Methods of Analysis for Tall Oil Products

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THE TALL OIL INDUSTRY in the United States has grown at a phenomenal rate during the past 10 years. Highly refined products are now being produced from tall oil, such as very light-colored fatty acids, substantially free from rosin acids and rosin substantially free from fatty acids. Manufacturers of paint, varnish, soap, detergents, linoleum, and paper have adopted these products as raw materials and depend on their quality and uniformity. It is therefore not surprising that, in the United States, considerable attention has been given to, and a lot of work has been done on the development of suitable methods of analysis for these products.

Most of this work was carried out in laboratories of producers and users of tall oil products in collaborative tests under the auspices of the American Society for Testing Materials (Committee D-17) with the support of the Tall Oil Division of the Pulp Chemical Association. Some methods developed by committees of the American Oil Chemists' Society for the analysis of fatty acids have also found application for tall oil fatty acids. It is the purpose of this paper to give a short review of some of the A.S.T.M. work and to discuss present methods for the analysis of tall oil products in general.

Tall Oil and Tall Oil Fatty Acids

Analytical values which are often or occasionally determined on crude tall oil, acid-refined tall oil, distilled tall oil, and tall oil fatty acids are as follows:

Chemical Values. Acid number, saponification number, rosin acids, fatty acids, unsaponifiables, polyunsaturated fatty acids (conjugated and total linoleic acid), saturated fatty acids, oleic acid, and iodine value.

Physical Values. Color, moisture, specific gravity, refractive index, viscosity, flash point, pour-point, cloud-point, and titer.

Values for typical tall oil products in the United States are given in Table I.

Acid values and saponification values are determined according to the time-honored methods of the oil and fat chemists. Methanol is universally used as a solvent and methanolic KOH as titrant. While potentiometric titration is specified in the referee methods of the A.S.T.M., the use of thymol blue or phenolphthalein as indicator is popular in many laboratories because of speed or convenience.

The determination of rosin acids is more complicated and has a long history of development. The first to solve this problem was Twitchell (1). By bubbling hydrochloric acid gas through solutions of rosin and fatty acids in alcohol, he made use of their different esterification rates and was able to convert the fatty acids into their respective esters while the rosin remained unesterified and could be titrated. This principle of selective esterification is still the basis of all present methods, which in the meantime have undergone many changes to make them simpler and faster. Wolff (2) in 1910 introduced the use of sulfuric acid as an esterification catalyst. There were a number of investigations in Germany, Sweden, and the U.S.A., which contributed to methods of rosin acids determination. While in Europe the slower gravimetric methods, in which the fatty acid esters are isolated and weighed, became standards of the industry; in the U. S. emphasis was placed on simple manipulation and speed. A simple and fast modification of the Wolff method was developed by Hastings and Pollak and published in 1939 (3). It consisted in refluxing a sample of tall oil in methanol in the presence of sulfuric acid for 2 min., cooling, and titrating the unesterified rosin acids by using a thymol blue indicator. This indicator, because of its two color changes, allows measurement of the rosin acid aside from the mineral acid in one titration. The A.S.T.M. adopted this method and added potentiometric titration, which eliminates difficulties in determining the end-points, particularly in such dark-colored products as crude tall oil (4).

The McNicoll method (5), which uses naphthalene sulfonic acid as a catalyst and titrates unesterified rosin acids with phenolphthalein as indicator against a blank was first employed for the determination of rosin in soap. It too became an A.S.T.M. method for tall oil.

By 1953 experience in our own laboratory and investigations by Sprengling (6) and Hezel (7) indicated that the reflux time of 2 min. for the Wolff Method was too short. We decided to determine the reflux times necessary for rosin acid mixtures of 30 to 50%, corresponding to the crude and refined tall oil products of commerce. The mixtures were prepared from rosin-free distilled soybean fatty acids and from tall oil rosin acids repeatedly recrystallized from methanol. A Beckman Model K automatic titrator was used. To determine the end-points which would give the most accurate results in connection with automatic titrators, potentiometric titration curves were first plotted with 10 different commercial crude tall oils, four distilled tall oils, and two acid-

TABLE I

Analysis Values of Typical U. S. Tall Oil Products

Product	Acid No.	Sap. No.	Rosin acids	Unsap.	Fatty acids	Color, Gardner	Specific gravity 25°/25°C.	Refractive index 25°C.
Crude tall oil			%	%	%			
Low rosin	170	174	40.0	6.9	52.5	17	0.960	1.5030
High rosin	166	172	49.0	7.1	43.1	18	0.975	1.5100
Distilled tall oil	190	194	29.0	1.2	69.8	7+	0.947	1.4860
Acid refined tall oil	169	173	40.0	6.8	53.1	8	0.980	1.5025
Tall oil fatty acids	192	194	4.0	4.0	92.0	7+	0.901	1.4710
	196	197	1.3	1.5	97.2	5+	0.900	1.4670
	198	199	0.4	0.4	99.2	3	0.897	1.4645
Tall oil heads	172	177	0.5	15	84.4	12+	0.905	1.4754
Tall oil rosin	168	176	94[a]	4.0	2.0	WW[b]	1.060	—
Tall oil pitch	55	115	32	32	30	17[c]	1.005	—

[a] Includes rosin esters and anhydrides. [b] U. S. rosin color standards. [c] 10% solution in benzene.

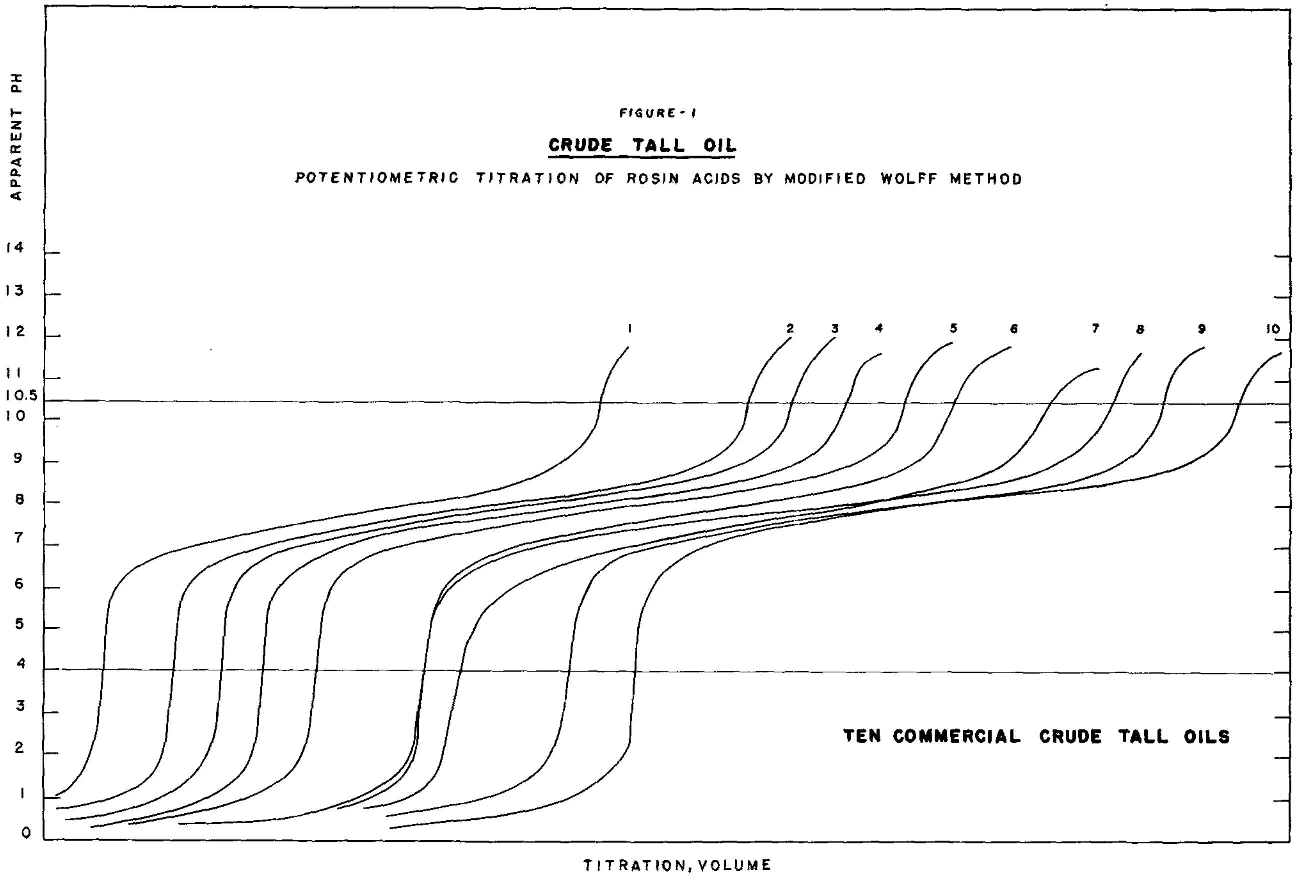

FIGURE - 1

CRUDE TALL OIL

POTENTIOMETRIC TITRATION OF ROSIN ACIDS BY MODIFIED WOLFF METHOD

TEN COMMERCIAL CRUDE TALL OILS

refined tall oils (Figures 1 and 2). The results show inflection points of pH 4 and 10.5 for either crude tall oil, distilled tall oil, or acid-refined tall oil. With most tall oil products titration to definite end-points is satisfactory, and interpretation of individual titration curves is not necessary. It was found that a 15- to 30-min. esterification time is necessary with mixtures containing between 30 to 50% rosin acids. The tests were repeated and confirmed in a collaborative testing program by members of A.S.T.M. in 1954. As a result of this work the Wolff method was changed to the present A.S.T.M. D 803-55T, which specifies a 30-min. reflux time and allows the use of an automatic titrator with pH 4 and 10.5 end-points as an alternate to plotting a titration curve.

One of the greatest challenges to the tall oil chemist was to provide an accurate enough method for the determination of the small percentages of rosin acids in the highly fractionated tall oil fatty acids produced in modern distillation plants. The Herrlinger-Compeau method (8) solved this problem by using a relatively large sample of fatty acid (40 g.), refluxing it in methanol in the presence of sulfuric acid, cooling, adding ether, extracting the mineral acid with salt solution, and titrating the remaining unreacted rosin acids dissolved in the ether. This method was adopted by the A.S.T.M. for the determination of rosin acids in fatty acids and is now A.S.T.M. D-1240-54.

The testing of this method by the A.S.T.M. in 1951 is one of the best examples of the type of collaborative work carried out by its members. Samples of fatty acids containing 0 to 15% rosin acids were sent to 19 laboratories, including those of producers and users of tall oil products, government laboratories, commercial testing laboratories, and research institutions. With the exception of one laboratory none had previous experience with this method.

TABLE II

Results of Collaborative Test of Herrlinger-Compeau Method

A.S.T.M. member laboratory	Rosin acids content of samples					
	0.00	1.00	3.00	6.00	10.00	14.80
	Rosin acids found					
1	0.02	1.03	3.05	6.03	9.95	14.80
2	0.04	1.00	2.99	6.00	9.88	14.74
3	0.05	1.06	2.99	6.08	9.95	14.78
4	0.01	0.99	2.94	5.99	9.84	14.53
5	0.38	1.16	3.18	6.27	9.84	14.93
6	0.45	1.28	3.79	5.37	9.95	14.95
7	0.09	1.06	3.07	6.00	10.70	14.80
8	*nil*	0.96	2.99	5.99	9.83	14.58
9	0.01	0.811	3.09	6.09	9.94	14.91
10	0.076	1.02	3.03	6.80	10.7	15.30
11	—	0.81	3.08	6.03	10.15	15.03
12	0.00	0.93	2.97	5.98	9.94	14.81
13	0.145	1.08	3.15	6.16	9.76	14.5
14	0.21	0.99	3.07	6.06	9.83	14.88
15	0.25	1.16	3.30	6.23	10.12	14.62
16	-0.04	1.29	2.94	5.81	9.75	14.25
17	0.02	0.98	2.97	5.98	9.88	14.80
18	0.02	1.06	3.05	6.06	10.06	14.80
19	-0.14	1.00	2.93	5.92	9.94	14.80

The results of the collaborative tests are given in Table II. They can be summarized as follows:

Samples tested 114
Number of collaborative laboratories.......... 19
Rosin acids range..0–15%

Determinations		Accuracy
Number	Percentage	Rosin acids content
76	67	±0.1%
19	17	±0.2%
9	8	±0.3%

TABLE III
A.S.T.M. Methods for Determination of Rosin Acids

Method		Principle of method	Range rosin acids	Application		
				Tall oil	Fatty acids	Rosin
			%			
Wolff	D 803-55T	Methanol, sulfuric acid, 30-min. reflux	15–55	X	—	—
Wolff[a]	—	Methanol, sulfuric acid, 5-min. reflux	55–100	—	—	X
Linder Persson[a]	—	Butanol, sulfuric acid, azeotropic removal of water	0–100	X	X	X
Herrlinger-Compeau	D1240-54	Methanol, sulfuric acid, 40-g. sample extraction of sulfuric acid before titration	0–15	—	X	—
McNicoll	D 803-55T	Methanol naphthalein sulfonic acid	15–55	X	—	—

[a] A.S.T.M. designation to be issued.

A new method for the determination of rosin acids applicable over the whole range of rosin content from tall oil fatty acids to tall oil rosin is the revised Linder Persson Method (9). The sample is esterified with butyl alcohol in the presence of benzene and sulfuric acid. The water formed during the esterification is removed by azeotropic distillation and collected in a specially constructed moisture trap. After titration, using either a thymol blue or phenolphthalein indicator, a correction factor is applied to the result. In the U. S. this method is being tried with good results by a few people for tall oil products. It has been tested by the A.S.T.M. in connection with the determination of fatty acids in rosin and found to give results equivalent to the Wolff method. Since it is claimed that the Linder Persson method has the advantage of applicability to products with widely varying rosin content, it will undoubtedly be further investigated by the A.S.T.M. A summary of the A.S.T.M. Methods for rosin acids determination is given in Table III.

The method which is used for the determination of unsaponifiables in tall oil and tall oil fatty acids, A.S.T.M. D 803-55T, has been carefully worked out over the years by the members of A.S.T.M. It consists of refluxing a 5-g. sample in 15 ml. of 2N alcoholic potassium hydroxide for 1.5 hrs., followed by extraction of the unsaponifiables from the soap solution with ether by using conventional separatory funnels. The conditions for dilution, extraction and isolation of the unsaponified matter are critical for obtaining reproducible results. The higher alkali concentration assures complete saponification of the rosin esters present, and the small volume of the alcoholic alkali eliminates the need for alcohol removal prior to extraction. For removal of the soap the ether extract is washed with gradually increasing quantities of water. This prevents the formation of emulsions. After weighing, the unsaponifiables are dissolved in isopropyl alcohol and titrated with alkali to correct for rosin carried over through hydrolysis of the rosin soap. Collaborative work was carried out by A.S.T.M. members from 1952 to 1954 to bring this method to its present form and to adopt it as an alter-

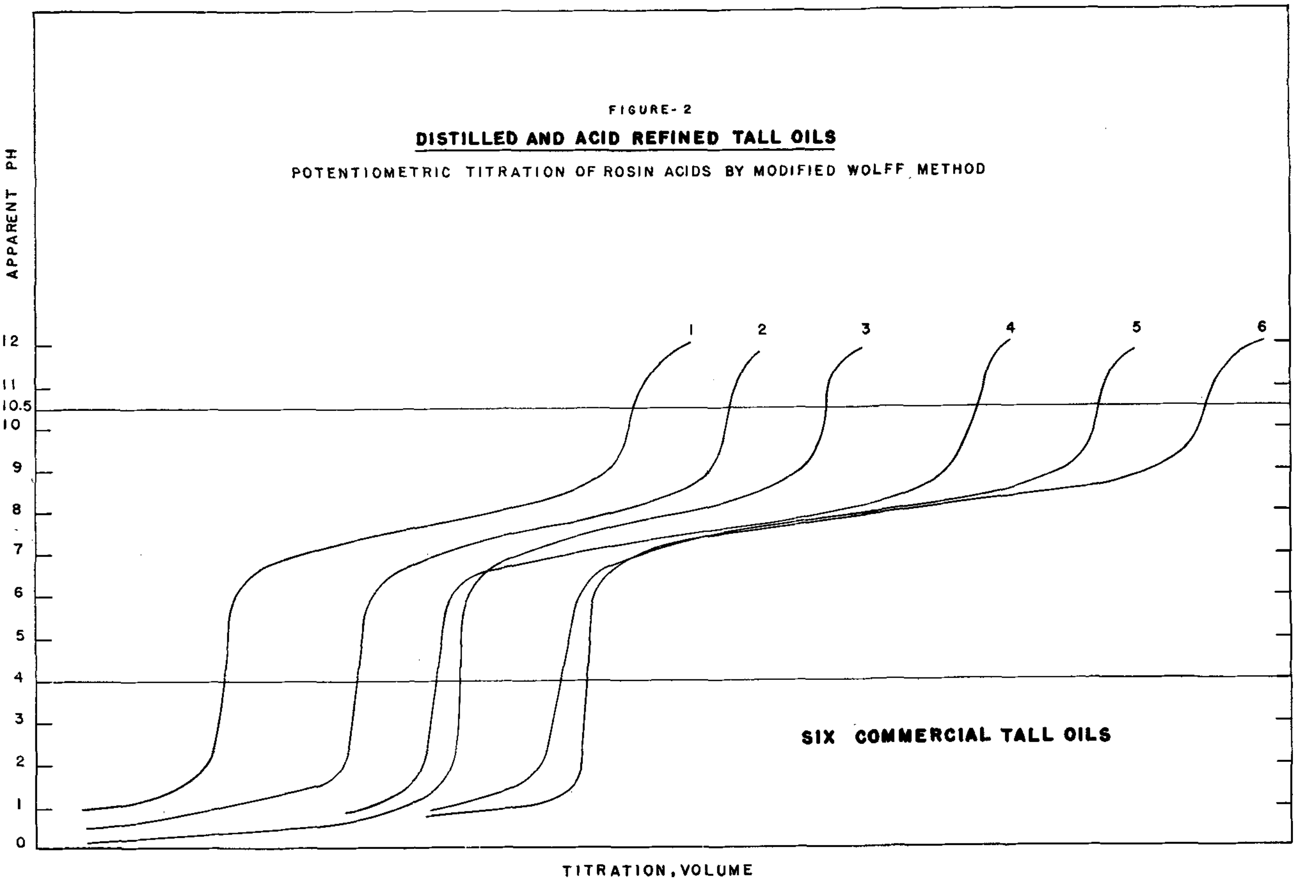
FIGURE-2

DISTILLED AND ACID REFINED TALL OILS

POTENTIOMETRIC TITRATION OF ROSIN ACIDS BY MODIFIED WOLFF METHOD nate method for the analysis of unsaponifiables in rosin.

Moisture is determined by azeotropic distillation of a large sample with xylene and collection of the water in the Dean Stark Trap. Only crude tall oils contain moisture. Distilled and refined products are dry.

The fatty acid content of crude tall oil, distilled tall oil, acid-refined tall oil, and tall oil fatty acids is calculated from the difference between 100 and the sum of rosin acids, unsaponifiables, and moisture. This is in contrast to the determination of *fatty acids* in rosin, which is calculated from the acid number and the rosin acids content.

Individual fatty acid constituents are quite often determined to furnish product specification data and to judge the effect of operational variables and seasonal changes in the raw material. These are conjugated, nonconjugated, and total polyunsaturated fatty acids (which are usually expressed as linoleic acid), oleic acid,and saturated acids (mainly palmitic acid). The determinations can be carried out directly on highly refined tall oil fatty acids if they are low in both unsaponifiables and rosin. On products with higher rosin and unsaponifiable content and for most accurate results, the fatty acids must first be isolated. To separate the fatty acids a sample is esterified with methanol and the rosin is extracted with alkali. The ester is saponified, and the unsaponifiables are removed by extraction with ether. The fatty acids are then liberated from the remaining soap solution, taken up in ether, washed acid-free, and dried.

Conjugated and nonconjugated polyunsaturated fatty acids are determined according to the modified Brice and Swain ultraviolet spectrophotometric method A.O.C.S. L12a-55 and Cd 7-48, using a Beckman Model DU quartz spectrophotometer. This method is based on the measurement of conjugated linoleic acid by ultraviolet absorption before and after isomerization of the sample by heating with a glycol or glycerol sodium hydroxide solution, which converts the nonconjugated linoleic acid to the conjugated type. Since the polyunsaturated acids consist mainly of dienoic acids with less than 1% of trienoic acids and no acids of higher unsaturation, readings are taken at wavelengths of 233, 262, 268, and 274 mμ only.

Saturated fatty acids, which in tall oil fatty acids consist mainly of palmitic acid, are determined according to the lead salt method A.O.C.S. Cd 6-38. Since rosin is also precipitated, a correction for the rosin content of the sample must be applied. With certain products the lead salts do not crystallize readily. A method which is sometimes better but is also subject to a lot of complications is the separation of the solid acids by low-temperature crystallization from a methanol-water mixture. The determination of palmitic acid can also be carried out by a quantitative fractional distillation of the methyl esters. None of these methods is very satisfactory. It is expected that vapor chromatographic separation of the methyl esters will not only allow an accurate determination of palmitic acid but also the direct determination of oleic acid, linoleic acid, and higher molecular saturated and unsaturated fatty acids. Oleic acid is, at present, determined as the difference between the total fatty acids and the sum of saturated and polyunsaturated fatty acids.

As with most refined products, color has become an important criterion of quality. It is at present determined with a Hellige color comparator and the Gardner Varnish scale. This has so far been the most satisfactory method even for the extremely pale-colored tall oil fatty acids. The determination of color by using the Lovibond Scale has not found adoption among users and producers of tall oil products. The reason is that the method is cumbersome, and the color standards are expensive to maintain. However there is room for an improved method, particularly for the determination of very light colors where a more discriminating method is needed. Spectrophotometric measurement of color promises to eliminate the human factor of visual determinations. A committee of the A.O.C.S. is working on this problem.

Specific gravity is important for weight-per-gallon information needed for shipping and storage. Viscosity and flash-point are usually given in a typical analysis for customers' information.

Refractive index is one of the most useful values for production control in tall oil refining plants. It takes less than one minute to run a refractive index, yet the value obtained is highly significant in judging quality changes in the finished and intermediate products. The refractive index of a specific product is influenced mainly by the rosin and the unsaponifiables content and to a minor degree by the composition of the fatty acids. While the relationship between refractive index and composition varies from product to product, as well as for the same product made at different times, it can nevertheless be used to determine changes in the rosin and unsaponifiable content of still products by using factors determined from time to time by actual chemical tests. For example, the total of the rosin acids and unsaponifiable content can be determined by refractive index, using the latest factor for the product in question. Then if the rosin acids content is known (*i.e.,* recently determined by chemical analysis) the unsaponifiable content can be calculated by the difference, or, if the unsaponifiable content is known, the rosin acids can be calculated. A typical curve showing the relationship between the refractive index and the total for rosin acids and unsaponifiables during a certain production period is shown in Figure 3.

Pour-point, cloud-point, and titer are often requested by customers who are concerned with the storing qualities of tall oil and tall oil fatty acids. Unfortunately none of these values can be accurately determined in tall oil products, or, if determined, the data are of no value in judging the behavior of the products on storage. There are two constituents in tall oil and tall oil fatty acids which at low temperature can crystallize and settle from solution. One is rosin, which readily forms supersaturated solutions. These may remain liquid for days and then unpredictably set up solid even at room temperature. Neither the pour-point nor the titer would detect supersaturation. The other constituent is palmitic acid. It comes out more readily on cooling, first as a fine cloud and finally settling out as a bottom layer after 24–48 hrs. A titer test which is determined by the heat of crystallization of the solid acid, in this case palmitic acid, will not show up unless the concentration of the solid acid is high enough. Most distilled tall oils and tall oil fatty acids contain less than 3% of palmitic acid, a concentration too low to give a noticeable exotherm on cooling of the sample. The cloud-point will vary and not tell the story either. The most reliable test

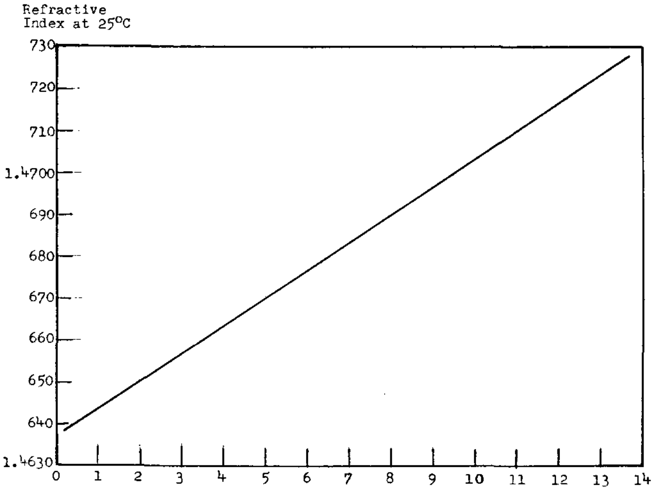

FIG. 3. Refractive index vs. rosin acids and unsaponifiables.

for storage behavior is to place the sample in a refrigerator at the desired temperature for testing, shaking, and examining daily for several days.

Another test which is not suitable for tall oil and tall oil fatty acids is the Iodine Number. While this value is of considerable significance in judging the unsaturated fatty acid content of vegetable and marine oils in connection with their drying qualities, it cannot be used to judge tall oil products because both rosin and unsaponifiables greatly influence the iodine test. A better method for judging the quality of tall oil fatty acids in connection with drying properties is to determine the conjugated and total linoleic acid content by spectrophotometric analysis.

Tall Oil Rosin

Analytical values usually or occasionally determined on tall oil rosin are the following:

Chemical Values. Acid number, saponification number, rosin acids, fatty acids, unsaponifiables, ash, iron, abietic acid, and dehydroabietic acid.

Physical Values. Color, hardness, optical rotation, and softening point.

Acid number and saponification number are carried out according to A.S.T.M. D 465-51 and A.S.T.M. D 464-51, respectively. Referee methods use potentiometric titration, and the alternate indicator methods use phenolphthalein as an indicator. Solvents are ethyl or methyl alcohol with the addition of some benzene, to effect a clear solution. The acid number is perhaps the most important criterion for rosin quality. It is a measure of the acid equivalents available for chemical reactions and indicates whether the rosin has been subjected to heat treatment or other modification such as neutralization.

Since tall oil rosin is separated from fatty acids by a fractional distillation process, the determination of residual fatty acids is of great importance for the purpose of plant control during production to assure a high quality product. Producers regulate their processes so as to obtain a clear, hard, vitreous high-melting rosin containing usually less than 3% of fatty acids.

The method used for the determination of fatty acids in rosin had originally been developed in our laboratories. Its principle is to calculate the fatty acids content from the difference between the total acidity of the sample, determined as acid number, and the acidity contributed by the rosin acids, determined either according to a modified Wolff method or the Linder Persson method. Since the fatty acids remaining in tall oil rosin consist of oleic acid and higher molecular fatty acids of varying compositions, it has become customary to compute and report the fatty acids content as oleic acid.

The A.S.T.M. has recently carried out a collaborative testing program on modifications of this method, which are now in the process of being adopted as standards. A short outline of the method is as follows:

a) Determine the acid number of the rosin;
b) determine rosin acids by using either a Wolff method with 5 min. of reflux time or the Linder Persson method;
c) calculate fatty acids content from acid number and rosin acids content as follows:

$$\underset{\text{(as oleic acid)}}{\text{Fatty acid \%}} = \frac{\text{AN} - (\%\ \text{RA} \times 1.855)}{1.986}$$

where

AN = acid number
RA = rosin acids

There are two methods for the determination of unsaponifiables in rosin, A.S.T.M. D 1065-56, Methods A and B. Method A is a continuous-extraction method; Method B, a separatory funnel method identical to A.S.T.M. D 803-55T for tall oil. For some time the continuous-extraction method has been the only standard. Many users of rosin and private testing laboratories did not have the continuous-extraction equipment. Tall oil producers who entered the rosin field in 1950 used their funnel method for the determination of unsaponifiables in tall oil. The A.S.T.M. therefore decided to develop an alternate funnel method for rosin which would give values identical to the continuous method. The A.S.T.M. subcommittee on rosin carried out considerable work during 1952–1954 on these methods. It was found that a higher alkali concentration (2N) during the saponification step gave more reliable results in both methods and allowed some simplification in the extraction method. The revised methods were tested on gum rosin, wood rosin, and tall oil rosin. The results obtained by eight analysts of six A.S.T.M. member laboratories with tall oil rosin, comparing the revised continuous-extraction method with the separatory funnel method, Method D 1065-56, Methods A and B, are shown in Table IV.

The method for ash is A.S.T.M. D 1063-51 and for iron, A.S.T.M. D-1064-51. Neither method is used often on tall oil rosin. Since tall oil rosin is made by distillation, it should be very low in both ash and iron unless iron is picked up from the still, which then indicates the existence of a serious corrosion problem for the producer.

TABLE IV

Results of A.S.T.M. Collaborative Tests of Method for Unsaponifiables in Rosin

	Results with tall oil rosin							
Analyst	1	2	3	4	5	6	7	8
Method A	3.3 3.3 3.3	3.4 3.3 3.4	3.5 3.3 3.5	3.4 3.4 3.5	3.4 3.5 3.4	3.8 3.7 —	3.5 3.6 —	3.4 3.4
Method B	3.8 3.7 3.7	3.7 3.6 3.7	3.7 3.7 3.7	3.1 3.2 3.4	3.4 3.4	3.6 3.7	3.8 3.6	3.6 3.7

Method A. Separatory funnel method.
Method B. Continuous extraction method.

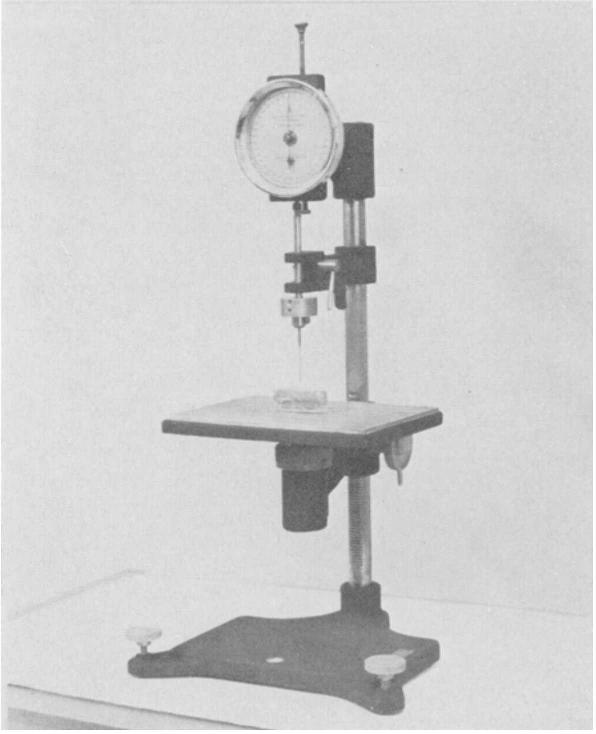

FIG. 4.

Abietic and dehydroabietic acid is determined on tall oil rosin which has been subjected to some treatment such as disproportionation or dehydrogenation to produce rosin specialties. In general, a modification of the method developed during World War II by the Rubber Reserve (10) is used. A sample is dissolved in either ethanol or methanol, and its absorption is measured at wavelengths 241, 273, 276, 279, and 300 mμ, using a Beckman Model DU quartz spectrophotometer.

Color is determined according to A.S.T.M. D 509-55, using U. S. government rosin standards.

The hardness of tall oil rosin is a good criterion for low fatty-acid content. It is not satisfactory for quantitative determinations but can be used with advantage as a quick test for control of still operations. We adopted for this purpose a Precision Universal A.S.T.M. Penetrometer. The rosin is poured into a mold consisting of a ring ¼ in. high and ¾ in. in diameter. The rosin held by the ring is cooled to 25°C. in a water bath, and the penetration is determined by using a penetrometer needle, a 150-g. weight, and a 10-second release time. (The rosin cubes used for color determinations, suitably cooled, may also be used.) We have recommended this method to our friends, and it is now used by several producers of tall oil rosin. The needle must be replaced frequently to assure uniformity of results. While it is a good qualitative method, all efforts to make it a quantitative measure for fatty acid have failed because of the many factors that influence hardness in rosin.

Optical rotation is very useful for the control of processing rosin by heat treating, disproportionation, and dehydrogenation. We dissolve the rosin in chloroform and determine its rotation in a 1-decimeter tube, using a Rudolf Model 60 Polarimeter with a sodium lamp. The results are expressed as specific rotation. The rotation can also be measured on the solid rosin, which is poured into a special metal and glass cuvette and allowed to cool. The results are not as accurate because strains set up in the rosin during cooling influence the rotation.

The softening point of rosin is determined by the ring and ball method A.S.T.M. E 28-51T.

Summary

The principal standard methods used by the American industry for the analysis and quality control of tall oil products have been discussed, and some of the work of the A.S.T.M. in developing these methods has been reviewed.

Further growth of the tall oil industry will undoubtedly result in new products of greater refinement and wider utilization. New and improved methods of analysis will be required. These can be worked out by the industry in continued collaborative work under the auspices of the A.S.T.M. and A.O.C.S. Undoubtedly instrumental test methods such as infrared and ultraviolet spectroscopy and gas chromatography will play a role of increasing importance in the analysis of tall oil products.

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Continuous Acidulation Process for Tall Oil Production

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THE ORIGINAL METHOD for producing tall oil was a batch system, developed in Sweden and Finland (1) about 1905, which consisted simply of reacting the black liquor skimmings with sulfuric acid in a large wooden tank at temperatures near 200°F.(93°C.). The acidified mixture was gravity-settled; and the upper layer, the crude tall oil, was skimmed off leaving a residue of lignin, spent sulfuric acid, and salt cake. Until recently this batch method, with minor improvements, has been the only system available; and, for that matter, some companies are still using it (2).

As a result of a cooperative program between Newport Industries and De Laval, a nozzle type of centrifuge was installed and placed in commercial operation in 1953 at Newport's plant in Alabama. This

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[1] Presented at the Spring Meeting, American Oil Chemists' Society, Memphis, Tenn., April 21–23, 1958.