# A New Method for the Determination of Neutral Fat in Sulphonated Oils*

By RALPH HART

IN A paper by the writer on the "Determination of Neutral Fat in Sulphonated (sulfated) Oils,"[1] it was suggested that instead of finding the neutral fat gravimetrically, the determination of the saponification number corresponding to the neutral fat might be sufficient. Since then Nishizawa and Winkuti[2] have investigated the effect of alkali on sulfonated oils and find that boiling for five hours with 1.oN alcoholic caustic has only a negligible effect on the sulfate radical. Hence, saponification tests on sulfonated oils may be carried out without fear of interference from the organically combined sulfate group. Herbig[3] also has made saponification tests on the neutral fat extracted from sulfonated castor oil by means of cold acetone—a method developed by himself.

While the present A.L.C.A. method for the analysis of sulfonated oils are quite complete, it would seem desirable to include the saponification test outlined below; which by calculation would furnish the following additional information; (1) the saponification value of total fatty matter—useful in identifying the origin of the sample, (2) saponification equivalent of neutral fat, and (3) the approximate percentage of neutral fat.

In this discussion the following terms will be employed:

(a) "Fatty Matter" — animal or vegetable oils, fats and waxes which react with alkali.

(b) "Unsaponifiable Oil or Grease" — mineral oil and waxes not affected by alkali.

(c) "Oil or Grease"—a mixture of the first two, or fat of unknown composition.

There will also be made the following distinction between the different saponification data:

(a) "Saponification Figure (F)" will refer to the mgms. KOH required to saponify the total oil, or any of its components, in one gram of the original sample.

(b) "Saponification Value (V)" will indicate the mgms. KOH required to saponify one gram of the water-free total oil, or any of its components.

(c) "Saponification Number (N)" will refer to the mgms. KOH required to saponify any component contained in one gram of total fatty matter.

Thus the neutral fat in a sample composed of 50 per cent total fatty matter containing 20 per cent (based on the sample) neutral fat, one gram of the latter requiring 190 mgms. KOH for its saponification, will show a saponification figure of 38, saponification value of 190 and a saponification number of 76, all expressed as mgms. KOH.

The following procedure for the determination of neutral fat by the saponification method is suggested:

1. *Free and combined fatty acids (B)*[4]—Weigh 8 grams of the sample into a 500 cc. beaker, add 50 cc. of 95 per cent alcohol and several drops of phenolphthalein indicator. Run in N/2 NaOH until end point is reached; boil gently until no more $NH_3$ is given off (to be tested for, with moist red litmus paper), cool, add N/2 NaOH again until the pink color persists; again boil to drive off any remaining $NH_3$ and add N/2 NaOH after cooling to bring to end point. Record the total number of cc. of N/2 NaOH required. Add 150 cc. water and 5 cc. methyl orange indicator and titrate to acid end point with N/2 $H_2SO_4$. The number of cc. of N/2 $H_2SO_4$ required for this titration, corresponds to the combined and free fatty acids. Calculate to mgms. KOH per gram of sample = B.

2. *Alkali minus ammonia or fixed alkali (C)*[4]—In the test for combined and free fatty acids, the number of cc. N/2 $H_2SO_4$ minus total number of cc. of N/2 NaOH used to make alkaline corresponds to the alkali minus $NH_3$ (in the case of the presence of ammonium salts this may be a minus quantity). Preserve the sign and calculate to mgms. of KOH per gram of sample = C.

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[1] *Jour. A. L. C. A.* 24, 120 (1929).
[2] *Chem Umschau* 36, 97 (1929).
[3] *Fäber-Ztg.* 25, 169 and 194 (1914).
[4] *Jour. A. L. C. A.* 22, 588 (1927).

3. *Saponification figure of total fatty matter* ($F°$)[5]—2 to 2.5 grams of oil are boiled in an Erlenmeyer flask (Jena glass) of 200 cc. capacity for 30 minutes under a reflux condenser with 25 cc. of N/2 alcoholic potash measured from a pipette; a blank test with 25 cc. of this solution is run simultaneously, every operation being exactly the same as with the sample. The blank test is necessary in view of changes of temperature and the solubility of the glass in alkali. After saponification, 50 cc. of neutralized alcohol are added to the sample, boiled gently until no more $NH_3$ is given off (to be tested for with moist red litmus paper), and then titrated back with N/2 hydrochloric acid in the presence of phenolphthalein; the amount of acid necessary to neutralize the 25 cc. is also determined. Calculate the amount of alkali absorbed by the fat to mgms. KOH per gram = F°.

4. *Total fatty matter*—Usual procedure.

It will be noticed that the saponification figure of total fatty matter is the only new determination; the others are taken from the present A.L.C.A. methods. From the above data, the following formulas were derived:

Formula 1. Saponification figure of total fatty matter plus fixed alkali of sample, mgm. KOH per gram = $F° + C$.

Formula 2. Saponification value of total fatty matter, mgm. KOH per gram;

$$V° = \frac{100\ (F° + C)}{\text{Per cent total fatty matter}}$$

Formula 3. Saponification figure of neutral fat, mgm. KOH per gram; $Fn = (F° + C - B)$.

Formula 4. Neutral fat, approximate per cent of sample;

$$p = \frac{100\ Fn}{V°}$$

Formula 5. Approximate saponification value of neutral fat, mgms. KOH per gram;

$$Vn = (V° - 10 + \frac{p}{10}$$

Formula 6. Neutral fat, corrected, per cent of sample;

$$P = \frac{100\ Fn}{Vn}$$

Formula 7. Neutral fat, corrected, per cent of total fatty matter

$$= \frac{100\ P}{\text{Per cent total fatty matter}}$$

Formula 8. Saponification number of neutral fat, mgm. KOH per gram

$$= \frac{100\ Fn}{\text{Per cent total fatty matter}}$$

In formula 4, the saponification value ($V°$) of total fatty matter or mixed fat has been used instead of the saponication value of the neutral fat, which is not known. Hence the per cent neutral fat (p) so calculated is only approximate and is always lower than the correct value, from which it may differ by as much as 5 per cent. In formula 5, an attempt has been made to calculate the saponification value of the neutral fat (Vn) in the mixture; this can be determined approximately only, as follows: It can be shown that the difference in the saponification values between neutral fat and the corresponding fatty acids is approximately 10 mgms. With this assumption—and with the approximate per cent neutral fat (p) and the saponification value of total fatty matter ($V°$) given—the derivation of the following equation will be evident:

$$\frac{p}{100} Vn + (1 - \frac{p}{100}) (Vn + 10) = 100\ V°$$

which reduces to the following simple formula:

$$Vn = V° - 10 + \frac{p}{10}$$

If we assume no lactones, anhydrides or other neutrals fats that do not contain glycerine, formulae 6 and 7 are probably correct to within the experimental error. Tables I and II below show the accuracy with which the saponification value of neutral fat, as well as the present neutral fat, may be calculated by means of the above formulas. Tables I represents known mixtures of neutral fat and fatty acids, having saponification values of 190 and 200 respectively; Table II (corresponding to a castor oil product) represents similar mixtures with saponification values of 170 and 188 respectively.

G. W. Priest, chairman of the A.L.C.A. Committee on sulfonated oils for 1929 and who instigated this paper, has kindly furnished the writer with the preliminary results of the work by his laboratory on the determination of neutral fat by various methods. In Table III is listed part of this data, from which were calculated, by means of Formulas 1 to 8 inclusive, the results given in Table IV. In Table V the neutral fat by extraction methods and the new method are compared.

It is evident from Table V that the results obtained by the saponification method are about twice as great as that by extraction with ether, and even greater when the extraction is made with petroleum ether. It seems therefore that extraction of the original undecomposed oil by solvents does not yield all of the neutral fat, or all the fat that will react with alkali. It would also seem to be established that some of the neutral fat must be sulfonated and, hence, partly soluble in water; consequently is only incompletely if at all extracted by solvents.

[5] Holde-Mueller, *First Eng. Ed.*, *p.* 342, 1915.

TABLE I.—SHOWING ACCURACY OF CALCULATING Vn

Saponification value neutral fat = 190
Saponification value fatty acids = 200

| Mixture No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Neutral fat, actual per cent | 00 | 20 | 50 | 70 | 100 |
| Fatty acids, actual per cent | 100 | 80 | 50 | 30 | 00 |
| Theoretical saponification value of mixture (V°), mgm. KOH | 200 | 198 | 195 | 193 | 190 |
| Theoretical saponification no. of neutral fat, mgm. KOH | 00 | 38 | 95 | 133 | 190 |
| Neutral fat (p) calculated, approximate per cent (Formula 4) | 00 | 19.2 | 48.7 | 68.9 | 100 |
| Difference between actual and approximate per cent neutral fat | 00 | —0.8 | —1.3 | —1.1 | 00 |
| Calculated saponification value neutral fat (Vn), mgm. KOH (Formula 5) | 190 | 189.9 | 189.9 | 189.9 | 190 |
| Neutral fat, corrected, per cent (Formula 6) | 00 | 20 | 50 | 70 | 100 |
| Difference between actual and corrected per cent neutral fat | 00 | 00 | 00 | 00 | 00 |

TABLE II.—SHOWING ACCURACY OF CALCULATING Vn

Saponification value neutral fat = 180
Saponification value fatty acids = 188

| Mixture No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Neutral fat, actual per cent | 00 | 20 | 50 | 70 | 100 |
| Fatty acids, actual per cent | 100 | 80 | 50 | 30 | 00 |
| Theoretical saponification value of mixture (V°), mgm. KOH | 00 | 36 | 90 | 126 | 180 |
| Theoretical saponification no. of neutral fat, mgm. KOH | 00 | 36 | 90 | 126 | 189 |
| Neutral fat (p) calculated, approximate per cent (Formula 4) | 00 | 19.3 | 48.9 | 69.1 | 100 |
| Difference between actual and approximate per cent neutral fat | 00 | —0.7 | —1.1 | —0.9 | 00 |
| Calculated saponification value neutral fat (Vn), mgm. KOH (Formula 5) | 178 | 178.3 | 178.9 | 179.3 | 180 |
| Neutral fat, corrected, per cent (Formula 6) | 00 | 20.2 | 50.3 | 70.3 | 100 |
| Difference between actual and corrected per cent neutral fat | 00 | 0.2 | 0.3 | 0.3 | 00 |

TABLE III.—ANALYSES OF SULPHONATED OILS

| Sample No. | 215 | 216 | 243 | 244 |
|---|---|---|---|---|
| Free and combined fatty acids (B), mgm. KOH | 72.36 | 77.10 | 77.61 | 54.34 |
| Fixed alkali (C), mgm. KOH | —4.32 | —21.17 | 38.40 | 17.50 |
| Saponification figure of total fatty matter (F°), mgm. KOH | 128.1 | 143.2 | 76.14 | 98.58 |
| Total fatty matter, per cent | 63.01 | 67.02 | 63.46 | 58.12 |
| Neutral fat (petroleum ether extraction), per cent of sample | —— | —— | 5.02 | 8.78 |
| Neutral fat (ether extraction), per cent of sample | 13.05 | 16.64 | 9.14 | 15.06 |

TABLE IV.—NEUTRAL FAT BY CALCULATION

| Sample No. | 215 | 216 | 243 | 244 |
|---|---|---|---|---|
| Saponification figure total fatty matter plus fixed alkali, mgm. KOH | 123.8 | 122.1 | 114.5 | 116.1 |
| Saponification value total fatty matter (V°), mgm. KOH | 196.5 | 182.2 | 180.4 | 199.8 |
| Saponification figure neutral fat (F), mgm. KOH | 51.42 | 44.93 | 36.93 | 61.74 |
| Neutral fat, (p) approximate per cent of sample | 26.18 | 24.66 | 20.47 | 30.90 |
| Approximate saponification value neutral fat (Vn), mgm. KOH | 189.1 | 174.7 | 172.5 | 192.9 |
| Neutral fat, corrected, per cent of sample | 27.2 | 25.8 | 21.4 | 32.0 |
| Neutral fat, corrected, per cent of total fatty matter | 43.2 | 38.5 | 33.7 | 55.1 |
| Saponification number of neutral fat, mgm. KOH | 81.7 | 67.0 | 58.2 | 106 |

TABLE V.—NEUTRAL FAT METHODS COMPARED

| Sample No. | 215 | 216 | 243 | 244 |
|---|---|---|---|---|
| Method: | | | | |
| Petroleum ether, extraction per cent sample | —— | —— | 5.02 | 8.78 |
| Ether extraction, per cent sample | 12.05 | 16.64 | 9.14 | 15.06 |
| Saponification or new method | 27.2 | 25.8 | 21.4 | 32.0 |

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## American Maize Income

The American Maize Products Company has reported for 1929 a net income of $1,548,440, or $4.81 a common share after preferred dividend requirements. This compares with $589,205, or $1.61 a share, in 1928.

Current assets at the end of 1929 were $3,700,852, and current liabilities, $355,112, leaving a net working capital of $3,345,740, compared with $4,182,038 in June, 1929. During 1929 the company acquired 9,432 shares of preferred stock, which is held in the treasury. The common stock was changed from $100 par to no-par and 300,000 new shares were issued for 30,000 old $100 par stock.

Total assets at the end of 1929 were $7,482,687.

Penick & Ford, Ltd., will add two buildings to its plant at Cedar Rapids, Iowa, this summer. One building will be a 50-by-70-foot two-story addition to the dry starch plant, and the other, a three-story structure for office, assembly and recreational uses. Equipment in the starch plant addition will represent further investment of $70,000, and that for the office building about $60,000.

Swift & Co., have contracted for the erection of a lard refinery at Nuevo Laredo, Mexico, to which crude lard will be shipped from the United States in bulk. The new plant will facilitate distribution to meet the steadily growing demand in Mexico for lard.

# New Books

Publication 276, of the Botanical Series of the Field Museum of Natural History, Chicago, is entitled "A Study of Some Characteristics of Vegetable Oils," by James B. McNair, Assistant Curator of Economic Botany. The publication discusses the possibility of relationship between characteristics of oils and fats, with particular reference to their melting points and the climatic habitat of the parent plants. Comprehensive tables, grouping the oils and fats according to progressive values of the more important characteristics, are included, the various plants being referred to according to accepted botanical names only.

The Soybean Oil of China and Its Manifold Uses, by A. A. Horvath, published by the Bureau of Industrial and Commercial Information, Ministry of Industry, Commerce and Labor, National Government of the Republic of China, Booklet Series No. 13.

This brochure gives a quick picture of the history of soybean oil production in China, the present methods of producing the oil, and the various uses to which the oil may be put, including edible, paint-making, soap-making, rubber substitute and other uses. An interesting chapter discusses the possibility of producing artificial petroleum products from soybean oil.

## Neutral Fat Determination

(*From Page* 305)

It is also interesting to note that Herbig[6] extracted a sample of sulfonated castor oil (containing 59.9 per cent total fatty matter and 5.8 per cent organically combined $SO_3$) with cold acetone and found that the extract, supposedly the neutral fat, was 26.51 per cent of the oil—a result more closely in agreement with the writer's method than with the present extraction method.

Neutral fat may conveniently be expressed in any one of the following ways:

(a) Saponification figure, *i. e.*, mgm. KOH per gram of sample.

(b) Per cent of sample.

(c) Saponification number or "neutral fat-number" *i. e.*, mgm. KOH per gram of total fatty matter.

(d) Per cent of total fatty matter.

Results expressed by the last two methods are obviously more complete than by the others, since they already take into account the per cent total fatty matter in the sample; they offer also the advantage in that the composition of the fatty matter in different samples may be more directly compared. As the "neutral fat-number" (c) is more readily calculated than the per cent neutral fat and furnishes almost as much information, it would seem to offer the best means for reporting the latter.

A new method is suggested for estimating neutral fat in sulfonated oils by means of saponification tests. Detailed procedures are outlined and the necessary formulas developed.

Mention has already been made of the courtesy extended by Priest in supplying the data in Table III. The writer is also greatly indebted to Priest and to J. W. Harnly for many helpful suggestions and corrections.

[6] *Loc. cit.*