Designation: D 1065 – 96 (Reapproved 2001)

Standard Test Method for Unsaponifiable Matter in Naval Stores, Including Rosin, Tall Oil, and Related Products[1]

This standard is issued under the fixed designation D 1065; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the percentage of material in Naval Stores products as defined in Terminology D 804[2] including rosin, tall oil and related products, other than insoluble dirt or similar visible foreign matter that does not yield a water-soluble soap when the sample is saponified with potassium hydroxide.

1.2 *This standard does not purport to address all of the safety concerns, 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 509 Test Methods of Sampling and Grading Rosin[2]

D 803 Test Methods forTesting Tall Oil[2]

D 804 Terminology Relating to Naval Stores, Including Tall Oil and Related Products[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

3. Significance and Use

3.1 This test method is designed to broaden the scope of the previous edition of the test method by the inclusion of tall oil and tall oil derived from products as test materials. Test Methods D 803 currently includes a method for the determination of unsaponifiable matter.

3.2 The amount of unsaponifiable matter in tall oil and other related products is important in characterizing such products as it indicates the level of nonacidic material, both free and combined, present in the test material. The unsaponifiable in naval stores products is primarily composed of higher molecular weight alcohols, sterols, and hydrocarbons.

4. Apparatus

4.1 *Erlenmeyer or Other Flat-Bottom Flask*, of 125-mL to 250-mL capacity, with standard-taper 24/40 joint.

4.2 *Erlenmeyer Flask*, of 250-mL to 300-mL capacity, with wide mouth.

4.3 *Separatory Funnels*, of 300-mL to 500-mL capacity, with glass or polytetrafluoroethylene (PFTE) stoppers.

4.4 *Graduated Cylinder*, one of 10 to 25-mL and one of 50 to 100-mL capacity.

4.5 *Beaker*, of up to 250-mL capacity.

5. Reagents

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.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled, or deionized water.

6. Preparation of Sample

6.1 Procurement and handling of samples will vary depending upon the physical state of the material. In all instances, the sampling should conform to accepted sampling techniques which ensure the sample is representative of the material being sampled.

6.2 Uniform liquid material should be mixed well and an aliquot removed for analysis. Titer in fatty acid samples should be resolubilized by gentle heating and agitation. Rosin crystallization in liquid samples, such as distilled tall oil (DTO), should be resolubilized by heating to 160°C with periodic agitation. Homogeneous representative samples are imperative.

6.3 Solids that melt at relatively low temperature (that is,

[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.34 on Naval Stores.

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[2] *Annual Book of ASTM Standards*, Vol 06.03.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *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.

tall oil pitch) should be warmed to liquification to facilitate mixing and pouring. Homogeneous representative samples are imperative.

6.4 Solids that melt at relatively high temperatures (that is, rosin) should be fractured and chipped if possible, (see Test Methods D 509). The sample taken for analysis shall consist of small pieces of rosin chipped from a freshly exposed part of a lump of lumps, and thereafter crushed to facilitate weighing and solution. The sample shall be prepared the same day on which the test is begun in order to avoid changes in properties due to surface oxidation that is very pronounced on ground rosin having a large surface area exposed to the air.

7. Reagents

7.1 *Alkali (titrant), Standard Alcoholic Solution* (0.1 *N*)—Dissolve 6.6 g KOH or 5.2 g NaOH, preferably in pellet form, in 1 L of methanol (99.5 %) or ethanol (95 %) denatured by Formula No. 3A or No. 30 of the U.S. Bureau of Internal Revenue. Standardize this solution to ± 0.001 *N* using potassium acid phthalate, or another accepted primary standard for alkaline titrant, according to accepted quantitative practice.

7.2 *Ethyl Ether* (diethyl ether).

7.3 *Isopropyl Alcohol (Isopropanol) (91 to 99 %)*—If not neutral, make neutral to phenolphthalein by adding 0.1 *N* alkali solution dropwise.

7.4 *Phenolphthalein Solution*—Dissolve 1.0 g of phenolphthalein in 100 mL of alcohol conforming to 6.1.

7.5 *Potassium Hydroxide, Ethanolic (Saponification) Solution (132 g KOH/L)*—Dissolve 132 g of KOH (preferably pellets) in 150 mL of water and dilute to 1 L with ethanol (95 %) denatured by Formula No. 3A or No. 30 of the U.S. Bureau of Internal Revenue.

7.6 *Thymol Blue Indicator Solution*—Dissolve 0.1 g of thymol blue in 100 mL methanol (99.5 %).

8. Procedure

8.1 Weigh 5.0 ± 0.1 g (to 0.01 g) of the sample into the 125-mL (250-mL) Erlenmeyer or other flat-bottom flask, using the 10 or 25-mL graduated cylinder add 15 mL of the *ethanolic* KOH solution (132 g KOH/L), attach to the condenser, and heat to reflux and maintain for 1.5 h. Remove the flask, add 30 mL water, transfer to a separatory funnel, and rinse the flask with an additional 20 mL of water that is added to the separatory funnel. Rinse the flask with 40 mL of ethyl ether, adding the ether rinse to the separatory funnel. Stopper and shake the separatory funnel, then allow to stand until the ether layer separates from the water/soap layer. Drain the aqueous soap layer (lower layer) into a second separatory funnel, allowing a few drops of the aqueous layer to remain above the stopcock to prevent loss of ether extract by creepage through the stopcock joint.

8.2 To the aqueous soap layer in the second funnel, add 30 mL ether and extract as before. Drain the aqueous soap layer into the original saponification flask. Add the ether layer from the second separatory funnel to the first separatory funnel, thereby combining the extracts. Pour the aqueous soap layer from the original saponification flask into the second separatory funnel, add 30 mL ether and extract for the third time. Drain the aqueous soap layer from the second separatory funnel into the original saponification flask again, and add the ether layer to the first funnel as before, thereby combining it with the two previous extracts. Now drain off, and add to the soap solution already in the original saponification flask, all but a few drops of aqueous soap solution that has collected at the bottom of the *first* separatory funnel below the combined ether extract layers. Add 2 mL of water to the first separatory funnel and drain off all but a few drops, combining it in the saponification flask.

8.3 Again pour the combined aqueous soap layers from the original saponification flask into the second separatory funnel, add 30 mL ether, and extract for the fourth time. After separation of the layers, discard the aqueous soap layer (lower layer) from the second separatory funnel and add the ether layer to the combined ether extracts in the first separatory funnel. Carefully drain off any remaining aqueous soap layer that may have collected above the stopcock under the ether extracts in the first separatory funnel. Add 2 mL of water, swirl the separatory funnel gently, allow the water to settle, and then drain off and discard the water layer (lower). Repeat this washing once with 5 mL of water, followed by three washes with 30 mL of water. Drain a portion of the third 30-mL water wash into a beaker, add 2 drops of phenolphthalein solution, and examine for any pink color. If pink color is observed, wash once more with 30-mL water. The absence of pink color indicates the wash is neutral to phenolphthalein.

8.4 Drain the neutral washed, combined ether extracts into a dry, tared (to 0.001 g or 0.0001 g), wide-mouth Erlenmeyer flask, rinse the separatory funnel with 15 mL ether and add this to the tared Erlenmeyer flask. Evaporate the ether from the flask using a steam bath. If any water droplets collect in the flask, add a few millilitres of acetone, and continue to evaporate on the steam bath until a clean, dry residue is obtained. Place the flask in a forced convection drying oven at 100 to 105°C for 15 to 30 min. Inspect for solvent vapor, if none, cool in a desiccator, and weigh (to 0.001 g or 0.0001 g).

8.5 Dissolve the contents of the flask with 50 mL of isopropyl alcohol conforming to 6.3, add 4 or 5 drops of thymol blue or phenolphthalein indicator solution, and titrate with the standardized 0.1 *N* alkali solution in 6.1. When the solution is too colored to detect with certainty the endpoint internally, titrate until a faint color change is noted. Then withdraw approximately 0.5 mL of the solution to a porcelain spot plate, and to the portion on the spot plate add 1 drop of the indicator solution. Continue titrating with 0.1-mL increments of titrant, followed by testing on the spot plate, until a definite color change that persists for at least one minute is obtained.

9. Calculation and Report

9.1 Calculate the percentage of unsaponifiable matter in the sample as follows, and report the results to the nearest 0.1 %:

$$\text{Unsaponifiable matter, \%} = [(A - (CN \times 0.302)) / B] \times 100 \quad (1)$$

where:

A = dried residue, g,
B = sample used (dry basis), g,
C = alkali titrant solution used, mL, and
N = normality of the alkali titrant solution.

10. Precision and Bias [5]

10.1 *Precision—Interlaboratory Test Program:* An interlaboratory study of the unsaponifiable matter content of three substances, tall oil fatty acids, distilled tall oil, and rosin, were run in 1994. Results for determinations for tall oil fatty acids were reported for 17 laboratories, determinations for distilled tall oil for 16 laboratories and determinations for rosin from 6 laboratories. The design of the experiment, similar to that of Practice E 691 and a within-between analysis of the data are given in Research Report No. D01-1102.

10.2 *Test Results*—The precision information given below for the unsaponifiable matter content of naval stores products is for a comparison of two test results, each of which is the average of three test determinations as follows:

10.2.1 *Repeatability Limit*, 95 % (within laboratory) = 0.3 %.

10.2.2 *Reproducibility Limit*, 95 % (between laboratory) = 1.1 %.

10.3 These terms (repeatability limit and reproducibility limit) are used as specified in Practice E 177. The respective standard deviations among test results, related to the above numbers by the factor of 2.8 are as follows:

10.3.1 Repeatability standard deviation = 0.1 %.

10.3.2 Reproducibility standard deviation = 0.4 %.

10.4 *Bias*—This test method has no bias because unsaponifiable matter content is defined only in terms of this test method.

11. Keywords

11.1 rosin; tall oil; tall oil fatty acids; unsaponifiable matter

[5] Supporting data are available from ASTM Headquarters. Request RR:D01-1102.