Continued from opposite page.

"The Conflict of Politics with Science and Economics in the Fat and Oil Industry"—J. D. Craig.

"Votator"—R. C. Dawson.

"Oil Refining Practice in Latin America"—R. D. Oilar.

We will also have a paper by H. Aspegren, one or two from the Swift & Company Laboratories, and several others which have been promised, but the title of which have not yet been announced. The final program of the meeting will be published in the October issue of OIL AND SOAP.

In addition to the scientific program which is being prepared, the Local Committee has arranged for a preview of a Century of Progress Exposition, giving especial attention to the exhibits in the Hall of Science. The Ladies' Committee is also arranging enjoyable entertainment for the visiting and local ladies.

There will also be the annual Bowling Tournament which has been a feature of the last two meetings. Mr. King, chairman of this committee, will announce the time, place and events in the next issue of OIL AND SOAP.

There will also be golf for those who care to play if the weather permits, the usual football games, a visit to the famous Adler Planetarium, etc.

Come, bring your family, and enjoy an educational treat and entertainment at another of our fine Chicago meetings.

Why Not Hydroxyl Value?

By J. T. R. ANDREWS and R. M. REED

The Procter & Gamble Company

The Acetyl Value

THE hydroxyl content of oils and fats has long been recognized as a characteristic comparable in importance to the iodine number, saponification number, etc. Efforts to measure this "constant" quantitatively have resulted in the well known "acetyl value," which *Lewkowitsch*[1] has defined as "the number of milligrams of potassium hydrate required for the neutralization of the acetic acid obtained on saponifying one gram of an acetylated fat or wax."

In the estimation of acetyl value according to the Andre-Cook method, adopted by both the American Chemical Society Committee on Analysis of Commercial Fats and Oils[2] and the American Oil Chemists' Society,[3] the saponification values before and after acetylation are determined and the acetyl value calculated with the aid of the following formula:

$$A = \frac{S^1 - S}{1 - 0.00075\,S}$$

in which

A = acetyl value

S = saponification value before acteylation

S^1 = saponification value after acetylation

Weakness of the Acetyl Value

THE usefulness of the acetyl value in calculation has been somewhat diminished by the fact that it is based on a weight of acetylated substance, whereas most other constants, such as saponification value, are based on a weight of original sample.

DeGroote[4] pointed out that, contrary to the statement of *Lewkowitsch*,[5] acetyl values (since they are based on acetylated samples) cannot be used in interpolations to determine percentages of hydroxylated material in admixture

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with nonhydroxylated substances. *DeGroote* stated that this difficulty could be obviated through the replacement of acetyl value by "hydroxyl value," which he defines as "the milligrams of KOH required by the acetic acid from the acetylation and subsequent saponification of a l-gram sample of the oil or fat under examination." He suggested that in determining the hydroxyl value the sample be weighed before acetylation and the necessary precautions observed to prevent loss during acetylation and saponification.

The American Chemical Society Committee on Analysis of Commercial Fats and Oils[2] reported that the filtration and distillation methods for the determination of acetyl value were difficult and gave inaccurate results. These procedures are similar to that recommended by DeGroote for the determination of hydroxyl value, so that his proposed method does not appear to be advantageous.

This is the same hydroxyl value as that proposed by *Twitchell,*[6] who defined it as the "milligrams of potassium hydroxide having the same amount of hydroxyl as has 1 gram of the alcohol." Twitchell esterified hydroxyl groups with stearic acid in the presence of a catalyst and determined the hydroxl value of the substance by measuring the amount of stearic acid used.

Definition and Determination

THE definitions of Twitchell and DeGroote, although differing slightly in form, are identical in principle and may be restated as follows:

"The hydroxyl value of a substance is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram." This value may be determined from the saponification values before and after acetylation in the same manner as the acetyl value, the calculation being made with the aid of the following formula:

$$H = \frac{b - a}{1 - 0.00075\,b}$$

in which

H = hydroxyl value
a = saponification value before acetylation
b = saponification value after acetylation

The derivation of this formula may be carried out as follows:

On acetylation, one gram of hydroxyl will be changed to

$$\frac{17.008 + (60.032 = 18.016)}{17.008} \text{ or } 3.470$$

grams of acetate.

Let C = per cent hydroxyl in original sample. Then $0.0347\,C + (1 - C/100)$ = weight of acetylated oil obtained from one gram of original sample. Simplified, this becomes:

$$0.0247\,C + 1$$

Since by definition, hydroxyl value (H) is equal to $\frac{561.08}{17.008}\,C$, the weight of acetylated oil obtained from one gram of original sample may be expressed as: $0.00075\,H + 1$.

Let b = saponification value of acetylated oil. Then $b\,(0.00075\,H + 1)$ = saponification value of acetylated oil based on one gram of unacetylated oil = b_a.

Let a = saponification value of unacetylated oil. Then $b_a - a$ = increase in saponification value due to acetylation = H.

Substituting: $b(0.00075\,H + 1) - a = H$

$$\text{Or } H = \frac{b - a}{1 - 0.00075\,b}$$

The relationship between the hydroxyl value (H) and the acetyl value (A) may be calculated as follows:

$$\text{If } H = \frac{b - a}{1 - 0.00075\,b} \qquad (1)$$

$$\text{and } A = \frac{b - a}{1 - 0.00075\,a} \qquad (2)$$

Letting $0.00075 = K$

$$\text{Then } H = \frac{b - a}{1 - Kb} \qquad (3)$$

$$\text{and } b = \frac{H + a}{HK + 1} \qquad (4)$$

$$\text{Also } A = \frac{b - a}{1 - Ka} \qquad (5)$$

$$\text{and } b = A - aAK + a \qquad (6)$$

Equating (*4*) and (*6*):

$$\frac{H + a}{HK + 1} = A - aAK + a \qquad (7)$$

Solving (7) for H:

$$H = \frac{A}{1 - AK} = \frac{A}{1 - 0.00075A} \qquad (8)$$

Solving (8) for A:

$$A = \frac{H}{1 + 0.00075H} \qquad (9)$$

Equations (1), (2), (8), and (9) may also be expressed as follows:

$$H = \frac{1335.4\,(b - a)}{1335.4 - b} \qquad (10)$$

$$A = \frac{1335.4\,(b - a)}{1335.4 - a} \qquad (11)$$

$$H = \frac{1335.4\,A}{1335.4 - A} \qquad (12)$$

$$A = \frac{1335.4\,H}{1335.4 + H} \qquad (13)$$

Previous Formulas for Calculation of Hydroxyl Content

COCKING,[7] in 1918, published a formula for the calculation of the alcohol content of essential oils which is identical in principle with that given above for the calculation of the hydroxyl value and was derived in a similar manner.

Andre,[8] in 1921, suggested a formula for the calculation of the acetyl value using the saponification values obtained before and after acetylation. This was revised by *Cook,*[9] who gave a simple derivation for the formula and expressed it in the form now commonly used in the calculation of acetyl values. Cook also published a formula for the calculation of the alcohol content of oils which was essentially the same as the formula given above for the calculation of the hydroxyl value.

Advantages Over Acetyl Value

DEGROOTE[4] pointed out that the acetyl number of a mixture of 10 per cent of hydroxystearic acid with 90 per cent of material inert toward acetic anhydride would not be 16.4 (10 per cent of 164, the acetyl number of hydroxystearic acid), but would actually be 18.4. Thus an error of 12 per cent would be introduced if the hydroxystearic acid content of this mixture were calculated from the acetyl value according to the proportional relationship assumed by *Lewkowitsch.*[5] The relatively greater usefulness of the hydroxyl value is recognized when it is noted that the above mixture would have a hydroxyl number of 18.7, which is one-tenth that of hydroxystearic acid.

Accordingly it is recommended that acetyl value be replaced by the more rational constant, the hydroxyl value. Since the difference is in method of calculation, no change in analytical procedure is necessary. Adoption of this change will place this determination on the same basis as saponification value, acid value and ester value.

Limitations of Determination

THE determination of hydroxyl value presents no complications and gives accurate results when applied to oils consisting wholly of glycerides. When applied to hydroxy fatty acids, however, errors result due to two different and partially compensating causes. *Lewkowitsch*[10] pointed out that acetic anhydride converts fatty acids into their anhydrides, the resultant loss in weight causing acetyl values to be too high. *DeGroote*[4] showed that low acetyl or hydroxyl values are obtained when this method of analysis is applied to hydroxylated fatty acids (especially ricinoleic) due to the esterification of such materials on heating.

For these reasons, the determination of the hydroxyl content of fatty acids by the present method is unsatisfactory, and further work should be done to devise a method or procedure suitable for such substances. A step in this direction has been taken by *Zerewitinoff*[11] who has proposed a method for the determination of the hydroxyl content of fatty acids by utilizing the reaction between hydroxylated substances and methyl magnesium iodide in which methane is evolved. The methane is measured, and the total hydroxyl content (both alcoholic and carboxylic) of the fatty acid is then calculated. By titration the carboxylic hydroxyl may be determined and the alcoholic hydroxyl content is then calculated.

Applicability of Hydroxyl Value

IT should be noted that hydroxyl value may be determined upon other materials containing alcoholic hydroxyl groups, as well as on fixed oils, fats and waxes, provided other substances affected by acetic anhydride (notably aldehydes, phenols and acids) are not present. It is especially applicable to essential oils, many of which contain mixtures of various alcohols. In such cases, it may be preferable to express hydroxyl content by means of hydroxyl value rather than in terms of percentage of any one alcohol. Whenever the hydroxyl content is determined by formylation as proposed by *Glichitch*,[12] the hydroxyl value will be given by the following formula:

$$H = \frac{b - a}{1 - 0.00050\,b} = \frac{2003.8\,(b - a)}{2003.8 - b}$$

in which

H = hydroxyl value
a = saponification value before formylation
b = saponification value after formylation

References

(1) *Lewkowitsch, "Oils, Fats, and Waxes," Vol. I, 6th ed., p.* 437, *MacMillan* (1921).
(2) *Ind. & Eng. Chem.* 18 (1926), 1346.
(3) *Official Methods of Chemical Analysis of the American Oil Chemists' Society* (1929), 41.
(4) *DeGroote, et al., Ind. & Eng. Chem., Analytical Edition* 3 (1931), 250.
(5) *Lewkowitsch, "Oils, Fats, and Waxes," Vol. I, 6th ed., p.* 439, *MacMillan* (1921).
(6) *Twitchell, J. A. C. S.* 29 (1907), 568.
(7) *Cocking, Perf. & Ess. Oil Record* 9 (1918), 317.
(8) *André, Bull. soc. chim.* (4) 29 (1921), 745.
(9) *Cook, J. A. C. S.* 44 (1922), 392.
(10) *Lewkowitsch, "Oils, Fats, and Waxes," Vol. I, 6th ed., p.* 445, *MacMillan* (1921).
(11) *Zerewitinoff, Z. für Anal. Chem.* 52 (1913), 729.
(12) *Glichitch, Perf. & Ess. Oil Record* 14 (1923), 401.

Note

A paper entitled "Determination of Hydroxyl Number of Oils, Fats, and Waxes," by Willard L. Roberts and H. A. Schuette, presented during the spring meeting of the American Chemical Society at New Orleans, March 28-*April* 1, 1932, *and published in the Analytical Edition of Industrial and Engineering Chemistry, July* 15, 1932, *has come to our attention since the above was written. These authors describe and recommend a new procedure for determining the hydroxyl number of oils (e. g. rancid corn oil) which yield soluble, volatile acids likely to be lost during washing and drying of the acetylated oil in the usual procedure for determining acetyl value.*

Without questioning the usefulness of the Roberts and Schuette procedure in special cases, we believe that the Andre-Cook method as adopted by the A. O. A. C., the A. O. C. S., and A. C. S. is a better procedure for general use.

Although we have worked entirely independently, priority must of course be accorded Roberts and Schuette for such new subject matter as is common to the two papers, the chief item being the formula for conversion of hydroxyl value to acetyl value. In preferring hydroxyl value, based on weight of original sample, rather than acetyl value, based on weight of acetylated sample, the authors of both papers are merely following the lead of earlier workers. We sincerely hope that others in our field will interest themselves in this subject, and that acetyl value will eventually be displaced by the more useful hydroxyl value.

THE AUTHORS.

Cottonseed Oil Food Manufacturers Organize Institute

LEADING refiners of cottonseed oil and manufacturers of cottonseed oil foods, at a recent meeting in Chicago, organized an association to be known as the Institute of Cottonseed Oil Foods.

Concerns participating in the meeting, and which will be members of the Institute, were the Procter & Gamble Company of Cincinnati, the Southern Cotton Oil Company of New Orleans, the South Texas Cotton Oil Company of Houston, Tex., the Interstate Cotton Oil Refining Company of Sherman, Tex., International Vegetable Oil Company of Memphis, Tenn., Swift & Company, Armour and Company, Wilson & Co. and the Cudahy Packing Company of Chicago.

The packing companies are large refiners of cottonseed oil and producers of cottonseed oil foods, with plants scattered throughout the South. It is expected that other refiners and