The Analysis of Sulphonated Oils*

Report of American Leather Chemists' Association Committee

By G. W. PRIEST

WHEN I made my committee report a year ago on a method for the determination of neutral oil in sulphonated castor oil, the work was more or less incomplete and I requested further time for study. Some question has arisen since then concerning what was meant by neutral oil in this particular case. I assumed that, as there was no difficulty in determining the unsaponifiables by the usual methods and that neutral oils other than castor were separable by petrolic ether or by calculation according to our A.L.C.A. methods, the problem of the committee was to work out an accurate method for the determination of neutral oil due to castor oil alone, and if possible one that was reasonably rapid and foolproof.

In order to find a definition of neutral oil in a sulphonated oil I consulted several oil chemists and we came to the conclusion that the following would be a good one. In using the term neutral fat the A.L.C.A. uses the right term. Neutral fat then may be defined as all neutral saponifiable matter which exists in a sulphonated oil. This does not include such materials as ammonia soaps and salts, because the ammonia soaps are already saponified and cannot be classed a ssaponifiable matter and the latter are not soaps and the reaction is not one of saponification. In spite of this broad definition we proceeded to study sulphonated oils which we knew contained nothing at the start but pure castor oil.

Most of my business life has been spent in the manufacture of patent leather and the study of chemical problems which are related to it. My experience with castor oil in the plant and laboratory leads me to believe that there is a loose hydroxyl group in the molecule which wanders, often into combinations which are injurious and in the laboratory exceedingly difficult to detect and isolate. After my experience of last year I approached the problem with many misgivings. Before starting on the study I got in touch with several manufacturers of sulphonated castor oil to ascertain what their neutral fat control was, and found the situation to be about as follows. They buy a technically pure castor oil and sulphonate it according to their usual procedure, assuming that they get from two to three per cent neutral fat in a highly sulphonated oil and ten to fifteen in a less highly sulphonated one. They rarely analyze it for neutral fat on account of the length of time required for the analysis and its complications. They use, when a determination is essential the method of Lewkowitsch which was suggested by Bumcke and which I retained as a tentative method until I found something as good or better. One of the members of this committee who is technical director of a large laboratory later corrected his statement about the use of the Lewkowitsch method as follows and suggested the trial of a modification of method No. 5 of last year. He writes that "in using petroleum ether rather than sulphuric ether in this determination we are choosing the lesser of two evils. Whereas the petroleum ether will tend to give high results by dissolving some of the soap, we have found that in attempting to make corrections for the soaps dissolved by the sulphuric ether, greater losses were involved which brought the results close to those attained by petrolic ether." Below are the two methods.

Modified method of Lewkowitsch — Ten grams of the sample are dissolved in 50 cc. of water, 20 cc. of ammonia and 30 cc. of glycerine are added and the mixture is extracted twice with ether, using 100 cc. for each extraction. The ethereal solution is then washed three times with water to remove small quantities of dissolved soap and the ether evaporated off. The residue is transformed to a small tared beaker, dried at first on the water bath, then at 100° C. and weighed to constant weight.

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	215 mg KOH per gram	%	216 mg KOH per gram	%
Total Alkali (A)	44.83		25.78	
(R)	—14.86		—8.65	
SO_3 .1426 (A + F)		4.274		2.24
Neutralized Combined SO_3		6.37		3.56
Moisture		26.55		24.34
Ash		4.00		1.96
Unsaponifiable		.66		1.69
Saponification No. (Uncorrected) E°	128.13		143.23	
Free and Comb. Fatty Acids (B)	72.36		77.10	
Alkali Minus NH_3 (C)	—4.32		—21.17	
NH_3[.030357 (A-C)]		1.49		1.43
Free Fatty Acids (B-A)	27.53		51.32	
Sodium Sulphate in Ash due to combined SO_3		3.25		0
Sodium Carbonate in Ash due to combined fixed alkali comb. as soap		0		0
Total salts and impurities		.75		1.96
Sodium bound as soap		0		0
Total fatty matter		64.18		67.02
Oleic Acid		36.40		38.78
Neutral Fat		27.78		28.24
Neutral Fat (Extraction method)		13.05		16.64
Neutral Oil (Extraction method)	(sulfuric ether)	13.71		18.33
Neutral Fat (Extraction method)				13.31
Neutral Oil (Extraction method)	(petrolic ether)			15.00
Sapon. Equiv. of Fatty Matter E°	128.13 mgms KOH		143.23 mgms KOH	
Sapon. Equiv. Neutral Fat En	51.45 mgms KOH		44.96 mgms KOH	
Neutral Fat Hart Method		26.18		24.68

	←No. 243 lot 2657→ mg KOH per gram	%	←No. 244 lot 2681→ mg KOH per gram	%
Total Alkali (A)	38.40		17.50	
(F)	—4.09		18.55	
SO_3 .1426 (A + F)		4.89		5.14
Neutralized Combined SO_3		7.28		7.66
Moisture		26.50		32.14
Ash		10.03		7.98
Unsaponifiable		0.25		0.27
Saponification No. (This En does not include Free Fatty Acids, Ammonia as Soap or Ammonia as Salts)	36.93		61.74	
Free and Comb. Fatty Acids (B)	77.61		54.34	
Alkali — NH_3 (C)	38.40		17.50	
NH_3 [.030357 (A-C)]		0.00		0.00
Free Fatty Acids	39.20		36.84	
Na_2SO_4 in Ash due to combined SO_3		8.70		6.79
Na_2CO_3 in Ash due to combined fixed alkali combined as soap		0.39		0.00
Total Salts and Impurities		0.94		1.19
Sodium bound as soap		1.57		0.72
Total Fatty Matter		63.46		58.12
Oleic Acid		39.04		27.33
Neutral Fat		24.42		30.79
Neutral Fat (Ether extraction)		9.14		15.06
Neutral Oil (Ether extraction)		9.39		15.33
Neutral Fat (Petrolic Ether ext.)		5.02		8.78
Neutral Oil (Petrolic Ether ext.)		5.27		9.05
Saponification Equivalent of Fatty Matter	E° 76.14 mgms KOH		98.58 mgms KOH	
Saponification Equivalent of Neutral Fat	En 36.93 mgms KOH		61.74 mgms KOH	
Neutral Fat Hart Method		20.45		30.91

NEUTRAL FAT EXTRACTION METHODS

	215	216	243	244
Ether	13.05	16.64	9.14	15.06
Pet. Ether	——	13.31	5.02	8.78

Petrolic ether method—Weigh 10 grams of sample into a 250 cc. Erlenmeyer flask. Add 50-70 cc. of Alcohol and a few drops of phenolphthalein, then add slowly N/2 NaOH until neutral. Extract three times in a separatory funnel. Wash extract three times with water. Evaporate and dry with usual precautions. The only other suggestion which I had received was that the ether extract in the Lewkowitsch method should be corrected for dissolved soap.

Before sending samples of oil out to the committee for study, I determined to do some work in order to test out further the two methods and in particular the correction for soap included in the ether extract. I had prepared for me by manufacturers of sulphonated castor oils four samples made from pure castor oil numbered as follows: 215-216-243-244. I had hoped that I might also find some new volatiles or mixtures which might be used successfully for separation of neutral oil but everything tried failed. Below I quote from our laboratory report.

"We believe that these four oils have been prepared from technically pure castor oil. Judging from the performance of these oils under the two methods in our laboratory alone we would have been fairly well satisfied. No. 216 gave us the greatest trouble in the separation of the emulsions. However, we succeeded in completing the analysis in about ten days. The other oils gave us little trouble in the extractions, but we found it more or less difficult to wash the extractions with water and get good separations." "Prolonged and careful study of soap in the ether and petroleum ether extract showed that each carried over the same amount, to the extent of about 1 per cent. As we are not sure that this is soap we have not shown the correction."

At this time it appeared that if a determination of neutral fat was to be made on a sulphonated castor oil, there was only one thing to be done and that was to take the necessary time and precautions for the ether or petrolic ether methods which would mean as far as time went from three days to a week. For control work I was willing to do this. On page 266 is a tabulation of the results of continuous work extending over more than two month. This work was done in triplicate and the checks were very close. The work was as carefully and painstakingly done as in any research laboratory and performed by two very skilful oil chemists. I have every confidence in the accuracy of the results as far as the limitations of our laboratory equipment goes.

This corroborates our work of a year ago that petrolic ether while speeding up the work by giving sharper breaking emulsions was too low in results for accuracy.

The manufacturer of oils Nos. 243 and 244 recommended the petrolic ether method for determination of neutral fat reported the following figures.

	243	244
Neutral Fat	12.27	20.85

I have great confidence in his laboratory technique and have never had more than a fraction of a per cent difference in our check ups on other oil analyses, and am at a loss to explain this difference. Many complications can and do occur during analysis of castor oils which cause polymerization. In some cases the ether residue after complete aqueous wash and drying to constant weight was not soluble in alcohol and in other cases it was. The drying of such oily residues should be done either in vacuo or in a stream of inert gas. I had no such apparatus. It became apparent as time went on that I was dealing with a very complicated problem, but as I was about to send out samples to the committee, Ralph Hart published his paper in A.L.C.A. JOURNAL and I immediately got in touch with him and sent him the results of our analytical work so that he could figure out the percent of neutral fat by his titration method. I was a bit skeptical when the results came back, but noticed that there was a relationship between his figures and ours. In a paper written by him which will shortly appear are quotations from reports of research work which is being done abroad and which would make it appear that our conceptions of neutral fat in a sulphonated castor oil will have to be changed. During sulphonation some polymerization takes place which makes a water soluble castor product, and also leaves some unchanged castor oil. The titration method shows both of these products and is a true value of the oil. While we get by our regular method a figure by calculation, Hart's new method gives us one which is obtained directly. It will be observed in the paper which he is about to publish that our A.L.C.A. method of which he is the father, does not differ more than two or three per cent from this direct titration method.

Conclusions

THE method of Lewkowitsch as outlined, using ether, in skilled hands and with the use of vacuum drying ovens or one having a stream of inert gas during the drying period of the ether extract gives a partial measure of neutral fat in a sulphonated castor. The

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The true iodine number of a fat or fatty acid denotes the amount of iodine absorbed to give a saturated halogen compound without any substitution. The iodine number of the constants is not necessarily the true iodine number since it represents a chemical equilibrium, where the iodine is divided between several fatty acids. The Wijs method for the determination of iodine numbers gives the true value. *Chem. Umschau Fette, Oele, Wachse u. Harze* 37,85-7 (1930).

The antioxidizing power of alpha-naphthol on linseed oil is stronger than that of beta-naphthol and the higher the temperature the greater the activity of the former. Because of volatility, it is difficult to make either naphthol hold its antioxygenic activity for a long time at elevated temperatures. *J. Soc. Chem. Ind. Jap.* Suppl. Bind. 33, 107-9 (1930).

Minute quantities of nitrous oxide and ammonia are said to act as negative catalysts in the hydrogenation of oils when nickel is used as the active catalyst. Prior treatment of the nickel catalyst with various anesthetics, such as urethan, barbital, brucine, cocaine hydrochloride and the like, retard the catalytic activity of the nickel. *J. Soc. Chem. Ind. Jap.* Suppl. Bind. 32, 318-23 (1930).

A qualitative test recommended for the detection of free caustic soda in toilet and grained soaps is as follows: add a few drops of phenolphthalein to 25 cubic centimeters of 96 per cent alcohol, then neutralize to a light rose tint; dissolve two grams of the finely divided sample in this alcohol with heat and exclusion of air. Cool, and if free caustic soda is present, the solidified mass will retain a distinct red color for at least one hour. *Seifensieder-Ztg.* 56, 402-3 (1929).

The potassium soaps of most oils and fats split off approximately one-half of their alkali content on hydrolysis, except the potassium soaps of castor oil, coconut oil or rosin, which split off from 6.1 to 26.3 per cent. Sodium soaps hydrolyze somewhat less than the corresponding potassium soaps. *Seifensieder-Ztg.* 56, 386-8 (1929).

According to Herbert G. French, vice-president of Procter & Gamble Company, business has been very much above average in all departments during the past three weeks. It is reported that an additional disbursement in the form of a stock dividend of possibly 2 or 3 per cent is likely to be forthcoming during the latter part of this year, in view of the company's excellent earnings prospects.

El Dorado Oil Co., which crushes copra, with mills at San Francisco, has been taken over by the Colgate-Palmolive-Peet Co., according to recent announcements. The acquisition of El Dorado by Colgate-Palmolive-Peet, negotiations for which were reported a month ago, gives the soap company a source of coconut oil independent of Philippine imports.

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time needed for the analysis is so long and the care and patience required so great that many sources of error can creep in while the final figure is not an exact one. The modification using petroleum ether gives results much too low and should not be recommended as a standard method. Hart's method is a quick accurate method and appears to have behind it the weight of research work now being done overseas. It is evident that we are going to be obliged to change our ideas about the amount of neutral oil in a pure sulyhonated castor oil and to recognize that there is about 26 per cent of a fatty matter unsulphonated but saponifiable. I recommend that the committee make a study of this method for the coming year after Hart has published his paper.

The association is indebted to The Griess-Pfleger Tanning Company for its permission to allow its laboratory to give so much time to this work in spite of the fact that it uses practically no sulphonated castor oil. I am indebted to John W. Harnly, research chemist, of the above firm for the amount of work which he did and Kenneth Matzinger. Ralph Hart has met me in a spirit of rare cooperation and I am glad that it has fallen to his lot to help out the tanning laboratories once more, and to strengthen a seemingly weak spot in the A.L.C.A. method.

Referee Applicant

W. M. Black, of Augusta, Georgia, has applied for certification as Referee Chemist of the American Oil Chemists' Society. (*Second publication.*)