The Determination of Rosin in Fatty Acids

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IN the United States the production of fatty acids from tall oil has been perfected to a high degree. Tall oil fatty acids of very low rosin content are produced by the industry and are used in ever-increasing quantities in the manufacture of surface-coating materials, detergents, and soaps. There has consequently been a great need for a method which would allow an accurate determination of low percentages of rosin acids in tall oil fatty acids and in the products manufactured from them.

This need became apparent to us during the development of a distillation process for separating tall oil into rosin and fatty acids. It was necessary to determine the rosin content of the fractions with great accuracy in order to control still operations, which were designed to produce a fatty acid containing approximately 1% rosin.

The most widely used methods for the determination of rosin acids in fatty acids are the Wolff method (14, 5, 1) and the McNicoll method (1, 8, 10). The Wolff method is largely used for the analysis of crude and refined tall oil while the McNicoll method is used for the analysis of tall oil fatty acids and for the determination of rosin in soaps and detergents. Both methods are similar in principle; the rosin acids are determined after the fatty acids present have been converted to methyl esters in the presence of a strong acid catalyst. The rosin acids remain largely unesterified since their carboxyl groups react very slowly under the conditions employed. The free rosin acids are then determined by titration with alkali.

In the Wolff method the titration is either carried out potentiometrically, in which case the inflection points define the alkali consumed by the rosin acids, or with the use of a thymol blue indicator, which by virtue of its two color changes allows a distinction between rosin acids and the sulfuric acid catalyst.

The McNicoll method uses phenolphthalein as an indicator. The rosin acids and the catalyst, β-naphthalenesulfonic acid, are titrated together against a blank containing the catalyst.

Gravimetric methods, in which both rosin acids and fatty acids are determined by weight, have been developed and are used in Germany, Sweden, and Finland (4, 9). The gravimetric methods are claimed to be more accurate than the volumetric methods but are very time-consuming.

None of the methods discussed above is entirely satisfactory. Despite many efforts to improve them (2, 3, 11, 6, 13, 12), they result in errors of at least $\pm$ 1% when analyzing mixtures containing small amounts of rosin.

Some improvement is achieved by the method of Linder and Persson (7), in which a more complete esterification of the fatty acids is achieved by the azeotropic removal of water during the esterification. This, with some empirical corrections, gives higher accuracy than the Wolff method. However while the Linder and Persson method appears to give excellent results in the range of 10-100% rosin acids, precise values are not obtained in the lower range of rosin acids. Another drawback is its long esterification time of 1-1½ hours, which makes it unsuitable for plant control purposes.

In order to work out a more accurate method for rosin acids in the range of 0-15%, consideration was given to the following factors:

a) Because of the small rosin content a large fatty acid sample was needed for a rosin titration of sufficient magnitude. A correspondingly larger quantity of acid catalyst was required to assure a complete esterification of the fatty acids. It was therefore decided to remove the catalyst before titration by washing an ether solution of the esterification mixture with salt solution. This is the established practice in a number of European methods (14, 4).

b) Sulfuric acid was chosen as catalyst in preference to aromatic sulfonic acids because it can be more readily removed by washing, and, being a stronger catalyst, it allows a shorter esterification time. Since speed is essential for a plant control method, a concentration of catalyst was chosen which gives maximum esterification in 10 minutes.

c) Visual determination of the titration endpoint using phenolphthalein indicator was adopted because we found it more accurate in a small titration range and more rapid than the potentiometric method.

d) To obtain accurate results in any method of this type, corrections must be made for such factors as incomplete esterification of the fatty acids, partial esterification of the rosin acids, and unavoidable mechanical loss of titratable rosin acids in the salt washes. Rather than to apply individual corrections for each of these, it was decided to use a single empirical correction factor, experimentally determined for the desired rosin acids range. This factor, which represents the algebraic sum of all errors, was determined by titrating known mixtures of pure abietic acid and fatty acids after selective esterification and removal of acid catalyst under the specified conditions of the method.

Reagents

a) Methanol (99.5% or better). Anhydrous synthetic methanol is satisfactory.

b) Standard Alcoholic Potassium Hydroxide Solution (0.5 N or 0.2 N).

c) Sodium Sulfate Solution (10%). A reagent grade of sodium sulfate, using 110 g. Na_2SO_4 dissolved and diluted to 1 liter with distilled water.

d) Ether. A reagent grade of ethyl ether.

e) Sulfuric Acid, Concentrated. A reagent grade containing 96% H_2SO_4 (Sp. Gr. 1.84).

f) Phenolphthalein Indicator. 1 g. dissolved in 100 ml. of methanol.

g) Methyl Orange Indicator. 0.1 g. dissolved in 100 ml. of distilled water.

h) Ethyl Alcohol. Neutral 95% ethyl alcohol, or neutral denatured alcohol conforming to U.S.S.D. Formula No. 30 or No. 3-A.

Analytical Procedure

Dissolve 40.0 $\pm$ 0.1 g. of the sample in 100 ml. of methanol in a 300-ml. flask. Twirl the flask to dissolve the oil and add a boiling chip. Add slowly 5 ml. of concentrated sulfuric acid while swirling the

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flask vigorously and connect the flask to a condenser. Heat the flask and reflux for 10 minutes. Cool the flask to room temperature with cold water.

Add 250 ml. of the sodium sulfate solution to a 500-ml. separatory funnel. Pour the cooled esterification mixture from the flask into the funnel and complete the quantitative transfer of the flask contents with 100 ml. of ether. Shake the funnel mixture thoroughly. Allow to settle, draw off the aqueous salt layer, and discard. Wash the contents of the funnel twice again with 250-ml. portions of the sodium sulfate solution. The last washing should not react pink to methyl orange indicator.

After removing the last washing, drain the contents of the separatory funnel into a 500-ml. Erlenmeyer flask. Add 20 ml. of ethyl alcohol and 1 ml. of the phenolphthalein indicator. Titrate to the appearance of a pink-red color, using 0.5 *N* alcoholic KOH if the rosin content is over 5% and 0.2 *N* alcoholic KOH if under 5%.

Calculations

This method requires the use of a correction factor dependent upon the amount of rosin acids present. The general equation for the correction has been established for a rosin acids range of 0-15% as follows:

$$\text{Rosin acids, percentage} = (1.031 \times \text{apparent rosin acids}) - 0.74.$$

Using this correction the calculation for rosin acids becomes:

$$\text{Rosin acids,}^{2} \text{ percentage} = \frac{1.031 \times A \times 30.2 \times N}{S} - 0.74.$$

Since the sample weight is 40 grams, the equation is simplified to:

$$\text{Rosin acids,}^{2} \text{ percentage} = 0.778 \times A \times N - 0.74$$

where A = milliliters of KOH solution used for titration of sample

where N = normality of KOH solution

where S = grams sample used.

Development of Correction Factor

To standardize the method and to develop the correction factor, known mixtures of pure fatty acids, free from rosin, and pure rosin acids, free from fatty acid, were prepared. Esterification experiments in our laboratory showed but a slight difference in the esterification rates of stearic, oleic, and linoleic acid with methanol. However we felt it advisable to use a commercially available rosin-free fatty acid similar in composition to tall oil fatty acids and to compare this material with rosin-free tall oil fatty acids. For this purpose samples were prepared using Wecoline S, distilled soya fatty acids made by E. F. Drew and Company Inc., and Acintol FA No. 2, distilled tall oil fatty acid made by the Arizona Chemical Company (freed completely of rosin by esterification and extraction). The composition of the two materials, Wecoline S (as used) and Acintol FA No. 2 (before the rosin removal), is shown in Table I.

TABLE I

Analyses of Fatty Acids Used for Preparing Standards

	Wecoline S	Acintol FA No. 2
	(Soya fatty acid as used)	(Tall oil fatty acid before rosin removal)
Acid Number	197.8	193.5
Saponification Number	204.3	196.0
Iodine Number	132.0	130.0
Unsaponifiables	2.3%	2.0%
Rosin Acids	None	1.0%
Linoleic Acid	50.3%	46.0%
Linolenic Acid	6.2%	0.5%
Saturated Acids (as Palmitic)	14.8%	3.0%
Oleic Acid	26.4%	47.5%

Rosin-free tall oil fatty acids were prepared by selective esterification of the fatty acids, using methanol and sulfuric acid, extraction of the rosin acids with potassium hydroxide solution, saponification of the fatty acid esters, and splitting of the soaps with acid to liberate the rosin-free fatty acids.

Pure rosin acids were separated from distilled tall oil by centrifuging, then recrystallizing five times from methanol, each time freeing the crystals from the mother liquor by means of a centrifuge, and finally drying them under vacuum. The purified rosin acids had an acid number of 184.6 to 185.0. To prevent the oxidation of the rosin acids, they were immediately dissolved in the fatty acids to produce the desired mixtures.

The rosin-fatty acid mixtures were adjusted to contain 1-15% rosin acids and were analyzed according to the method described. The titration values, expressed as apparent percentage rosin acids, were then plotted against the corrections necessary to obtain the true rosin acids content. The values obtained with soya fatty acids and tall oil fatty acids are shown in Table II.

TABLE II

Comparison of Corrections for Rosin Acids in Soya Fatty Acids and Tall Oil Fatty Acids

Apparent rosin acids, %	Correction % rosin acids[a]		
	Soya fatty acids	Tall oil fatty acids	Difference tall oil less soya
1	0.72	0.73	0.01
2	0.68	0.70	0.02
4	0.62	0.65	0.03
8	0.50	0.55	0.05
10	0.43	0.50	0.07
13	0.34	0.43	0.09
15	0.28	0.38	0.10

[a] To be subtracted.

It can be seen that there is but a slight difference between the corrections for soya fatty acids and tall oil fatty acids and that for all practical purposes the corrections can be used interchangeably.

The curve for rosin acids-soya fatty acid mixtures is shown in Figure 1. The equations given above are based on this curve.

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[2] Rosin acids are expressed as abietic acid, using a molecular weight of 302. If the method is used to determine the amount of commercial rosin in such products as soap, it may be desirable to express the results as *rosin* instead of *rosin acids*. In this case a molecular weight of 346 may be used. This value has been accepted as the apparent average molecular weight of rosin of commerce by the American Oil Chemists' Society in the determination of rosin in soap (10). Conversion of rosin acids to rosin is as follows: Rosin percentage = rosin acids × 1.146.

TABLE IV

Comparison of New Method With McNicoll and Wolff Methods

Abietic acid present, %	McNicoll Method				Wolff Indicator Method				New Method
	Analyst No. 2, % RA	Analyst No. 3, % RA	Analyst No. 4, % RA	Mean, % RA	Analyst No. 2, % RA	Analyst No. 3, % RA	Analyst No. 4, % RA	Mean, % RA	Mean, % RA
0	0.0	0.0	0.0	0.0	3.6	1.5	2.6	2.6	0.02
1	0.6	0.0	0.65	0.4	....	4.1	3.6	3.9	1.03
3	2.94	1.27	2.28	2.16	6.4	4.4	5.3	5.4	3.05
6	5.51	4.79	5.23	5.18	....	7.5	8.5	8.0	6.03
10	9.40	8.55	9.20	9.05	12.1	11.9	11.9	12.0	9.95
15	14.5	13.5	13.9	14.0	16.9	17.3	18.5	17.6	14.97

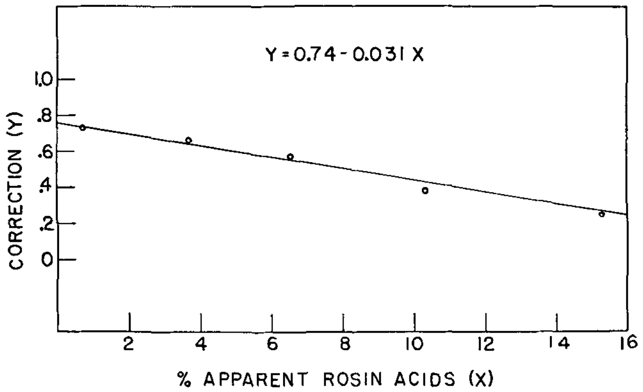

FIG. 1. Correction curve.

Accuracy and Precision of the Method

To test the method, kilogram batches of standard mixtures of pure rosin acids and soya fatty acids were prepared over the range 0-15% rosin acids. Each standard mixture in the series was analyzed by four analysts with the results shown in Table III.

TABLE III

Accuracy and Precision of the Method in the Analysis of Soya Fatty Acid—Rosin Acid Mixtures[a]

Rosin acids present, %	Analyst No. 1, % RA	Analyst No. 2, % RA	Analyst No. 3, % RA	Analyst No. 4, % RA	Mean, % RA	Mean deviation
0	0.03	0.00	0.00	0.03	0.02	±0.02
1	1.01	1.01	0.97	1.13	1.03	±0.05
3	3.05	3.05	2.97	3.14	3.05	±0.04
6	5.97	5.95	5.99	6.21	6.03	±0.09
10	9.91	9.81	9.93	10.14	9.95	±0.10
15	14.90	14.81	14.99	15.19	14.97	±0.12

[a] Single determinations by four analysts.

Analysts No. 1, 2, and 3 were experienced in the method while Analyst No. 4 had no prior experience in the determination. Since the values are single determinations and not averages of multiple tests, the agreement is remarkably good.

The method permits the determination of rosin acids in samples containing 0-15% rosin acids to within ± 0.1%. The relative error is 5% of the rosin acids content at the 1% level and improves to better than 1% of the rosin acids content at the 15% level.

It should be noted that rosin-free materials use a small amount of alkali in this titration. Therefore the presence of rosin should be checked qualitatively (Liebermann-Storch test) in cases when the rosin acids content is determined by this method as less than 0.1%.

A comparison of the method with the McNicoll and Wolff methods is shown in Table IV.

These results show that the McNicoll method gives results which are from .5 to 1% too low and that agreement between single determinations of various analysts is only fair. The Wolff indicator method gives values which are 2-3% too high and the agreement between analysts is, in general, poor.

Summary

A new method is described for the determination of rosin acids in fatty acids over a range of 0-15%.

The method is based on an acid-catalyzed selective esterification of a large sample, removal of the acid catalyst, titration of the unesterified rosin acids, and application of an empirical correction factor to the results.

Excellent agreement is obtained between various analysts, and the rosin acids content can be determined to within ± 0.1%.

Examination of the McNicoll and Wolff indicator methods showed these methods unreliable in the range of 0-15% rosin acids. The McNicoll method gave values which were from .5-1% low and the Wolff method 2-3% high.

It is anticipated that the new method, which covers a rosin acids range that is becoming more important industrially as the technology of tall oil separation advances, will prove useful to workers in this field and to those interested in the accurate determination of rosin acids in other products.

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