



Standard Test Methods for Saponification Number of Naval Store Products Including Tall Oil and Other Related Products¹

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1. Scope

1.1 These test methods cover the determination of the saponification number of tall oil and products obtained by the fractionation of tall oil such as rosin, fatty acids and distilled tall oil as defined in Terminology D 804.² These test methods are also applicable to gum and wood rosin. Two test methods are covered as follows:

1.1.1 Test method using a potentiometric method, and

1.1.2 Test method using an internal indicator method.

1.2 The potentiometric method is suitable for use with both light- and dark-colored test samples. It should be considered the referee method. The internal indicator method is suitable for use only with light- and medium-colored test samples. It should be considered the alternate method.

1.3 *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 803 Test Methods for Testing Tall Oil²

D 804 Terminology Relating to Naval Stores, Including Tall Oil and Other Related Products²

E 70 Test Method for pH of Aqueous Solutions with the Glass Electrode³

3. Significance and Use

3.1 These test methods are designed to broaden the scope of the previous edition of the test method by the inclusion of tall oil and tall oil derived products as test materials. Test Methods D 803 currently includes a method for the determination of saponification number. The details of that procedure will be

deleted when test methods D 803 are revised. Test Methods D 803 will reference these test methods.

3.2 The saponification number is an important property of tall oil and the products obtained by the fractionation of tall oil. It is the test method widely used to determine the total acid content, both free and combined, of these products.

3.3 The potentiometric test method should be used when the most reproducible results are required.

4. Preparation of Sample

4.1 If the sample for analysis is rosin, it shall consist of small pieces of rosin chipped from a freshly exposed part of a lump or lumps, and thereafter crushed to facilitate weighing and dissolution. Prepare the sample the same day on which the test is begun in order to avoid changes in properties due to surface oxidation. Changes are very pronounced on ground rosin that has a large surface area exposed to air. Existing rosin dust and powdered rosin must not be used.

4.2 If the sample is a nonhomogeneous liquid, heat the entire sample in a closed container fitted with a capillary vent or the equivalent. Some kind of agitation, even if done occasionally by hand, saves much time. Heat by immersion in open steam or hot water bath to avoid overheating. When dealing with crystallized rosin, a higher temperature of approximately 160°C may be needed. Remove samples for testing only when the entire sample is homogeneous and has been well stirred.

5. Purity of Reagents and Water

5.1 Unless otherwise indicated, it is intended that all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society,⁴ where such specifications are available. References to water shall be understood to mean distilled or deionized water.

¹ These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and are 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 15.05.

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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

POTENTIOMETRIC TEST METHOD (Referee Method)
6. Apparatus

6.1 *Erlenmeyer Flask*, 250-mL, of chemically resistant glass⁵ with standard-taper glass joint.

6.2 *Hot Plates*.

6.3 *Water-Cooled Reflux Condenser*, with standard-taper joint to fit the Erlenmeyer flask.

6.4 *Buret*, with 0.1 mL divisions.

6.5 *Stirrer*, variable-speed, with a polytetrafluoroethylene (PTFE) coated magnetic stir bar.

6.6 *Delivery or Volumetric Pipet*, 50-mL constant.

6.7 *PTFE Boiling Stones*, or glass beads.

6.8 *Beaker*, 400-mL tall-form.

6.9 *Glass Electrode pH Meter*, conforming to the requirements of Test Method E 70. Use either standard or alkali-resistant electrodes for this test. Alternatively, an automatic potentiometric titrator may be used.

7. Reagents

7.1 *Ethyl Alcohol (95 %)* denatured by Formula No. 3A or No. 30 of the U.S. Bureau of Internal Revenue.⁶

7.2 *Isopropyl Alcohol*, Reagent grade.

7.3 *Toluene*, Reagent grade.

7.4 *Alkali Solution, Standard Alcoholic (0.5 N)*—Dissolve 33 g of potassium hydroxide (KOH), preferably in pellet form, in ethyl alcohol conforming to 7.1 and dilute to 1 L with 3A ethyl alcohol. Standardize to $\pm 0.001 N$ by dissolving potassium acid phthalate ($C_6H_4 COOKCOOH$) in 60 mL of water followed by the addition of 40 mL of isopropyl alcohol. Once the potassium acid phthalate has dissolved, 2.553 g of potassium acid phthalate will be neutralized by 25.0 mL of 0.5 N KOH solution. Protect the standardized solution against evaporation and absorption of carbon dioxide (CO_2) from the air. The solution should be standardized either potentiometrically or colorimetrically using either phenolphthalein or thymol blue as the indicator. The standardization should use the same equipment and techniques as used in the actual saponification number determination.

7.5 *Acid, Standard (0.5 N)*—Standardize a 0.5 N solution of HCl to $\pm 0.001 N$ by any accepted procedure.

7.6 *Borax Buffer, Standard Solution (0.01 M, pH 9.18 at 25°C)*—Dissolve 3.81 ± 0.01 g of disodium tetraborate ($Na_2B_4O_7 \cdot 10 H_2O$) in water and dilute to 1 L in a volumetric flask. Use the special grade⁷ of borax prepared specifically for use as a pH standard. As an alternative, commercially available buffer with a pH between 9 and 11 may be used.

8. Procedure

8.1 Transfer 2.95 to 3.05 g of the sample, weighed to the nearest 0.001 g, to the Erlenmeyer flask. If necessary, 10 mL of

isopropyl alcohol-toluene solution (1:1) can be added to the flask to predissolve the sample. Using a constant delivery pipet or volumetric pipet add 50.0 mL of the alkali solution. Add several PTFE boiling stones or glass beads and connect the flask to the condenser.

8.2 Place the flask on a hot plate and maintain the solution at reflux for 1 h. At the end of the reflux time, while the sample is still warm, transfer the contents of the Erlenmeyer flask into a 400-mL tall-form beaker rinsing with 100 mL of isopropyl alcohol in three washings. Place samples on a heated surface until they can be titrated. In order to avoid highly variable results, make sure that the temperature of the samples is approximately 60 to 70°C when titrated.

8.3 Titrate with 0.5 N acid, recording the buret and pH meter readings. Sufficient acid may be added initially to bring the pH of the solution to about 12. Allow sufficient time for the electrode system to reach equilibrium. Add acid in 1.0-mL portions until the change in pH per addition exceeds 0.3 pH units. Reduce the additions of acid to 0.1 mL or smaller until the end point has been passed, as indicated by a significant decrease in pH units per 0.1 mL of acid added. Continue the titration with 1.0-mL portions until it becomes apparent that the inflection point has been well defined.

8.4 Determine the inflection point (point of maximum change in pH per millilitre of acid) to the nearest 0.05 mL. This may be found by inspection of a plot of pH against millilitres of acid added. For greater accuracy, a plot may be made of the change in pH per millilitre of acid added, against the pH. The inflection point is considered as the end point of the titration. Alternatively if an automatic titrator is used, the endpoint is either the inflection point from the plotted curve or the pH determined to coincide with the inflection point in the laboratory performing the analysis. The value of 10.8 is the average pH encountered at the inflection point by this procedure.

8.5 *Blank*—Make duplicate blank determinations using 50.0 mL of the alkali solution. If 10 mL of isopropyl alcohol-toluene solution (1:1) is used as a solvent in 8.1, then use the same amount in the blank determination.

9. Calculation and Report

9.1 Calculate the saponification number, expressed as milligrams of KOH per gram of sample as follows:

$$\text{Saponification number} = [(B - A) N \times 56.1] / C$$

where:

B = acid required for titration of the blank, mL,

A = acid required for titration of the sample, mL,

N = normality of the acid, and

C = sample weight, g.

Report the saponification number to the nearest whole number.

INTERNAL INDICATOR TEST METHOD (Alternative Method)
10. Apparatus

10.1 Same apparatus as 6.1-6.7.

11. Reagents

11.1 *Phenolphthalein Indicator Solution*—Dissolve 1 g of

⁵ Alkali-resistant glasses, or equivalent, are suitable for this purpose. Borosilicate flasks may be used, but they should either be new or be cleaned by rinsing with a hot solution of HF (2 or 3 %). This removes from the flasks the adhering partially disintegrated silicates that would interfere with the determination.

⁶ Available from the U.S. Bureau of Alcohol, Tobacco, and Firearms, Distilled Spirits and Tobacco Branch, 1200 Pennsylvania Ave., NW, Washington DC 20226.

⁷ The National Institute of Standards and Technology standard sample of borax No. 187 is satisfactory for this purpose.

phenolphthalein in 100 mL of methanol.

11.2 *Thymol Blue Indicator Solution*— Dissolve 0.1 g of thymol blue in 100 mL of methanol.

11.3 Same as 7.1-7.5.

12. Procedure

12.1 Transfer 2.95 to 3.05 g of the sample, weighed to the nearest 0.001 g to the Erlenmeyer flask. If necessary, 10 mL of isopropyl alcohol-toluene (1:1) can be added to the flask to predissolve the sample. Using a constant delivery pipet or volumetric pipet, add 50.0 mL of the alkali solution. Add several PTFE boiling stones or glass beads, and connect the flask to the condenser.

12.2 Place the flask on a hot plate and maintain the solution at reflux for 1 h. At the end of the reflux time, place samples on a heated surface until they can be titrated. In order to avoid highly variable results, make sure that the temperature of the samples is approximately 60 to 70°C when titrated.

12.3 Titrate with 0.5 N HCl using either 4 to 5 drops of phenolphthalein indicator to a clear endpoint or 4 to 5 drops of thymol blue indicator. With thymol blue, the end point is indicated when the color undergoes the first change from a distinct blue to a blue-green, just short of clear yellow. If needed, more indicator may be used. Read the buret to 0.05-mL titrant. If less than 20 mL of titrant is consumed, decrease the sample size.

12.4 *Blank*—Make duplicate blank determinations using 50.0 mL of the alkali solution and following the same procedure as for the sample. If 10 mL of isopropyl alcohol-toluene solution (1:1) was used as a solvent in 12.1, then use the same amount in the blank determinations.

13. Calculation and Report

13.1 Calculate the saponification number as described in Section 9. Report the results to the nearest whole number.

14. Precision and Bias ⁸

14.1 *Precision*—The precision of these test methods was determined through a multilaboratory round-robin testing program using two substances: tall oil fatty acid and distilled tall oil. The results were combined to give the conclusions given below.

14.1.1 Single operator precision—The single operator standard deviation was found to be 0.9 %. Therefore, results of two properly conducted tests by the same operator on the same sample should not differ by more than 2.5 %.

14.1.2 Multilaboratory precision—The multilaboratory standard deviation was found to be 2.2 %. Therefore, results of two properly conducted tests on the same sample from two laboratories should not differ by more than 6.1 %.

14.2 *Bias*—The procedure in this test method for measuring acid number has no bias because the value of the acid number is defined only in the terms of these test methods.

15. Keywords

15.1 rosin; saponification number; tall oil; tall oil fatty acids

⁸ Supporting data are available from ASTM Headquarters. Request RR: D01-1091.

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