.65 per cent. and, on solution in the requisite amount of water and filtration to remove insoluble matter, will yield a syrup which has an ash above 0.45 per cent. This insoluble matter or "nitre" gives an ash which is just as much "maple" as the mineral matter which is in solution in the syrup.

During the season just past, several samples of maple sugar were examined from one locality of a large maple-producing section from which, although they conformed to the U. S. Stds., it was impossible to make legal syrups. The average ash was 0.79 per cent., well above the limit prescribed in the standards, but syrup made from the samples had an average ash of 0.42 per cent.—below the standard. It was suspected that some one had taken advantage of the fact that, although 0.65 per cent. maple sugar ash is necessary for a legal sugar, it is not necessary, in order to comply with the standards, that all this ash-giving matter shall go into the syrup made from the sugar. It is therefore possible to take a maple sugar containing a large quantity of this "nitre," and a correspondingly high ash, and add cane sugar to it in such proportion that the resulting sugar will still have an ash above the limit of 0.65 per cent. As the standards are now placed the sugar is legal if it contains 0.65 per cent. maple sugar ash on the water-free substance. But owing to the large amount of "nitre" this sugar will not yield a legal syrup on solution in water and filtration.

A careful analysis of the ash for water-soluble and insoluble portions and the alkalinity of each may show that cane sugar has been added to a maple sugar containing a large amount of "nitre," but a simpler method and one which conforms to actual practice is the placing of the ash of a maple sugar on a syrup basis instead of a water-free basis as at present. There can be no objection to leaving a proper lower limit on the ash determined as it exists in the sugar and expressing it on a water-free basis for uniformity, but the result desired, the stopping of adulteration, is not prevented. It simply shows how low in ash a maple sugar may be and still be pure. The ordinary maple sugar of commerce has not been clarified beyond the possible skimming off of impurities that come to the surface during concentration; accordingly all the "nitre" or salts rendered insoluble by boiling and concentrating remain in the mixture and are sold as sugar. When a syrup is made from this sugar, this insoluble portion has to be removed in order to produce a clear merchantable article. If the syrup is put up for consumption direct from the sap without going through the sugar stage, this insoluble matter, or "nitre" is removed, although occasionally it is found in the bottom of cans of syrup which have been carelessly prepared.

From the above it is easily seen that the ash of a commercial sugar may be much higher than if made from a filtered syrup, and, conversely, the ash of a filtered syrup made from a commercial sugar will be much lower than that of the sugar when both are calculated on the water-free basis. The amount of insoluble matter present in a sugar, which must be removed to make a clear syrup, varies with the condition of the sap and the method of preparation, long-continued boiling being a chief factor. Whatever the amount, the larger part of it consists of lime salts, which show up as total ash in the analysis. Therefore, as above stated, the careful analysis of the ash of many pure sugars would tend to establish standards which would to a certain extent check adulteration; but the limits would necessarily be wide and a simpler method is as follows: To 50 grams of the sugar in a small glass stoppered flask add 26 cc. (25 grams) of boiling water. Dissolve by shaking thoroughly. Filter, while still warm, through ordinary filter paper into a small narrow-necked flask, keeping the funnel covered with a watch glass to prevent undue loss by evaporation. Determine the specific gravity of the syrup thus made at standard temperature and from this calculate the amount of total solids as sugar by reference to tables, the balance being water. De-

termine the ash and calculate to a uniform basis of water content, for instance the U. S. Std. of 32 per cent. This is necessary because of the varying amount of moisture present in the original

Description.	Moisture.	Ash. Total.	Ash. Water-soluble.	Ash. Water-in-soluble.	Alkalinity, cc. N/10 acid per 100 grams sample. Water phenolphthalein.	Soluble methyl orange.	Water-insoluble methyl orange.	Total.	Ash, dry basis.	Ash, syrup basis (32% water).
New York maple sugar (pure)	2.70	1.116	0.392	0.724	29.0	53.0	128.0	181.0	1.147	0.800
New York sugar syrup (filtered) 50 gm. sugar, 25 gm. water	41.28	0.455	0.311	0.144	16.0	38.0	41.0	79.0	0.775	0.527
New York sugar—60 parts Cane sugar—40 parts	1.5	0.723	0.302	0.421	17.5	31.0	75.0	106.0	0.779	0.499
Syrup of above (filtered) Mixed sugar—50 gm., Water—25 gm.	34.8	0.322	0.184	0.138	7.0	15.5	31.0	46.5	0.494	0.336
Canadian maple sugar (pure)	6.1	0.861	0.853	0.476	36.0	....	88.0	....	0.917	0.624
Canadian sugar syrup (filtered) 50 gm. sugar, 25 gm. water	39.44	0.476	0.301	0.175	18.0	35.0	40.0	75.0	0.786	0.554
Canadian sugar—75 parts Cane sugar—25 parts	2.0	0.643	0.302	0.341	29.0	40.0	61.0	101.0	0.656	0.450
Syrup of above (filtered) Mixed sugar—50 gm., Water—25 gm.	35.3	0.373	0.206	0.167	12.5	26.0	39.0	65.0	0.576	0.382

50 grams of commercial sugar. The per cent. of moisture can be calculated roughly from the amount of water present in the weak syrup in excess of $33^1/_3$ per cent. which would result from the solution of 50 grams anhydrous sugar in 25 grams water. If no cane sugar has been added the total ash will be over 0.45 per cent., usually 0.50 per cent. If cane sugar has been added, the amount can be determined approximately, by calculation with 0.45 per cent. as a basis.

The analyses of two sugars of known purity are given in the following table, together with the syrups made from them as above outlined. The same table contains comparable results on mixed sugars made from each by the addition of the stated amounts of cane sugar.

It will be seen that both mixed sugars would have to be passed as pure under the present standards. The other methods commonly in use for the detection of adulterated maple products depend for their accuracy on the same substances as does the ash, hence are unreliable in detecting this particular condition.

In the following table are given the results on fourteen samples of commercial maple sugars, analyzed by the above method.

The samples were carefully taken by boring with a long auger through the center of tubs holding about 60 lbs. sugar each, and then mixing thoroughly the sugar brought up by the auger. A syrup made commercially from these tubs would not have an ash much above 0.40 per cent. and the analyses show the reason. Before giving suggestions as to the wording of the standard which it is believed would prevent sophistication of maple sugar, a word should be said about the water content of maple syrup.

Sample No.	Solids.	Moisture	Ash on original sugar.	Ash on dry basis (0.65% std.).	Alkalinity to phenolphthalein, 100 g. sugar.	Alkalinity to methyl orange, 100 g. sugar.	Ash of syrup—50 g. sugar, 25 g. water.	0.45% ash on syrup containing 32% water.
1	89.95	10.05	0.59	0.655	20.0	103.0	0.31	0.35
2	83.0	17.0	0.77	0.93	33.0	134.0	0.46	0.56
3	87.4	12.6	0.70	0.80	29.0	116.0	0.42	0.48
4	89.1	10.9	0.80	0.90	32.0	153.0	0.39	0.44
5	87.57	12.43	0.45	0.51	8.0	43.0	0.16	0.18
6	87.9	12.1	0.83	0.94	32.0	154.0	0.43	0.49
7	88.3	11.7	0.66	0.75	26.0	123.0	0.36	0.42
8	87.5	12.5	0.68	0.78	30.0	113.0	0.44	0.51
9	87.6	12.4	0.81	0.92	29.0	143.0	0.38	0.44
10	89.0	11.0	0.66	0.74	18.0	118.0	0.31	0.36
11	90.4	9.6	0.81	0.90	32.0	145.0	0.36	0.40
12	88.2	11.8	0.72	0.82	34.0	145.0	0.37	0.43
13	91.3	8.7	0.76	0.83	31.0	147.0	0.40	0.44
14	91.0	9.0	0.25	0.27	8.0	49.0	0.12	0.13

The present U. S. Standard for syrup requires at least 0.45 per cent. maple ash and not more than 32 per cent. of water. Starting with a "pure" maple sugar containing just 0.65 per cent. maple ash on the water-free basis, which would be legal, it will readily be seen that even if all the ash-giving substances go into solution, a syrup made therefrom can only contain 30.75 per cent. moisture in order to have 0.45 per cent. ash. Such a syrup would be heavy and unpalatable and when exposed to the air for even a short time would readily crystallize. The ash of a syrup from any sap measures quite accurately the amount of solids-not-

sugar present and consequently the ability of the syrup to resist crystallization with a low water content. This fact was recognized by the Standards Committee when it made 30 per cent. the maximum water limit for cane syrup and molasses with 2.5 per cent. ash, as against 35 per cent. of water for a sugar syrup with no ash or solids-not-sugar. One-half per cent. ash represents approximately the solids-not-sugar that will permit the lowering of the water limit by 1 per cent. If the same reasoning were applied to maple syrups with an ash content of about ½ per cent., which all concede to be correct, the water limit would be placed at 34 per cent. This theory is borne out by practice. The maple syrups now on the market have an average water content of from 31½ to 32½ per cent., a fear of resulting crystallization keeping the manufacturers from going below this limit. This is too close to the legal limit to be comfortable. A slight variation in testing the degree in boiling down might make an otherwise pure syrup illegal. If the standard were raised to 34 per cent. a limit would be established that would be practical not because it enables the manufacturer to add 2 per cent. of water to his product but because it places a limit that would not have to be approached so dangerously near in order that a merchantable product may be obtained. The manufacturer would keep his syrup between 32 and 33 per cent. of water because fermentation and crystallization make very good watch-dogs to keep him from varying either way to any extent.

If the standard for the water content of syrup were 34, the ash of sugar on a water-free basis would have to be made 0.68 per cent. to correspond. The ash of the sugar may be higher than this, but at least 0.68 per cent. on a water-free basis must go into solution in water in order that a legal syrup may be made from it.

As standards, therefore, the following are suggested:

Maple sugar is the solid product resulting from the evaporation of maple sap or maple syrup and contains not less than 0.68 per cent. of maple sugar ash in the water-free substance, and on solution in water will yield a clarified maple syrup, containing not less than 0.45 per cent. maple syrup ash.

Maple syrup is the product resulting from the evaporation of maple sap or the solution of maple concrete or sugar and contains not less than 0.45 per cent. maple syrup ash and not more than 34 per cent. water.

ADDRESSES.

THE NEED OF METHODS OF ANALYSIS OF PHARMACOPOEIAL ARTICLES.[1]

By B. L. Murray.

The United States Pharmacopoeia is well and intimately known to all the pharmaceutical chemists here to-day. It is probably known in a general way to all the chemists of our association. But, notwithstanding this, the book is such an important one that it is worthy our close attention, for a short time at least. It is, without doubt, the most important law book that is written by laymen. While it is revised and put forth by a mere handful of men it is in effect the law for all our millions of population. It may safely be said that directly or indirectly it exerts its influence on each and every inhabitant of the United States and its possessions, for they all take medicine. Such a text is to be respected.

The pharmacopoeia lays down standards of purity and of strength for drugs and medicinal chemicals, and by virtue of the Food and Drugs Act these standards become in effect a part of the law. The book tells us what properties characterize preparations for medicinal use, how to make some of the preparations, how to test them, how much of them to take at a dose, etc. No better pharmacopoeia is published and for the greater part of it only praise can be offered. But like everything else artificial in its origin, it has defects, and, as is customary, the virtues will be dismissed with a mere mention, while the defects, or one of them, will be dwelt upon.

I have just said that the pharmacopoeia prescribes for us the quality and strength of our medicines, and how to test them. This statement must be modified. The pharmacopoeia tells us the required strength of practically all the articles within its purview, and tells us how to test *some* of them. The tests given, or, rather, those *not* given at all are the crux of this paper.

Whenever in the text freedom from chlorides, or sulphates, or phosphates, or iron, or most any of the simples is required, the appropriate qualitative test is given. But when it is required to employ a more important test, such as a quantitative assay method, the pharmacopoeia frequently gives no such test at all. Now this really is unfortunate, to put it mildly, for the purity requirements of the book are in the main high, and are all binding on those handling the preparations. If degrees of purity difficult to attain and maintain are required, of course in simple justice methods of ascertaining those degrees of purity should be stated. The selection of methods of analysis at random by different chemists is a poor practice.

The metallic mercury of the U. S. P. is an example of the condition mentioned. Metallic mercury to meet the requirements of purity must contain 99.9 per cent. of mercury. Only one-tenth of 1 per cent. of impurities allowed—and no official assay method given by which to test. This is rather an extreme case, but merely typifies many others. Metallic zinc, practically never taken internally, must contain 99

[1] Read before the Section of Pharmaceutical Chemistry of the American Chemical Society, at Detroit, June 30, 1909.

per cent. of zinc. No method of testing is given; that is, no quantitative method of determining the per cent. of zinc is given. There are many such instances.

We know why the present pharmacopoeia fails in many cases to give these most important methods. At the time the book was published it was not a national legal standard, but became so subsequently, with the passage of the Food and Drugs Act. The need of methods was formerly not so great, and when a relatively simple test such as a volumetric or an easy gravimetric method could not be found, none at all was put into the text. The idea was, also to employ tests requiring the minimum of apparatus and general equipment, on the assumption, it is said, that retail druggists are the principal users of the tests.

So much for the *present* pharmacopoeia—the U. S. P. 8th revision. The book has already been printed and distributed, has been revised and corrected by supplementary circulars, and has nearly served out its time. But what of the next revision, the ninth, the convention for which meets in May next? How shall the question of purity requirements in terms of per cent., and methods of assaying be handled? Are we again to fill the pages with tests for chlorides, etc., and omit the really important and more difficult methods of assay? Are we again to confine ourselves to easy volumetric or gravimetric determinations when there are better and more suitable, though less easy ones, at hand? Are we pharmaceutical chemists willing to be denied the privilege of making use of the latest advances in analytical chemistry? Must we forego the pleasure of using the modern oxidizers such as sodium peroxide and the persulphates? Do we not know the remarkable advances that have been made in electro-analysis? Can we close our eyes for another ten years and bring out a new pharmacopoeia, ignoring all these advantages at our service, and all for the sake of keeping things simple? It does not seem possible to me. In our next pharmacopoeia we need modern methods of analysis. Or at least we should accord ourselves the privilege of using such methods.

To incorporate full quantitative methods of determining gold, mercury, zinc, antimony, and all the others, would enlarge the book very materially, and this is possibly objectionable. For the pharmacopoeia to refer the chemist to some standard *text-book* for methods of analysis would hardly be justifiable or desirable. I suggest therefore that the Committee of Revision of the Pharmacopoeia follow the example of the Department of Agriculture in Washington. As all know this department accepts or adopts the methods of analysis of the Association of Official Agricultural Chemists. Let the Committee of Revision adopt as their methods of analysis the methods of the American Chemical Society. And it will be an excellent beginning for this the new Division of Pharmaceutical Chemistry to investigate, and if possible agree upon some or a few of the methods of analysis now entirely omitted from and so much needed in the United States Pharmacopoeia. Possibly the methods thus worked out and approved by the American Chemical Society could be made sufficiently attractive to tempt the Committee of Revision to use or refer to them.

I therefore offer the suggestion that this Division of Pharmaceutical Chemistry take up the investigation of methods of analysis of pharmacopoeial articles with the idea of selecting what may be termed standard methods of analysis.

BOOK REVIEWS AND NOTICES.

Metallography. By DR. W. GUERTLER. Volume I. Constitution. Part 1. Berlin: Gebrüder Borntraeger. Price, 4 Mk, 20 Pf.

This is the first part of what promises to be a comprehensive treatise on the subject of metallography. Necessarily future parts must decide as to the merits of the work as a whole, but the first part gives great promise. The chapters are: I, Introduction; II, Constitution in Relation to Temperature; III, Solid Solutions and Compounds; IV, Condition Diagrams; First Group. Paper, typography, illustrations and general appearance are the best.

OFFICIAL REGULATIONS AND RULINGS.

(T. D. 1524.) *Denatured Alcohol.*—Use of specially denatured alcohol prohibited in the manufacture of butyric and formic ether.

TREASURY DEPARTMENT,
OFFICE OF COMMISSIONER OF INTERNAL REVENUE,
WASHINGTON, D. C., August 5, 1909.

GENTLEMEN: Your letter of the 31st ultimo, addressed to the chief chemist, and making application for the authorization of formula No. 1 for use in the manufacture of butyric and formic ether, has been received, and the matter given careful consideration by this office.

The fact is recognized that the substances in question fulfil the conditions imposed by the amendatory act in being "definite chemical substances" produced from alcohol by molecular decomposition, and their manufacture from denatured alcohol could lawfully be permitted under Section 40, Part VI of Regulations No. 30.

In view of the fact, however, that these ethers are used mainly as flavoring material in beverages, and the further fact, which is apparent from your communication, that they must necessarily carry a considerable percentage of undecomposed alcohol, I do not consider it to be for the best interests of the Government, or in accord with the spirit and intent of the denatured alcohol law, to permit tax-free alcohol to be used in their manufacture. I must, therefore, deny your application.

Respectfully,
ROBT. WILLIAMS, JR.,
Acting Commissioner.

Messrs. ————————.

Judgment Nos. 92–99, Food and Drugs Acts.

92. Misbranding of canned peaches, plums, pears and apricots (underweight).

93. Misbranding of canned beans (underweight).

94. Misbranding of water (artificially lithiated water labeled as a natural product).

95. Misbranding of canned corn (underweight).

96. Misbranding of a cereal (as to quality and digestive properties).

97. Misbranding of canned tomatoes (underweight).

98. Adulteration and misbranding of syrup (as to presence of maple sugar).

99. Misbranding of syrup (as to place of manufacture and amount of maple sugar present).