

more testimony to that already collected on the injurious effect of soluble aluminum salts upon the human digestion. The consensus of opinion is that such salts retard the digestion, both in the stomach and intestines.

The only question to be answered then is as to the solubility of the salt present in the digestive fluids. As has been stated, it is insoluble in boiling water and dilute hydrochloric acid. If, however, 50 grams of the sausage be treated for four hours at 40° C. with 100 cc. of 0.33 per cent. hydrochloric acid containing 0.1 gram of Merck's pepsin, filtered, a portion of the filtrate ashed, and tested for aluminum, no small quantity of that metal will be found.

To determine the proportion of the preservative which would be dissolved in the stomach during digestion, the following experiments were tried: 50 grams of the two samples (Nos. 1 and 2), finely ground, were digested with 200 cc. of the above pepsin solution for twelve hours, an aliquot portion filtered off, and the aluminum determined. Sample No. 1 contained 14.9 mg. of aluminum oxide per 100 grams of the sausage, of which 12 mg. were dissolved by the solution, or 82.7 per cent. Sample No. 2 contained 34 mg. of aluminum oxide per 100 grams of sausage of which 24 mg. were dissolved, or 70.3 per cent., showing that a very large proportion of the compound is dissolved during the process of digestion and becomes a retarding factor. Acknowledgment is herewith made to Dr. W. D. Bigelow for valuable suggestions in planning this work.

FOOD LABORATORY, U. S. DEPT. OF AGR.

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## THE DETECTION OF MINERAL OIL IN DISTILLED GREASE OLEINES.

BY AUGUSTUS H. GILL AND STEPHEN N. MASON.

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IN THE woolen industry a large quantity of soap and oil is used in cleansing, oiling and milling the wool, yarn and cloth, during the different processes of manufacture.

Formerly all the waste from this washing went into the streams and was lost, also polluting the water, and making it unfit for other purposes. At the present time this waste is recovered, and after suitable purification, is used over again.

The soap-suds are collected in large tanks<sup>1</sup> (of 6,000 to 8,000 gallons' capacity) and a mineral acid, usually sulphuric or preferably hydrochloric acid, is added to precipitate the fatty acids, the mixture thoroughly stirred and allowed to settle. The fatty acids rise to the top, are skimmed off, and thrown upon cloth or sand filters to drain. The fatty matter, thus collected, which is known as the "magma" or "sake," is packed in cloth bags, and pressed hot. The dark greasy product thus obtained is known as "recovered grease," or under the trade name of "dégras." This is used for stuffing leather, making soap, in the manufacture of lubricating greases and wool oils. It is, however, particularly in England, often distilled, as is described below.

The distillation is carried on in cast iron stills (wrought iron cannot be used as it is rapidly corroded by the fatty acids), connected with suitable condensing apparatus. In most works, jets of superheated steam are used in addition to direct heat to lift the heavy vapors from the still, as it is claimed that this gives a larger yield of useful products, and that the quality is better than when direct heat alone is used. There are several fractions in the distillate, but the one that interests us is known as the "first distilled grease." This product may be redistilled for further purification, or it may be subjected directly to pressure, yielding as products a solid "stearine," and a liquid "oleine." It is to be noted that the name "oleine" is not indicative of the chemical composition of the oil, although it contains oleic acid, but is used to distinguish it from the solid stearine.

These distilled grease oleines are largely used for oiling wool, hence are generally known as "wool oils." The analyses of several distilled grease oleines, as given by Lewkowitsch,<sup>2</sup> are as follows:

Gravity.	Free fatty acids. Per cent.	Unsaponifiable matter.	Neutral oil.
0.9083	55.3	35.9	8.8
0.9031	55.02	34.66	9.2
0.8980	56.26	29.46	11.95
0.9000	59.83	38.92	1.25

Those upon which we worked showed the following composition:

<sup>1</sup> Condensed from Hurst: *J. Soc. Chem. Ind.*, 8, 90.

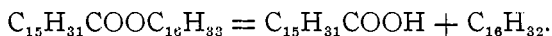
<sup>2</sup> "Analysis of Fats, Oils and Waxes," 2nd edition, p. 711.

	Fatty acid.	Unsaponifiable matter.	Neutral oil.
Oil A.....	50.7	46.5 <sup>1</sup>	2.8
	50.7	45.0 <sup>2</sup>	4.3
Oil B.....	36.3	40.6 <sup>1</sup>	23.1
Oil C.....	45.1	38.3 <sup>2</sup>	16.6
Oil D.....	45.5	41.4 <sup>2</sup>	13.1
	45.5	46.4 <sup>1</sup>	8.1

These four were from the following sources: Oil A, a pure oleine imported directly from the manufacturers by one of us. Oil B, a pure oleine from a local dealer. Oil C, a pure oleine from a manufacturer's agent. Oil D, an oleine of doubtful purity from a dealer in this country.

All but D were guaranteed pure and, in particular, free from any admixture with mineral oil.

The composition of the oleines varies greatly according to the grease from which they are prepared. They contain, in general, saponifiable esters of the fatty acids, *i. e.*, neutral fats, free fatty acid, and unsaponifiable matter, consisting of cholesterol, iso-cholesterol, and other higher alcohols characteristic of wool fat, and hydrocarbons formed by breaking up of the fatty acids during distillation; *e. g.*, cetyl palmitate splits into cetene and palmitic acid, according to the following equation:



These hydrocarbons resemble so closely those in mineral oils that the latter are difficult of detection when mixed with distilled grease oleines. Hence there is a temptation for dealers to adulterate these oleines with the cheaper mineral oil. The object of this work was to establish reliable means of detecting such adulterations of mineral oil in these distilled grease oleines. The method of procedure in obtaining the hydrocarbons from these oleines, consisted in saponification with alcoholic potash, extraction of the unsaponifiable matter with gasoline, and the treatment of this matter with boiling acetic anhydride to separate cholesterol and other higher alcohols, leaving the hydrocarbons pure. These hydrocarbons, prepared from different samples of distilled grease oleines, were compared directly with mineral oils, which would be likely to be used for adulteration.

<sup>1</sup> Unsaponifiable matter determined from saponification number.

<sup>2</sup> Unsaponifiable matter determined by extraction with gasoline.

The extraction of the unsaponifiable matter was carried out as follows: 200 grams of the oil were saponified by boiling on a water-bath two or three hours with an excess of alcoholic potash (120 grams to the liter) in a 750 cc. flask, provided with a return flow condenser. When the saponification was complete the solution was transferred to a liter separatory funnel and shaken several times with 300 to 400 cc. of redistilled gasoline (86° Bé). The soap solution was thrown away. The gasoline solution was concentrated to about one-half its volume and washed with warm water mixed with a little alcohol, in the separatory funnel until all the soap was removed. The remainder of the gasoline was distilled off in the water-bath, and the residue heated to 130° C. in a porcelain dish to drive off the water and last traces of gasoline.

From the saponification numbers of the different oils, the requisite amount of alcoholic potash was calculated, and 100 per cent. excess employed. After the saponification, when gasoline was first added and the mixture thoroughly shaken, no separation into two layers occurred, even after several hours' standing. Salt was added, but without effect. Finally water was added in small quantities until two distinct layers formed. In washing the gasoline solution water alone was tried, but did not appreciably dissolve the soap. When warm water, mixed with a little alcohol, was used the soap dissolved readily. In heating the oil to 130° C. to drive off water, a very small flame, or better, an electric stove should be used, and the oil constantly stirred to prevent bumping. A thermometer serves well as a stirring rod.

The unsaponifiable oil was freed from cholesterol and other higher alcohols by boiling for an hour with 100 cc. of acetic anhydride in a flask provided with a return flow condenser, and heated over a sand-bath. Water was added, and the solution transferred to a separatory funnel where it was washed with water and alcohol until the upper layer was clear and no odor of acetic acid was perceptible. The cholesterol and higher alcohols were dissolved by the acetic anhydride, leaving the hydrocarbons.

After submitting the oils to this process, a determination of their saponification number was made and if more than 0.2 cc. of alcoholic potash was used up, the treatment with alcoholic potash and acetic anhydride repeated.

The bromine numbers of the hydrocarbon oils were determined according to McIlhiney's process.<sup>1</sup>

TABLE I.—BROMINE NUMBERS OF HYDROCARBON OILS FROM DISTILLED GREASE OLEINES.

	Addition.	Substitution.	Total.
Oil A .....	28.8	14.2	57.2
Oil B .....	25.1	14.8	54.7
Oil C .....	21.5	16.8	55.1
Oil D .....	3.8	9.0	21.8
Mixture of 50 per cent. oil A and } 50 per cent. white rose oil.... }	9.0	12.85	34.7

TABLE II.—BROMINE NUMBERS OF PURE MINERAL "WOOL OILS."

Extra white rose oil.....	5.7	5.6	16.9
White rose oil .....	5.3	5.9	17.1
Eclipse white spindle oil .....	4.5	8.4	21.3
Eagle neutral oil .....	4.4	6.7	17.7
XX wool stock .....	5.9	7.5	20.9
Average for pure mineral oils....	5.2	6.8	18.8

The next means of distinguishing between the mineral oils and the hydrocarbon oils from the pure distilled grease oleine was the optical activity of the various oils, as shown by the Laurent polariscope. The undiluted oils were so cloudy and so much colored that it was impossible to obtain readings, hence they were diluted with ten parts of benzene. Even then readings were made with difficulty and were only accurate to within five minutes.

As the amount of rotation depends on the concentration of the optically active substance, the rotation for the pure oils would have been eleven times that of the actual readings. Mineral hydrocarbons are supposed to be optically inactive, but a small rotation was found in each case. This may have been due to the inaccuracy of the readings.

The results obtained with the polariscope are shown in the table below:

<sup>1</sup> This Journal, 21, 1084.

TABLE III.—ROTATION OF DISTILLED GREASE HYDROCARBONS AND MINERAL OILS.

Name of oil.	Average of actual readings.	Rotation for pure oil.
A .....	1° 38'	17° 58'
B .....	1° 36'	17° 36'
C .....	1° 23'	15° 13'
D .....	16'	2° 56'
E (mixture of A + rose).....	53.4'	9° 47'
White rose .....	6'	1° 6'
Venango neutral.....	11.2'	2° 3'
Eagle neutral.....	7'	1° 17'
2 Wool stock .....	6.8'	1° 15'
Average for pure distilled grease hydrocarbons.....		16° 56'
Average for pure mineral oils.....		1° 25'

The fluorescence of the oils is also a means of distinguishing the mineral oils, which give a blue color, from the distilled grease oleines, which give a green color. It was found that oils A, B and C gave a green fluorescence; oil D gave a blue fluorescence; oil E gave a greenish fluorescence. Of the mineral oils, White rose, Extra white rose, Eclipse white spindle, XX Wool stock and Venango neutral, all gave a blue fluorescence. The only exception to the fluorescence rule in the case of the oils used was the Eagle neutral oil, which was green, while all the other mineral oils were blue.

The specific gravities of the oils are so close together that this is not a reliable means of detecting mineral oil, although the mineral oils have a somewhat lower specific gravity. The specific gravities of the oils are shown in Table IV. The indices of refraction, as determined by the Abbé-Zeiss refractometer, show a decided difference between the two classes of hydrocarbons. This is also shown in Table IV.

The only exception to the rule was in the case of oil D, which all the other tests showed to be mixed with a mineral hydrocarbon oil. This oil had an index of refraction of 1.4921, nearly as high as the pure distilled grease hydrocarbons.

TABLE IV.—SPECIFIC GRAVITY AND INDEX OF REFRACTION OF DISTILLED GREASE, HYDROCARBONS AND MINERAL OILS.

Name of oil.	Specific gravity.	Index of refraction at 20° C.
A.....	0.896	1.4967
B.....	0.902	1.4991
C.....	0.895	1.4948

TABLE IV.—(Continued).

Name of oil.	Specific gravity.	Index of refraction at 20° C.
D .....	....	1.4921
E mixture .....	....	1.4850
Extra white rose .....	0.848	....
White rose.....	0.853	1.4735
Eclipse white spindle.....	0.855	....
Venango neutral .....	....	1.4662
Eagle neutral .....	0.859	1.4750
XX Wool stock .....	0.863	1.4709

The results of the various tests, as applied to the different pure oils and the mixture oil E, of 50 per cent. oil A and 50 per cent. White rose oil, seem to show that there are three or four reliable methods of detecting mineral oils in distilled grease oleines. First, the bromine numbers, and particularly the addition numbers, of the hydrocarbons from the pure oleines are much higher than those of mineral hydrocarbon oils. Second, the distilled grease hydrocarbons are optically active, giving a rotation for the undiluted oil of from 16° to 18°, while the mineral hydrocarbons are inactive, or give only a slight rotation, 1° or 2°. Third, the indices of refraction of mineral oils are lower than those of the distilled grease hydrocarbons. Fourth, the fluorescence of mineral oils is in general blue, while that of the oleine hydrocarbons is green. These tests, as applied to oil E, and a mixture of 50 per cent. oil A and 50 per cent. White rose oil, gave results from which the following percentages of mineral oil were calculated.

Test.	Mineral oil. Per cent.
Bromine number .....	56.7
Polariscope .....	48.6
Index of refraction .....	50.4

An investigation is in progress to determine the nature of these distilled grease oleine hydrocarbons.

In conclusion, we wish to express our indebtedness to Mr. Royal L. Wales for careful preliminary work leading up to this investigation.