THE ANALYSIS OF SULFONATED OILS

(SULFATED)

A COMMITTEE REPORT

Committee Report No. 1—The Determination of Moisture

Our former president, Mr. John P. Harris, at the suggestion of Mr. H. P. Trevithick, appointed a committee for "The Analysis of Sulfonated Oils with Particular Reference to the Modifications of the American Association of Textile Chemists and Colorists (A. A. T. C. C.)." A subcommittee of the A. A. T. C. C. Research Committee, of which Professor L. A. Olney is chairman, has been making a careful investigation of the various methods available for the analysis and the commercial grading of sulfonated oils and some of the findings have already been published.[1,2,3] The following men were appointed by Mr. Harris to serve on the new committee:

Ralph Hart, chairman, 1440 Broadway, New York.

J. Andrew Clark, Dutchess Bleachery, Inc., Wappingers Falls, N. Y.

A. H. Grimshaw, N. C. State College, Raleigh, N. C.

W. H. Irwin, Swift & Company, Chicago, Ill.

M. F. Lauro, N. Y. Produce Exchange, 2 Broadway, New York, N. Y.

C. P. Long, The Procter & Gamble Co., Ivorydale, Ohio.

Eugene R. Manning, Clemson College, South Carolina.

H. H. Mosher, Onyx Oil & Chemical Co., Jersey City, N. J.

R. A. Pingree, The U. S. Finishing Co., Providence, R. I.

W. H. Tiffany, United States Testing Co., Inc., 1415 Park Ave., Hoboken, N. J.

Ralph Wechsler, National Oil Products Co., Harrison, N. J.

Appreciation is also due to Mr. J. T. R. Andrews of Procter & Gamble Co., Mr. E. I. Birnbaum of Hart Products Corp., and Mr. E. Segessemann of National Oil Products Co., who are cooperating in this work.

Besides the investigation by the A. A. T. C. C. committee, the American Leather Chemists Association (A. L. C. A.)[4,5] had the matter investigated a number of years ago through one of its committees, leading to the present A. L. C. A.[6] tentative and official methods for the anlysis of sulfonated oils. More recently the Bureau of Standards, in conjunction with the Sulphonated Oil Manufacturers' Association, has been at work on methods of grading sulfonated oils, which has resulted in the promulgation of the Bureau of Standards Commercial Standard CS43-32.[7] Abroad standard tests for sulfonated oils are being proposed by the Wissenschaftliche Zentralstelle für öl-und Fettforschung ("Wizöff")[8] and by the International Society of Leather Trades' Chemists (I. S. L. T. C.)[9].

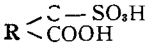
In this report, the commtitee presents experimental data on the determination of moisture by the A. A. T. C. C. distillation method and by a modification of the F. A. C. hot-plate method.[10] In view of the results obtained, the committee feels justified in recommending the distillation method as standard and the hot-plate method as an alternative method. The procedures for both methods will be found at the end of this report.

Sulfonated and Sulfated Oils

In this investigation it is proposed to study mainly the sulfated oils or the sulfuric acid esters of fatty oils, which are distinguished from true sulfonated oils by the fact that the former split off their sulfate radical when heated with mineral acids. Structurally the difference is shown by the following formulas:

$$R\begin{matrix} \diagup O-SO_3H \\ \diagdown COOH \end{matrix}$$

Sulfated oil

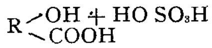


$$R\begin{matrix} \diagup C-SO_3H \\ \diagdown COOH \end{matrix}$$

Sulfonated oil

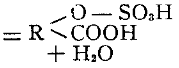
Thus in the sulfated oil or ester the SO_3H group is linked to the fatty radical by means of an oxygen atom, whereas in the case of a "true" sulfonated oil, it is connected to a carbon atom. Sulfated oil or ester is commercially known as "sulfonated" oil and the latter term will be retained in this report for that type of oil.

The sulfonated oils are commercially produced by treating hydroxy or unsaturated fatty acids or their esters with sulfuric acid. The following reactions take place:

1. 

$$R\begin{matrix} \diagup OH + HO\,SO_3H \\ \diagdown COOH \end{matrix}$$

Ricinoleic acid



$$= R\begin{matrix} \diagup O-SO_3H \\ \diagdown COOH \end{matrix} + H_2O$$

Ricinoleic hydrogen sulfate, or ricinoleic sulfuric acid ester

2. $R'C = CR''\,COOH + H\,OSO_3H =$

Oleic acid

$$R'C-\begin{matrix} CHR''\,COOH \\ \diagdown OSO_3H \end{matrix}$$

Oleic acid hydrogen sulfate, or oleic acid sulfuric acid ester

In the case of ricinoleic acid or hydroxy oil, a regular esterification takes place with the formation of water, but with unsaturated fats, such as oleic acid, addition to the double bond occurs. The end products, however, are sulfuric acid esters in both cases. The acid sulfonated oil contains two replaceable hydrogen ions—namely, one in the sulfate group and the other in the carboxyl group. The former is highly ionized and forms stable, neutral salts; the latter when neutralized behaves like soap—i. e., its water solution, in which it is readily hydrolized, is alkaline to methyl orange and the neutralized carboxyl group is readily regenerated with mineral acids. The names of the partly and completely neutralized sulfonated oleic acid are as follows:

$$R\begin{matrix} \diagup OSO_3Na \\ \diagdown COOH \end{matrix}$$

Oleic acid sodium sulfate, or sodium salt of oleic acid sulfuric acid ester

$$R\begin{matrix} \diagup OSO_3Na \\ \diagdown COONa \end{matrix}$$

Sodium oleate sodium sulfate, or disodium (normal) salt of oleic acid sulfuric acid ester

Distillation Method

The distillation method seems to be preferred as a standard method for moisture in sulfonated oils, soaps, etc. The method consists essentially in refluxing the sample with a water-immiscible solvent and collecting and measuring the water that distills over. It is comparatively rapid and accurate, and the least subject to theoretical errors. It is either the official or tentative method of the following organizations: American Association of Textile Chemists and Colorists[1], American Leather Chemists Association,[6] American Oil Chemists Society,[10] American Society for Testing Materials,[11] Association of Official Agricultural Chemists,[12] International Society of Leather Trades' Chemists,[10] and Wissenschaftliche Zentralstelle fü öl-und Fettforschung ("Wizöff").[8]

Bidwell and Sterling[13] prefer toluene to xylene as the distilling agent because the higher boiling point of the latter may decompose certain substances (such as sugars), liberating water. This objection, however, would not apply to oils. They also state that 75 cc. of toluene to which 1 cc. of water was added and then distilled retained 0.02 cc. of moisture, an amount which remained constant, however, when more water was added and distilled. The same authors state that several substances such as alcohol, glycerol, acetone, etc., which are volatile and miscible with water, may distill over and cause high results by this method.

To prevent foaming and to keep the mixture fluid and thin throughout the distillation, the addition of oleic acid is highly advisable, particularly with samples containing considerable amounts of soap. Hart[14] was the first to suggest the use of oleic acid to overcome this difficulty. Since then, lump rosin, sodium bisulphate, and other acid sales have also been recommended. In the presence of free alkali, the addition of oleic acid may introduce an error due to formation of water forming when oleic acid reacts with the excess alkali to form soap. However, the chances that a commercial sample of sulfonated oil may contain sufficient excess alkali to affect the moisture determination appreciably are very slight. Furthermore, by determining the free alkali, a correction factor may be applied to take care of the additional water.

Davidsohn[15] states that the determinations of water in fats and soaps by the distillation method are usually low, even with the new apparatus recently adopted (in Germany) in which the xylene is refluxed while the water distills over; and that apparently the soap retains some of the water and liberates it only after adding a quantity of water-free oleic acid. Schlenker[16] concludes that water determinations in soaps by the distillation method with petroleum benzine yield low results, unless a sufficient amount of oleic acid (20 grams per 30 grams of soap flakes) has been added before distillation. Schlenker prefers xylene to petroleum benzine, since the latter holds some of the water in minute suspension.

A. A. T. C. C. Distillation Method

In this method the Bidwell and Sterling moisture apparatus (Fig. 1A) is specified and the procedure embodies the following features: Ground-glass connections, thorough cleaning of the apparatus with soap and water before treating with chromic acid, specifications for calibrating the apparatus, an accurate method of weighing the sample to be taken for analysis, the addition of oleic acid and the amount, a convenient criterion for controlling the rate of distillation, definite end point when the distillation may be considered completed, and a precise method for measuring the condensed water and calculating the final result. In the A. O. C. S. method the Kingman moisture apparatus is specified. It seems, however, that the Bidwell and Sterling apparatus possesses a number of advantages, among which the following may be mentioned: The solvent is automatically taken care of, making it unnecessary to draw it off from time to time as required with the Kingman apparatus (removal of the solvent may also lead to losses due to entrained or dissolved moisture); acetylene tetrachloride recommended in the Kingman procedure is somewhat soluble in water, and finally in the Bidwell and Sterling apparatus there are no stopcocks to manipulate and only one meniscus to read instead of two.

Committee Results by the Distillation Method

The committee after investigating the A. A. T. C. C. distillation method recommends the following changes in the apparatus: The end of the condenser tube to be raised sufficiently so that it would not dip into the liquid in the trap and the dimensions of the ground joints to correspond to Interchangeable Ground-Glass Joint 25 of Commercial Standard CS21-30. The committee determined the moisture in two samples of sulfonated oils—namely, Samples 1 and 1-A, respectively, by this method and the results are given in Table I. It will be observed that the moisture contents of Samples 1 and 1-A were 25.78 and 42.12%, respectively; the greatest difference was 1.13 and 1.24%, respectively; and the average deviation, 0.24 and 0.33%, respectively. These results are in good agreement with those obtained by the A. A. T. C. C. committee on similar samples. The average deviation of approximately 0.3% may be assumed in this case to be equal to the probable precision of any one determination. The mean result is probably reliable to 0.1%.

The Hot-Plate Method

Upon the recommendation of Mr. Irwin, the committee has also investigated the F. A. C. hot plate method for moisture. This is one of the official methods of the Society and according to Mr. Irwin it has been in use for over 30 years. Jamieson,[17] who investigated the hot-air oven and hot-plate methods for fats, states that the hot-air oven method gives abnormally high results and after repeated heating the samples continue to lose weight indefinitely; the hot-plate method in most cases gave apparently satisfactory results, but several erratic results showed that more details should be given. He suggests that in using this method the sample to be tested be placed on an asbestos board (under which is a wire gauze to distribute the heat) alongside a "blank" sample of oil in which a thermometer is suspended, so that the temperature can be observed and controlled while the oils are gradually heated to 130° C. or to incipient smoking. After investigating the hot-plate method, the committee recommends that the temperature of the sample be controlled by a short thermometer which may also be used as a stirring rod, and that the beaker be heated in a hot-air oven for a short period before each weighing in order to remove any adsorbed moisture on the walls. The addition of oleic acid to keep the oil fluid is also recommended, particularly with samples containing considerable amounts of soap.

The committee determined the moisture of the same coöperative samples by the modified hot-plate method, using the procedure given at the end of this report, and the results shown in Table II more than justify Mr. Irwin's enthusiasm for the hot-plate method. The average moisture contents of Samples 1 and 1-A were 25.97 and 42.29%, respectively; the greatest difference was 1.29 and 1.03%, respectively; and the average deviation, 0.28 and 0.23%, respectively. The order of precision or reliability of this method may therefore be assumed to be about the same as for the distillation method. In Table III is shown a summary of the results by both methods, from which it will be noted that the difference in the means for Sample 1 by the two methods was 0.19%, and for Sample 1-A, 0.17%, or within the deviation or precision measure of the means. The average deviations by both methods were practically identical—namely, 0.24 to 0.33%.

Comments and Suggestions

Ralph Hart. In the hot-plate method we recommend the use of a short thermometer to serve as a stirring rod and to control the temperature. It was found that a considerable error was possible due to the improper taring of the beaker, since its comparatively large surface may absorb an appreciable amount of moisture, which the short heating on the hot plate may not be sufficient to remove. It is, therefore, suggested that after heating on the hot plate and before each weighing, the sample be heated in a hot-air oven for a short period. The following experiment was made to determine the necessity for this extra precaution:

A 150-cc. beaker was wiped dry, about 5 grams of oleic acid added, and weighed without heating. The oil was then heated on a hot plate at 130° C., cooled, and weighed. This was repeated until the weight was constant. The results, which follow, indicate that only after the third heating was constant weight reached:

	Weight (grams)	Difference (grams)
Before heating	48.229	....
After 1st heating......	48.217	0.012
After 2nd heating......	48.193	0.024
After 3rd heating......	48.190	0.003
After 4th heating......	48.190	0.000

The experiment was repeated with the exception that the beaker was heated in a hot-air oven for 15 minutes after heating on the hot plate. The following results indicate that constant weight was thus obtained after the first set of heatings:

	Weight (grams)	Difference (grams)
Before heating	55.512	....
After 1st heating on hot plate	55.491	0.021
After heating in oven..	55.468	0.023
After 2nd heating on hot plate and oven..	55.469	Negl.

Mr. Long and several others of the committee are strongly opposed to calcium chloride as a desiccant. A recent paper by J. H. Bower [Research Paper 649, *Bur. Standards J. Research*, **12**, 241-8 (1934)] on "A Survey of Commercial Drying Agents" seems to substantiate their objections. The method employed by Mr. Bower for determining the comparative efficiencies of the more common commercial drying agents, as well as some newer drying materials recently introduced, was to aspirate properly conditioned air through a train of U-tubes containing the drying materials in the order of their increasing drying powers. After a measured amount of air had passed through the system, the increase in the weights of the U-tubes following any one U-tube indicated the residual water escaping that tube.

The materials studied (with the amount of residual water in milligrams per liter of air dried), in the order of increasing efficiency at 30 C., follow: $CuSO_4$ (anhydrous), 2.8; $CaCl_2$ (granular), 1.5; $CaCl_2$ ("technical anhydrous"), 1.25; $ZnCl_2$ (sticks), 0.98; $Ba(ClO_4)_2$, 0.82; NaOH (sticks), 0.80; $CaCl_2$ (granular), (dehydrated), 0.36; $Mg(ClO_4)_2.3H_2O$, 0.031; silica gel, 0.030; KOH (sticks), 0.014; Al_2O_3, 0.003; $CaSO_4$ (anhydrous), 0.005; CaO, 0.003; $Mg(ClO_4)_2$, 0.002; BaO, 0.00065. The commercial names of some of the chemicals tested are as follows: $Ba(ClO_4)_2$, "Desichlora"; $Mg(ClO_4)_2.3H_2O$, "Dehydrite"; Al_2O_3, "Hydralo"; $Mg(ClO_4)_2$, "Anhydrone," and $CaSO_4$ (anhydrous), "Drierite."

W. H. Irwin. My reasons for recommending the hot-plate method for moisture in sulfonated oils as an alternative method are because it is so much quicker than the distillation procedure, it is official with the A. O. C. S., and it yields satisfactory results. We have used the hot-plate moisture method on thousands of samples of oils and fats, including many of high fatty acid content, and seldom if ever have a discrepancy.

The temperature registered by a thermometer placed horizontally on the hot plate should be between 215 and 225° C. and the temperature of the sample should at no time exceed 130° C. I had two different analysts check the effect of carrying the moisture determination by the hot-plate method beyond the smoking stage. In the case of Sample 1, one analyst found an increase in loss of 0.06% and the other 0.09%; with Sample 1-A, one analyst reported an increase in loss of 0.2% and the other, 0.3%. These differences, in my opinion, are not significant when dealing with samples containing as much water as these and indicate that there is not much danger of error due to overheating.

M. F. Lauro. Had great difficulty in the beginning with the distillation method because the end of the condenser tube dipped below the surface of the liquid in the trap and some of the liquid shot up into the condenser instead of flowing back into the distillation flask. I believe that

(*Continued on page* 238.)

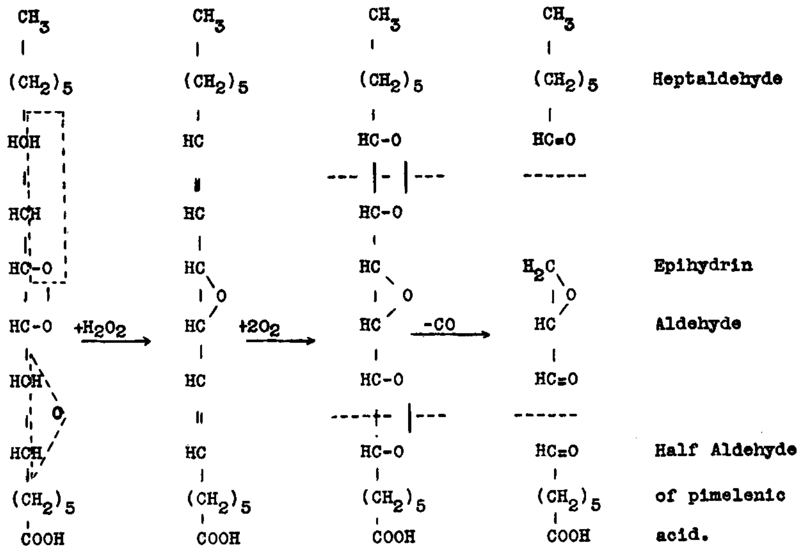


FIGURE VII

Oxidation of Oleic Acid According to Powick

cid lard at 100° C. and 3-5 mm. Hg pressure are inactive as catalysts of oxidation. These materials include the substances which are responsible for rancid odor and taste.

(2) That the peroxides are inactive as catalysts of oxidation.

Conclusion

The conclusion has been drawn that the active catalytic materials are of high molecular weight and not readily volatile at 200° C. and 3-5 mm. Hg pressure. This conclusion has been *tentatively* checked by the use of a synthetic product.

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(*Continued from page* 230.)

that part of the condenser tube should reach within 0.25 inch of the surface of the liquid.

C. P. Long. It is very desirable that the F. A. C. hot-plate method, which is one of the official methods of the A. O. C. S., be standardized much better than it is now. We believe that the size of the sample, the dish used, and the hot plate itself, and its temperature should be specified. We have set a limit of 130° C. as the maximum temperature to which the oil should be heated.

It has been our sad experience that calcium chloride will give up moisture to dry samples long before its physical appearance will give any indication of its condition. For this reason the committee should place some limit on the use of desiccating agents to be used in the desiccator.

H. H. Mosher. We have compared the hot-plate and distillation methods with ten samples of different oils and obtained practically check results when the time factor and the temperature of the hot plate was accurately controlled. We have found, however, that there is a small progressive deterioration of oil by the hot-plate method with a gradual loss in weight, so that some care and intelligence must be exercised in determining the end point. We have usually estimated this at the point at which the loss of weight flattens out.

R. H. Pingree. In order to eliminate the difficulty and expense of replacing parts of the distillation apparatus, I would recommend that both ground joints be "Standard Taper and Interchangeable Joints" and would suggest for this purpose Standard Joint No. 25 (Bureau of Standards, Commercial Standard CS21-30).

W. H. Tiffany. After making a number of tests with rapid evaporation methods, it would appear that the results are unreliable and subject to variations due to the speed of the determination, superheating at walls of vessel, or other unknown factors. However, after running a number of analyses according to the specifications of the hot-plate method as modified by the committee, I find that the results check well and are in good agreement with those by the distillation method.

Ralph Wechsler. Concerning the distillation apparatus, I fully agree with Mr. Lauro that the lower end of the condenser tube should not dip into the liquid of the trap, but should extend only to about 0.25 inch above the surface, in order to prevent the liquid from shooting up into the tube.

Summary

The committee finds that both the A. A. T. C. C. distillation method and the modified hot-plate method are satisfactory for the determination of moisture in commercial sulfonated oils that are free from other volatile matter. The agreement among different analysts was about the same for both methods, with an average variation of about 0.3%, which may also be considered as the probable precision or reliability of each method. Hence, the committee recommends the A. A. T. C. C. distillation method as a standard method and the modified hot-plate method as an alternative method. In the proposed procedures, the A. A. T. C. C. moisture apparatus has been modified so that the end of the condenser tube is raised above the level of the liquid in the trap, and the specifications for the ground joints have been changed to correspond to Interchangeable Ground-Glass Joint 25 of Commercial Standard CS21-30. The F. A. C. hot-plate method has been modified to include a short thermometer (for the control of temperature and to serve as a stirring rod), heating in an air-oven before weighing, and the addition of oleic acid to keep the sample homogeneous and liquid.

Proposed Standard Method of Test for Water in Sulfonated (Sulfated) Oils

A. O. C. S. Distillation Method

1. *Scope.* This method of test determines water existing in a sample of sulfonated (sulfated) oil by distilling the sample with a volatile solvent. It applies only to sulfonated oils that do not contain the following: mineral acids, free sulfonic acids, or free sulfuric acid ester; or alcohol, glycerol, diethylene glycol, acetone, or other water-miscible volatile compounds.

Apparatus

2. *General.* The apparatus shall consist of a glass flask, heated by suitable means and provided with a reflux condenser, discharging into a trap and connected to the flask. The connections between the trap and condenser and flask shall be ground joints. The trap serves to collect and measure the condensed water and to return the solvent to the flask.

Before use, the condenser and the receiving tube shall be thoroughly cleaned with soap and warm water, rinsed well, then treated with hot cleaning solution (a mixture of 10 ml. of saturated potassium bichromate and 990 ml. of concentrated sulfuric acid), and finally thoroughly washed and dried.

3. *Flask.* The glass flask (Fig. 1A) shall be of the short-neck, round-bottom type, made of well-annealed glass, having an approximate capacity of 500 ml.

4. *Heat Source.* An oil bath (stearic acid, paraffin wax, etc.) or an electric