Rapid Methods for the Estimation of Rosin and Fatty Acids in Tall Oil

By R. HASTINGS and A. POLLAK
RESEARCH LABORATORIES OF THE WEST VIRGINIA PULP & PAPER CO., NEW YORK, N. Y.

Abstract

A rapid method for the estimation of the rosin acids, and methods of calculating the composition of Tall Oil are described. The significance of the existing analytical methods for the estimation of fatty acids, rosin acids, and unsaponifiable matter in Tall Oil is given, together with a brief description of the properties of these three components.

Typical analyses of crude and refined tall oils, and a bibliography pertaining to the composition of Tall Oil are appended.

INTRODUCTION

Methods for the analysis of Tall Oil have not progressed as rapidly as its sales and uses. However, many investigators have demonstrated that tall oil consists of a mixture of rosin acids, fatty acids and unsaponifiable matter.

Our method for the estimation of these three components of tall oil, require determinations of the rosin acids, the unsaponifiable content and the acid number. Experience has proved this method to be both rapid and reliable. Various analysts have checked within two percent.

The Twitchell (1) and Wolff (2) methods, the latter being the official method of the American Oil Chemists Society, are based on the assumption that rosin acids do not esterify with anhydrous alcohol in the presence of hydrochloric or sulphuric acids. Our rapid method for the estimation of rosin acids is also based on this assumption.

The method used for the determination of the unsaponifiable content found best suited to tall oil is that by Wilkie (3) also described in Allen (4).

THE SIGNIFICANCE OF THE ANALYTICAL METHODS

UNTIL now, the modified Twitchell or modified Wolff method has been applied chiefly to estimate the rosin content of soaps and soap products. While we have found that this standard method applied to tall oil gives reproducible results, it must be pointed out that in the case of tall oil the results should not be interpreted by old standards. Thus, we may analyze a typical sample of tall oil and find it to contain 35% of rosin acids, 55% of fatty acids and 10% of unsaponifiable matter. This does not mean that a material of this composition could be duplicated by melting 35 lbs. of rosin into 55 lbs. of red oil and stirring in 10 lbs. of crank case oil. It would not be easy to tell the difference analytically, but in actual use the comparison would be startling to say the least. We know very little so far concerning the significance of the analytical results we can obtain.

The rosin acids present in tall oil appear to have an average molecular weight of 300. Abietic acid, $C_{20}H_{30}O_2$, molecular weight 302, melting point 182° C, has been isolated and is known to be present in considerable amount. Probably half the rosin acids indicated to be present by the Wolff method are abietic acid. The others have not been identified, but are liquid at room temperatures. Nothing is yet known concerning the properties of these liquid rosin acids.

The fatty acids as separated by the Wolff method have an average molecular weight of 280. They are unsaturated, the Wijs iodine number is usually near 150. The literature is contradictory about their nature.

The unsaponifiable matter is said to be a mixture of phytosterols, higher alcohols and some hydrocarbons. These are difficult to separate. The sterols form mixed crystals which will require much research before individual phytosterols can be isolated. At present most tests are generic, not specific.

On the other hand the properties of the unsaponifiable matter are unexpected. It does not separate out, even from dilute soap solutions. It appears to aid emulsification much as do some of the unsaponifiable constitutents of commercial rosin.

METHOD FOR ROSIN ACIDS

Reagents Required

METHANOL

The pure methanol (99.5%+) sold commercially by most of the leading producers of methanol is satisfactory.

METHYL SULPHURIC ACID SOLUTION

100 g of sulphuric acid (specific gravity 1.82-1.84) is slowly poured, stirring constantly, into 400 g of methanol (99.5%+). Preserve in a glass-stoppered bottle.

POTASSIUM HYDROXIDE IN METHANOL

30 g of potassium hydroxide, preferably in the pellet form, is dissolved in one liter of methanol (99.5%+) to form an approximately half normal solution. Potassium acid phthalate is preferable for standardizing the solution. 2.553 g of $C_6H_4COOKCOOH$ will be neutralized by 25.00 ml of 0.5000 N KOH.

THYMOL BLUE SOLUTION

0.10 g of thymol blue is dissolved in 100 ml of methanol.

PROCEDURE

4 — 5 grams of the tall oil sample are weighed in a tared 250 ml. conical flask on a scale having a sensitivity of 0.01 grams. 150 ml. of methanol are added, and the flask twirled to dissolve the oil. After 5 ml. of the methyl sulphuric acid solution are added, the entire mixture is boiled for two minutes under a reflux condenser. When the contents have cooled, a few drops of the thymol blue solution are added, and then titrated with the methanol solution of potassium hydroxide. This titration is continued until the thymol blue turns from red to yellow. (pH about 3) and the burette is either refilled or its reading is noted. The titration is further continued with the potassium hydroxide until the thymol blue turns from yellow to blue (pH about 9). The ml. of 0.500N potassium hydroxide consumed between the two and points are equivalent to the rosin acids present.

CALCULATIONS

1. The Rosin Acids Number

This value is convenient for calculations and corresponds to an acid number in that it expresses the mg. of potassium hydroxide consumed by the neutralization of the rosin acids in 1 g. of sample. It is

$$= 28.0 \frac{\text{ml. of 0.500 N KOH used}}{\text{g. of sample, dry basis}}$$

2. The Rosin Acid Content

   We have found that the rosin acids in tall oil have an average combining weight of 300, or nearly the molecular weight 302 of abietic acid. Consequently we compute

$$\%\ \text{rosin acids (calculated as abietic acid)} = \frac{302}{561} \times (\text{rosin acids number})$$

DETERMINATION OF STEROLS, HIGHER ALCOHOLS, ETC. AS UNSAPONIFIABLE CONTENT

Reagents Required

2.0 N-Potassium Hydroxide in Methanol Diethyl Ether

Procedure

5.00 grams of the tall oil sample are refluxed for 1.5 hours with 12.5 ml. of 2.0 N potassium hydroxide in methanol. This mixture is transferred to a separatory funnel with the aid of about 50 ml. of water. The contents are then extracted with ether using successive portions of 40, 30, 30 and 30 ml. The ether extracts are combined in a separatory funnel containing 20 ml. of water. The water is run off without shaking the funnel. The ether solution is washed by shaking it vigorously with 2, 5 and 30 ml. of water, and is then evaporated, dried and weighed.

Calculations

1. % sterols, alcohols, etc.

$$= (100)\ \frac{(\text{g. dry extract})}{(\text{weight of sample, dry basis})}$$

2. Express the result to one decimal.

DETERMINATION OF OTHER CONSTANTS

We have found that the Standard Methods of the American Oil Chemists Society for the determination of the Acid Number, the Saponification Number and the Wijs Iodine Number are quite satisfactory when applied to tall oil. In the case of the acid and the saponification numbers we prefer to use methanol instead of ethanol and thymol blue for indicator rather than phenolphthalein.

ESTIMATION OF THE COMPOSITION OF TALL OIL

We have found two methods useful for computing the composition of tall oil. The first method offers, so far as we know to date, the best estimates. The second more rapid method is satisfactory only when applied to distilled tall oil. In any case the first method is to be preferred.

PREFERRED METHOD FOR REFINED AND CRUDE TALL OIL

1. Rosin Acids, %

   Calculated as abietic acid

$$= \frac{302}{561} \times (\text{rosin acids number})$$

2. Sterols, Higher Alcohols, Etc., %

   As given above under determination of sterols, higher alcohols, etc.

3. Fatty Acids, %

   = 100 — (% rosin acids + % sterols, etc.)

RAPID METHOD FOR DISTILLED TALL OIL*

1. Rosin Acids, %

   Calculated as abietic acid

$$= \frac{302}{561} \times (\text{rosin acids number})$$

2. Fatty Acids, %

   Calculated as oleic acid

$$= \frac{282}{561} \times (\text{acid number} - \text{rosin acids number})$$

3. Sterols, Higher Alcohols, Etc., %

   By difference

   = 100 — (% rosin acids + % fatty acids)

VALIDITY OF THE METHODS

The rapid method we have described appears to check with the standard Wolff method of the American Oil Chemists' Society.

Assuming in both methods a combining weight of 302 for rosin acids, we found

Rosin acids, percent calc. as abietic acid	CRUDE TALL OIL	REFINED TALL OIL
By AOCS Wolff method	44.7	34.5
By our method	46.4	34.7

The isolation of the rosin acids in crude tall oil without affecting their chemical composition appears difficult. There is some evidence that the rosin acids in crude tall oil may have a higher combining weight than 302 but never so high as 346 which is used when the rosin acids are due to commercial rosin.

In the case of distilled tall oil the combining weight of the rosin acids appears to be 302 and the combining weight of the fatty acids about 282. This makes it possible to compute the amount of unsaponifiable matter by difference. Such a calculation of the unsaponifiable matter is usually within 10% of the determined value.

VARIATIONS IN ANALYSES

The composition of tall oil depends on its source and method of refining. Two general qualities are known, crude tall oil, the raw material obtained after acidifying the soaps salted out of pulp mill waste liquors, and distilled tall oil, the product obtained by vacuum distilling crude tall oil. Special processing methods applied to crude tall oil will of course produce grades of intermediate quality. Analyses may range as follows:

	CRUDE	DISTILLED
PHYSICAL DATA		
Specific gravity, 60°F/60°F	0.95-1.00	0.95-0.99
Color	brown to black	straw color to brown
Moisture, %	0-3	0-2
CHEMICAL DATA		
Acid Number	145-175	165-185
Saponification Number	145-175	165-185
Rosin Acids Number	40-120	10-80
Iodine Number (Wijs)	120-150	100-150
Ash, %	1.05-3.00	0.00-0.20
ANALYSIS		
Fatty Acids, %	25-60	40-90
Rosin Acids, % calculated as abietic	20-60	5-40
Sterols, higher alcohols, etc. %	6-20	3-15

The present specifications of the largest American producer are:

	CRUDE	DISTILLED
PHYSICAL DATA		
Specific gravity, 60°F/60°F	0.96-0.98	0.96-0.98
Pour Point, °F, not over	45	-
Viscosity, Saybolt Universal		
at 100°F, seconds	800-900	300-400
at 210°F, seconds	110-130	50-70
Flash Point, °F	350-370	350-380
Fire Point, °F	410-430	410-430

---

*This method cannot be applied to CRUDE TALL OIL or TALL OIL PITCH. It can only be used for REFINED TALL OIL and Abietic Acid.

Color	brown	
Lovibond using half column		
yellow, not more than		70
red, not more than		40
Moisture, %, less than	0.2	0.1
CHEMICAL DATA		
Acid Number	150-160	170-180
Saponification Number	160-170	170-185
Rosin Acids Number	76-82	60-67
Iodine Number (Wijs)	150-180	140
Ash, %, less than	0.3	0.1
ANALYSIS		
Fatty Acids, %	45-55	55-60
Rosin Acids, % calculated as abietic	40-45	34-38
Sterols (higher alcohols, etc.), %	6-10	6-10

REFERENCES

1. Twitchell — J. Soc. Chem. Ind. 10,804 (1891)
2. Wolff & Schloze — Chem. Ztg., 38, No. 34, 369-70
3. Wilkie — Analyst 42,200 (1917)
4. Allen — Commercial Organic Analysis II, 90, 769-75 (5th Ed.)

REFERENCES (APPENDED)

For those interested further in the composition of tall oil the following references to the literature are appended:

Alberti — Seifensieder Ztg. 55, 58-9 (1928)

Aschan — Berichte 45, 867-86 (1929)

Aschan — Finnish Paper Timber J. (1937), 324-28

Bergstrom — Jern-Kontorets Annaler 12, 507-18 (1911)

Boernstein — Seifensieder Ztg. 47, No. 5, 109 (1920)

Czerny — Bul. Soc. Chim., Romania, 7, 91-2 (1925)

Dittmer — Z. angew. Chem. 39, 262-9 (1926)

Duesberg — Seifensieder Ztg. 52, 873-74 (1925)

Fieser — Chemistry of Natural Products Related to Phenanthrene, Pp. 49-70, 344-47

Fleck and Palkin — J. Am. Chem. Soc. 59, 1593-5 (1937)

Fricke — Allgem. Oel-u. Fett Ztg. 24, 45-46

Frydlender — Rev. Produits chim. Actual Sci. reun. 37, 33-36, 65-70 15/II 1934

Hubscher — Der Chem. — Techn. Fabrikant 18, 12, 231-2 (1921)

Lewkowitsch — J. Soc. Chem. Ind. 12, 504 (1893)

Klatt — Fettchem. Umschau 41, 90-4 (1934)

Niesen and Ubbelohde — Fett u. Seifen 44, 426-32 (1937)

Phillips — Pulp & Paper Magazine of Canada, 211-19 (2/5/31)

Pollak — Oil and Soap 15, 33-34 (1938)

Pyhala — Chem. Umschau, 11, 145-7, 189-95 (5/25/27)

ABSTRACTS

Oils and Fats

Edited by

M. M. PISKUR and RUTH LINDAHL

Papers presented at D. G. F. meeting. Physical chemistry of emulsion formation and stability. F. Seelich. *Fette u. Seifen 46,* 139-42 (1939). Motion of emulsions and emulsifiers. H. Schmalfuss. *ibid.* 142-4. Fat containing salves for skin treatment and therapy. G. Hopf. *ibid.* 144-6. Emulsifying oil in technical margarine manufacture. L. Erlandsen. *ibid.* 147-50. Vitamin F. F. Grandel. *ibid.* 150-2. Marine animals as sources of vitamins A and D. F. Unger. *ibid.* 152-6. Soap machines. F. Tachman. *ibid.* 155-8. The papers are printed in full with illustrations.

Selective oxidation of animal and vegetable fats: A new constant. W. A. Alexander. *Analyst 64,* 157-164. (1939). Method: To 0.1 to 0.6 g. of oil, depending on I no. in a 150 cc. flask, add 2cc. CCl_4, warm to 60° C. in thermostat, add 10 cc. N $Na_2C_2O_7$ and leave in thermostat for 1 hr. A little water is added, then 25 cc. of 2.5 N $FeSO_4$ soln. and the contents titrated with 0.1 N $KMnO_4$. Run blank. The "oxidation equivalent" is defined as the cc. of 0.1 N $KMnO_4$ equiv. used by the oil times 0.3175 divided by the wt. of sample. This value when used in conjunction with I value can be used for detection of animal and vegetable fats. Data on several oils are tabulated.

The Wijs method for determining the iodine number. A proposed modification. Alfred Vossgord and Ernest Björsvik. *Z. anal. Chem. 115,* 195-204 (1939). — The method was subjected to critical examn. to det. the best conditions for carrying out the procedure; a sample of cod-liver oil was used at the start but 10 other kinds of oil were subsequently used to test the findings. The modified procedure can be used for I nos. between 8 and 190 with satisfactory agreement with nos. obtained by the unmodified procedure. The modified procedure is as follows: To the weighed sample (of wt. such that the halogen excess will lie between 65 and 400%) add 25 ml. of 0.2 N ICl soln. dissolved in a mixt. of 35% AcOH and 55% CCl_4 by vol. After 30 min. at about 20° add 10 ml. of 10% KI soln. and titrate excess I_2 with 0.1 N $Na_2S_2O_3$ in the usual manner. (*Chem. Abs.*)

Chemistry of fat spoilage. VI. The Rolls of "maltols" (2-methyl-3-oxypyron) *Fette u. Seifen 46,* 127-31 (1939). —2-methyl-3- oxypyron, a constituent of barley, which has a function similar to "Inhibitols," was found to possess no antioxidant properties.

Rancidity of fats. Butter. A. Romeo and R. Catalano. *Riv. ital. Profumi Piante officin 20,* 71-3 (1938). The sample is treated with hydroxylamine-HCl (I) and the HCl liberated by oxime formation is titrated with 0.1 *N, KOH.* The rancidity is expressed as the I no., i.e., amt. of I in mg. required to react with all the oxo-compds. in 100 g. of fat sample. Olive oil. A. Romeo and V. Crupi. ibid. 233-4. Good results with the use of the above method on olive oil were obtained. (*Chem. Zentr.*).

Hardening of oil at lower pressure with nickel-copper catalyst. S. Ueno, G. Inagaski and H. Kisaki. *J. Soc. Chem. Ind. Japan 41,* Suppl. binding 298-9 (1938). Seven tables of results are shown from which it is concluded that: (1) the unreduced