Designation: D 1469 – 93

Standard Test Method for
Total Rosin Acids Content of Coating Vehicles[1]

1. Scope

1.1 This test method covers the determination of total rosin acids content of rosin esters, varnishes, and alkyd resins, unmodified by such materials as maleic or fumaric acid, or phenols. Total rosin acids determined include free rosin, esterified rosin, and metallic salts of rosin.

1.2 This test method is primarily designed for material containing 0.5 to 5 % rosin on the nonvolatile basis.

1.3 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 1259 Test Methods for Nonvolatile Content of Resin Solutions[3]

D 1644 Test Methods for Nonvolatile Content of Varnishes[3]

3. Summary of Test Method

3.1 The specimen is saponified with potassium hydroxide-ethylene glycol reagent and acidified with hydrochloric acid. Heat is applied to hydrolyze metallic driers. This is necessary, especially when metallic rosinates are present.

3.2 The mixture described in 3.1 is extracted with benzene (Note 1). The rosin and fatty acids and unsaponifiables pass into the benzene layer. The aqueous layer will contain certain dibasic acids, polyhydric alcohols, and other water-soluble products of saponification.

NOTE 1—While it has not been evaluated for this procedure, toluene has been found to be an acceptable alternative in similar procedures.

3.3 The benzene is removed by evaporation, the residue weighed, and the rosin acids are determined by a selective esterification and titration method.[4]

4. Apparatus

4.1 *Air Condenser*, 30 in. (760 mm), with a 24/40 standard-taper joint.

4.2 *Buret*, automatic type, having a capacity of 25 mL, for the standard potassium hydroxide solution, fitted with soda-lime traps to protect against absorption of atmospheric carbon dioxide (CO_2).

4.3 *Erlenmeyer Flasks*, 250 and 500-mL capacity, with 24/40 ground joint.

4.4 *Separatory Funnels*, three of 1-L capacity.

4.5 *Steam Bath*, located in a fume hood, for evaporation of volatile solvents.

4.6 *Moisture Collection Trap*, constructed according to details shown in Fig. 1. Wrap with ½-in. (12.7-mm) asbestos tape.

4.7 *Pipet*, automatic, 50-mL capacity.[5]

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

5.3 *Benzene*—(Toluene may be an acceptable substitute, see Note 1.)

5.4 *Butyl Alcohol-Sulfuric Acid Esterification Reagent*—Add 500 mL of *n*-butyl alcohol, 500 mL of benzene, and 3.3 mL (6 g) of sulfuric acid (H_2SO_4) to a 2-L round-bottom flask with ground joint, connect to a moisture trap and condenser, and reflux on a hot plate for 30 min to distill out the water and

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[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

Current edition approved April 15, 1993. Published June 1993. Originally published as D1469 – 57 T. Last previous edition D1469 – 73 (1988)$^{\epsilon 1}$.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 06.01.

[4] Linder, A., and Persson, V., "Determination of Rosin Acids in Mixtures with Fatty Acids," *Journal*, Am. Oil Chemists' Soc., Vol XXXIV, No. 1, 1957, pp. 24−27.

[5] Pipets obtainable from the Arthur H. Thomas Co., W. Washington Square, Philadelphia, PA 19105 Catalog No. 8212, or from the Scientific Glass Apparatus Co., Catalog No. JP-6000, have been found satisfactory for this purpose.

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

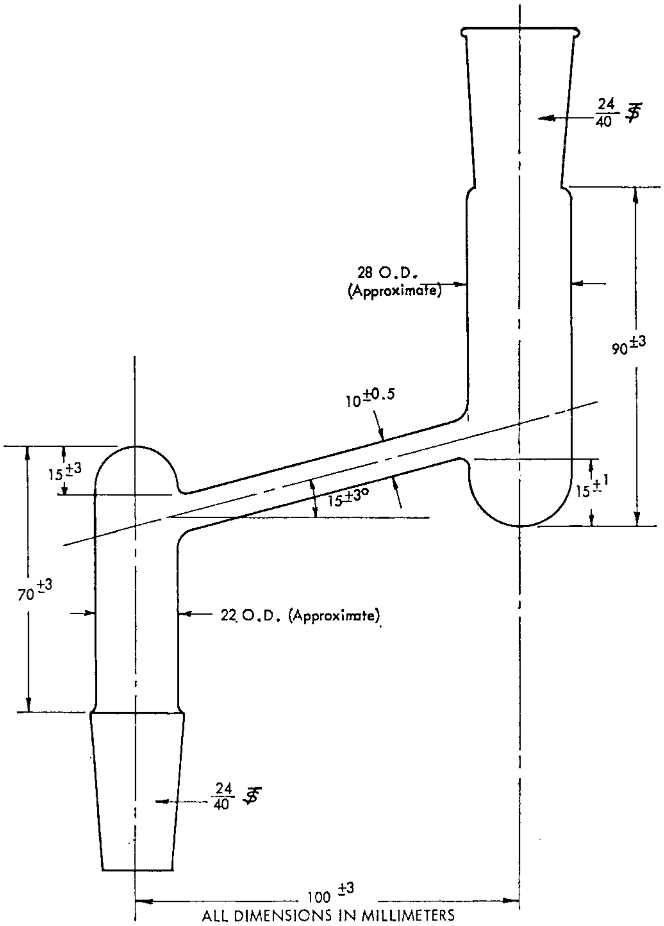

FIG. 1 Moisture Collection Trap

to form butyl-sulfuric acid. Cool and store in a glass-stoppered bottle.

5.5 *Ethyl Alcohol*, conforming to formula No. 30 or No. 3A of the U.S. Bureau of Internal Revenue.

5.6 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

5.7 *Potassium Hydroxide-Ethylene Glycol Solution (132 g/L)*—Dissolve 132 g of potassium hydroxide (KOH) pellets in 1 L of ethylene glycol in a 2-L Erlenmeyer flask. Insert a thermometer and boil to eliminate water until the temperature of the liquid reaches 190 to 195°C. Cool and store in a rubber-stoppered bottle.

5.8 *Potassium Hydroxide, Alcoholic Standard Solution (13.3 g/L)*—Dissolve 13.3 g of KOH pellets in 1 L of alcohol. Standardize against potassium acid phthalate primary standard.

5.9 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H_2SO_4).

5.10 *Thymol Blue Indicator Solution (10 g/L)*—Mix 1 g of thymol blue indicator with 100 mL of ethyl alcohol.

6. Procedure

6.1 Transfer to a 500-mL Erlenmeyer flask an amount of sample, weighed to the nearest 0.001 g, containing approximately 10 ± 1 g of nonvolatile material (Note 2). Add 150 mL of the potassium hydroxide-ethylene glycol solution and swirl to disperse the sample. Add a boiling stone, attach a condenser, and reflux on a hot plate for 2 h.

NOTE 2—Determine the nonvolatile content in accordance with either the foil method given in Test Methods D 1259 or the varnish method given in Test Method D 1644.

6.2 After refluxing, remove the flask from the hot plate and cool to room temperature under tap water. Add 100 mL of water, and while cooling under tap water, add 40 mL of HCl. Place on the hot plate again, reflux for 5 min, and cool under tap water.

6.3 Transfer the sample quantitatively to a 1-L separatory funnel with the aid of a total of 150 mL of water, followed by two 25-mL rinses with benzene. Shake, allow the layers to separate, and draw off the lower aqueous layer into a second 1-L separatory funnel. Extract the aqueous layer with a second 50-mL portion of benzene, and drain the aqueous layer into a third 1-L separatory funnel. Extract with a third 50-mL portion of benzene. Draw off and discard the water layer. Combine the benzene extracts, and wash with three 50-mL portions of water. Measure the pH of the third water wash. If it is less than 3.8, repeat with a fourth water wash. Discard the wash waters.

6.4 Transfer the washed benzene extract to a weighed (to the nearest 0.001 g) 250-mL Erlenmeyer flask, with the aid of 25 mL of benzene. Evaporate the benzene on the steam bath, preferably with the aid of a gentle stream of inert gas to a volume of approximately 20 mL. Add 5 mL of anhydrous ethyl alcohol and evaporate to dryness, to remove any water present by azeotropic distillation.

6.5 Cool and weigh to the nearest 0.001 g. To avoid oxidation, do not dry in an oven; also, the retention of a small amount of benzene does not affect the final calculation.

6.6 Using an automatic pipet, accurately measure 50 mL of the esterification reagent into the flask. Connect the flask to the moisture collection trap and condenser, place on a hot plate, heat to boiling, and reflux for 20 min. At the end of the heating period, allow the flask to cool somewhat, then remove and cool to room temperature.

6.7 Add 10 drops of thymol blue indicator solution and titrate with the alcoholic KOH solution to a blue end point.

6.8 Make a blank titration on 50 mL of the esterification solution, after refluxing it in the same manner.

7. Calculation

7.1 In order to apply properly the esterification correction factors to the isolated rosin acids-fatty acids mixture, it is necessary first to calculate the percent of rosin acids in the dried benzene extract, Y, and then to convert this value to the nonvolatile sample basis as follows (Note 3):

$$Y = [(A - B)N \times 30.24 \times 1.018]/S - 0.3 \qquad (1)$$

where:

A = alcoholic KOH solution required for titration of the sample, mL,

B = alcoholic KOH solution required for titration of blank, mL,

N = normality of the KOH solution used,

S = dried benzene extract, g,

30.24 = molecular weight of abietic acid multiplied by 100 and divided by 1000, 1.018 = experimentally determined factor to correct for the slight esterification of rosin acids, and

0.3 = experimentally determined factor to correct for unesterified fatty acids.

$$V = (S \times Y)/(W \times T) \quad (2)$$

where:

V = rosin acids in alkyd vehicle, nonvolatile basis, %,

W = original alkyd vehicle taken for analysis, g,

T = nonvolatile content of the vehicle, (Note 2) expressed as a decimal, and

S = dried benzene extract, g.

NOTE 3—If it is desired to express the total rosin acids as "commercial rosin," use 35.0 instead of 30.2 as the factor in the calculation.

7.2 Report the results to one decimal place.

8. Precision and Bias

TABLE 1 Precision

	Between Runs	Between Days	Between Labs
Degrees of freedom	17	11	4
Standard deviation	0.054	0.052	0.166
95 % confidence range	0.12	0.11	0.46

8.1 On the basis of an interlaboratory study of this test method in which one operator in four laboratories analyzed three samples containing different quantities of rosin, the within-laboratory standard deviation was found to be 0.05 % absolute at 11 df and the between-laboratory standard deviation was found to be 0.17 % absolute at 4 df (see Table 1). Based on these standard deviations, the following criteria should be used for judging the acceptability of results at a 95 % confidence level:

8.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 0.2 % rosin content.

8.1.2 *Reproducibility*—Two results each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.7 % rosin content.

8.2 *Bias*—No bias can be determined since no standard coating vehicle is available.

9. Keywords

9.1 alkyd resin; fatty acids; resin; resin acid; resin metallic salts