



Designation: D465 – 15 (Reapproved 2020)

Standard Test Methods for Acid Number of Pine Chemical Products Including Tall Oil and Other Related Products¹

This standard is issued under the fixed designation D465; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods are intended for determining the acid number of pine chemical products as defined in Terminology **D804** including tall oil products, wood and gum rosin, and other related materials. These test methods may not be applicable to all modified rosin products. Two test methods are covered, as follows:

- 1.1.1 Potentiometric method (referee), and
- 1.1.2 Internal indicator method (alternate).

1.2 The potentiometric method is suitable for use with both light- and dark-colored products. It should be considered the referee method. The internal indicator method is suitable for use only with light- and medium-colored products with a Gardner color of less than 12. It should be considered the alternate method.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ These test methods are under the jurisdiction of ASTM Committee **D01** on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee **D01.34** on Pine Chemicals and Hydrocarbon Resins.

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2. Referenced Documents

- 2.1 *ASTM Standards*:²
 - D803 Test Methods for Testing Tall Oil**
 - D804 Terminology Relating to Pine Chemicals, Including Tall Oil and Related Products**
 - E70 Test Method for pH of Aqueous Solutions With the Glass Electrode**
 - E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods**
 - E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method**

3. Significance and Use

3.1 These test methods are designed to broaden the scope of the earlier editions of the test method by the inclusion of tall oil and tall oil derived products as test materials and will be referenced in Test Methods **D803**.

3.2 The acid number is an important property of pine chemical products, such as tall oil, and the products obtained by the fractionation of tall oil. It is the test method widely used to determine the total free acid content 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. This is very pronounced on ground rosin having a large surface area exposed to the air. Existing rosin dust and powdered rosin must not be used.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

4.2 If the sample is a nonhomogenous 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 temperature of approximately 160°C may be needed. Sampling should take place only when the entire sample is homogeneous and has been well stirred.

4.3 For other products no special preparation is necessary except storage in a closed container prior to testing.

4.4 Guideline for sample size, solvent, and titrant:

Sample	Sample Size, g	Solvent I, mL	Solvent II, mL	Titration, KOH
Fatty acids DTO ^A Rosin soap	4.0 ± 0.05	Isopropyl alcohol, or methanol 100	None	0.5N
FA esters	20 ± 0.1	Isopropyl alcohol, or methanol 100	None	0.1N
Rosin CTO ^A Pitch	4.0 ± 0.05	Toluene 25	Isopropyl alcohol 75	0.5N
Rosin esters 10 ± 0.1 g	10 ± 0.1	Toluene 25	Isopropyl alcohol 75	0.1N

^A DTO represents distilled tall oil, while CTO represents crude tall oil.

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, where such specifications are available. References to water shall be understood to mean distilled or deionized water.³

POTENTIOMETRIC METHOD (REFEREE METHOD)

6. Apparatus

6.1 *Glass Electrode pH Meter*, conforming to the requirements of Test Method E70. Use either standard or alkali-resistant electrodes for this test. An automatic potentiometric titrator may be used in place of a pH meter.

6.2 *Buret*, 50 mL with 0.1 mL divisions.

6.3 *Stirrer*, variable-speed with polytetrafluoroethylene (PTFE) coated magnetic stir bar or other type mechanical stirrer.

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

7. Reagents

7.1 *Alkali, Standard Solution (0.5 N)*—Dissolve 33 g of potassium hydroxide (KOH) (pellets or sticks) in methyl

³ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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.

alcohol conforming to 5.1, and dilute to 1 L with the same solvent. Standardize to ± 0.001 N by dissolving potassium acid phthalate (KHP) in 60 mL of water followed by the addition of 40 mL of isopropyl alcohol once the KHP has dissolved; 2.553 g of KHP will be neutralized by 25.0 mL of 0.5 N KOH solution. Protect the standardized solution against evaporation and absorption of carbon dioxide (CO₂) from the air. The solution should be standardized frequently, 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 acid number determination.

7.2 *Alkali, Standard Solution (0.1 N)*—Dissolve 6.6 g of potassium hydroxide (KOH) (pellets or sticks) in methyl alcohol conforming to 7.4, and dilute to 1 L with the same solvent. Standardize to ± 0.001 N by dissolving potassium acid phthalate (KHP) in 60 mL of water followed by the addition of 40 mL of isopropyl alcohol once the KHP has dissolved; 0.5106 g of KHP will be neutralized by 25.0 mL of 0.1 N KOH solution. Protect the standardized solution against evaporation and absorption of carbon dioxide (CO₂) from the air. The solution should be standardized frequently, 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 acid number determination.

7.3 *Isopropyl Alcohol*, as in 5.1.

7.4 *Methyl Alcohol*, as in 5.1.

7.5 *Toluene*, as in 5.1.

7.6 *Borax Buffer, Standard Solution (0.01 M, pH 9.18 at 25°C)*—Dissolve 3.81 ± 0.01 g of disodium tetraborate (Na₂B₄O₇ · 10H₂O) in water and dilute to 1 L in a volumetric flask. Use the special grade⁴ of borax prepared specifically for use as a pH standard. As an alternative, a commercially available buffer with a pH between 9 and 11 may be used instead of self-prepared standard.

8. Standardization of Apparatus

8.1 Adjust the pH meter with the standard buffer solution from 7.6, following essentially the same procedure as described in Test Method E70.

9. Procedure

9.1 Transfer the prescribed amount of sample recommended in 4.4, weighed to the nearest 0.001 g, to a 400-mL tall-form beaker. Add the proper amount of solvent I (see 4.4) and swirl to dissolve. Heat gently if necessary to dissolve the sample.

9.2 Add the correct amount of solvent II (see 4.4), if required, and cool to near room temperature.

9.3 Adjust the beaker so the lower half of each electrode of the pH meter is immersed in the solution. Start the stirrer and adjust the speed so that there is vigorous stirring without spattering.

⁴ The National Institute for Standards and Testing standard sample of borax No. 187 is satisfactory for this purpose.

NOTE 1—Glass electrodes tend to dehydrate in nearly anhydrous solvent medium. Condition the electrode in water between tests and check with known pH buffers frequently.

9.4 Titrate with the standard alkali solution, recording the buret and pH meter readings. Sufficient alkali may be added initially to bring the pH of the solution to about 8. Allow sufficient time for the electrode system to reach equilibrium. Add alkali in 1.0-mL portions until the change in pH per increment added amounts to about 0.3 pH unit. Reduce the additions of alkali 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 added. Continue the titration with 1.0-mL portions until it becomes apparent that the inflection point has been well defined.

9.5 Determine the inflection point (point of maximum change in pH per millilitre of alkali solution) to the nearest 0.05 mL by plotting the pH readings against the millilitres of alkali used. For greater accuracy, a plot may be made of the change in pH per millilitre of alkali, against the pH. The peak of this curve will indicate the exact inflection point. The inflection point is considered as the end point of the titration. Alternatively, if an automatic titrator is used, the end point is either as inflection point from the plotted curve or the pH determined to coincide with the inflection point in the laboratory performing the analysis.

NOTE 2—The value of 10.8 is the average pH encountered at the inflection point by the above procedure using closely controlled conditions, solvent, etc.

10. Calculation and Report

10.1 Calculate the acid number of the sample, expressed as milligrams of KOH per gram of sample, as follows, and report to the nearest whole number:

$$\text{Acid number} = (A \times N \times 56.1) / B$$

where:

- A = alkali solution required for titration of the specimen, mL,
- N = normality of the alkali solution, and
- B = specimen weight, g.

INTERNAL INDICATOR METHOD (ALTERNATE METHOD)

11. Reagents

11.1 Prepare or use, as required, the reagents described in 7.1 – 7.5.

11.2 *Phenolphthalein Indicator Solution*—Dissolve 1 g of phenolphthalein in 100 mL of methyl alcohol.

11.3 *Thymol Blue Indicator Solution*—Dissolve 0.1 g of thymol blue in 100 mL of methyl alcohol.

12. Apparatus

12.1 Same apparatus as 6.2 and 6.3.

12.2 *Erlenmeyer flask*, 250-mL.

13. Procedure

13.1 Transfer the prescribed amount of sample recommended in 4.4, weighed to the nearest 0.001 g, to a 250-mL Erlenmeyer flask. Add the proper amount of solvent I (see 4.4) and swirl to dissolve. Heat gently if necessary to dissolve.

13.2 Add the correct amount of solvent II (see 4.4) if required and cool to near room temperature.

13.3 Titrate the solution with the standard alkali solution using 4 to 5 drops of either phenolphthalein or thymol blue indicator solution. Dark colored samples may require additional indicator to be added to the solution. With phenolphthalein titrate to the first persistent faint pink color, or with thymol blue titrate to a blue-green color. Read buret to 0.05-mL titrant.

NOTE 3—If less than 20 mL of titrant is consumed the sample size should be increased.

14. Calculation and Report

14.1 Calculate the acid number as described in Section 10 and report to the nearest whole number.

15. Precision and Bias

15.1 *Interlaboratory Test Program*—An interlaboratory study of the acid number of three substances, tall oil fatty acids, distilled tall oil, and rosin, was run in 1994. Each of 14 laboratories tested each of the three materials. The design of the experiment, similar to that of Practice E691 and a within-between analysis of the data are given in ASTM Research Report.⁵

15.2 *Test Result*—The precision information given below for the acid number of pine chemical products is for the comparison of two test results, each of which is the average of three test determinations as follows:

15.2.1 *Repeatability Limit*, 95 % (within laboratory) = 1.2.

15.2.2 *Reproducibility Limit*, 95 % (between laboratories) = 3.3.

15.3 These terms (repeatability limit and reproducibility limit) are used as specified in Practice E177. The respective standard deviations among test results, related to the above numbers by the factor of 2.8, are as follows:

15.3.1 Repeatability standard deviation = 0.4.

15.3.2 Reproducibility standard deviation = 1.2.

15.4 *Bias*—These test methods have no bias because acid number is defined only in terms of these test methods.

16. Keywords

16.1 acid number; rosin; tall oil; tall oil fatty acids

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1086. Contact ASTM Customer Service at service @astm.org.