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AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Method for Unsaponifiable Matter in Drying Oils, Fatty Acids, and Polymerized Fatty Acids[1]

1. Scope

1.1 This test method covers the determination of the unsaponifiable matter present in all natural and synthetic drying oils and their fatty acids and any other fatty acids or polymerized fatty acids used in protective coatings.

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 460 Test Methods for Sampling and Chemical Analysis of Soaps and Soap Products[2]

D 1193 Specification for Reagent Water[3]

D 1466 Test Method for Sampling Liquid Oils and Fatty Acids Commonly Used in Paints, Varnishes, and Related Materials[4]

2.2 *AOSC Standard:*

Specification H 2-41[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *unsaponifiable matter*—substances frequently found dissolved in fatty acids that cannot be saponified by sodium hydroxide or potassium hydroxide under the conditions prescribed but are soluble in the ordinary fat solvents. Included are the higher aliphatic alcohols, sterols, pigments, and hydrocarbons.

4. Significance and Use

4.1 The major components of drying oils and fatty acids can be saponified by reaction with alkali and converted to water-soluble soaps. This test method determines the amount of material present that is soluble in the oil but is not saponifiable. Under conditions of this test method, this material is not converted to a water-soluble soap and is extracted from the saponification mixture with petroleum ether.

4.2 A small amount of unsaponifiable material is characteristic of drying oils and fatty acids however a large amount indicates contamination with hydrocarbon materials such as mineral oils or hydrocarbon resins.

4.3 This test method is the referee method for unsaponifiable content. The exact amount of unsaponifiable matter obtained is governed by the partition coefficient of the matter between the soap solution and the solvent. Different results will be obtained if some other solvent, such as ethyl ether, is used.

NOTE 1—See relevant specifications for appropriate numeric ranges of unsaponifiable matter in specific drying oils or fatty acids.

5. Apparatus

5.1 *Glass-Stoppered Extraction Cylinder*, graduated at 40, 80, and 130 mL, about 300 mm in height and 35 mm in diameter.

5.2 *Erlenmeyer or Soxhlet Flasks*, 100 to 200-mL capacity.

5.3 *Separatory Funnels*, 500-mL capacity.

5.4 *Glass Siphon*.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests unless otherwise specified. 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming

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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 D01.32 on Drying Oils.

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[2] *Annual Book of ASTM Standards*, Vol 15.04.

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

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

[5] Available from American Oil Chemists' Society, 508 S. Sixth St., Champaign, IL 61820.

[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.

to Type II of Specification D 1193.

6.3 *Ethyl Alcohol, Neutral* (95 %)—Use 95 % ethyl alcohol or neutral denatured alcohol conforming to Formula No. 30 or 3A of the U. S. Bureau of Alcohol, Tobacco and Firearms. Boil and neutralize to the phenolphthalein end point with alkali just before using.

6.4 *Ethyl Alcohol* (1 + 9)—Mix 1 volume of alcohol conforming to 5.3 with 9 volumes of water.

6.5 *Phenolphthalein Indicator Solution* (10 g/L) (Note 2)—Dissolve 1 g of phenolphthalein in 100 mL ethanol (6.3), methanol, or isopropanol.

NOTE 2—A "masked phenolphthalein indicator" may be used with off-color materials. Prepare by dissolving 1.6 g of phenolphthalein and 2.7 g of methylene blue in 500 mL of denatured alcohol conforming to 5.3. Adjust the pH with sodium hydroxide (NaOH) or potassium hydroxide (KOH) solution so that the greenish-blue color is faintly tinted with purple. The color change is from green to purple when going from acid to alkaline.

6.6 *Petroleum Ether* conforming to the requirements given in Test Methods D 460.

NOTE 3—Petroleum ether conforming to the requirements of AOCS Specification H 2-41 also meets these requirements.

6.7 *Potassium Hydroxide Solution*(50 %)—Dissolve potassium hydroxide (KOH) in an equal weight of water.

6.8 *Sodium Hydroxide, Standard Solution (0.02 N)*—Transfer 40 mL of 0.5 *N* sodium hydroxide (NaOH) solution to a 1-L volumetric flask. Adjust to volume with recently boiled and cooled water. Standardize by titrating against potassium acid phthalate, using phenolphthalein indicator solution.

7. Sampling

7.1 The sampling of the material and sample preparation and handling shall be in accordance with Test Method D 1466.

8. Procedure

8.1 Transfer about 5 g of the well-mixed sample, weighed to 10 mg, to an Erlenmeyer or Soxhlet flask. Add 30 mL of alcohol and 5 mL of KOH solution. Boil gently but steadily under a reflux condenser for a minimum of 1 h and until completely saponified. Complete saponification is essential.

8.2 Transfer to the extraction cylinder and wash to the 40-mL mark with alcohol. Complete the transfer with warm and then cold water until the total volume is 80 mL. Wash out the flask with a little petroleum ether and add to the cylinder. Cool the cylinder and contents to room temperature (20 to 25°C) and then add 50 mL of petroleum ether.

8.3 Insert the stopper and shake vigorously for at least 1 min and allow to settle until both layers are clear. Use a glass siphon to remove the upper layer as completely as possible without including any of the lower portion.

8.4 Draw the petroleum ether fraction into a 500-mL separatory funnel containing 5 mL of ethyl alcohol (1 + 9) in order to minimize the possibility of leakage of petroleum ether.

8.5 Repeat the extraction at least six more times using 50-mL portions of petroleum ether each time, and, shaking vigorously with each extraction.

NOTE 4—There are some cases in which seven extractions may not be sufficient. This is best judged by making another extraction and evaporating this separately. Extraction should be discontinued when a single extraction shows less than 5 mg of residue.

8.6 Wash the combined extracts in a separatory funnel with 25-mL portions of alcohol (1 + 9), shaking vigorously and drawing off the alcohol layer after each wash. Discontinue washing when the wash solution is neutral to phenolphthalein. Be careful not to remove any of the ether layer.

8.7 Transfer the ether extract to a tared beaker and evaporate to dryness on a water bath under a gentle stream of clean, dry air. Complete the drying to a weight constant to 1 mg, preferably in a vacuum oven at 75 to 80°C and an internal pressure of not more than 200 mm of mercury, or in an air oven at 105°C for 15-min intervals. Cool in a desiccator and weigh.

8.8 After weighing, take up the residue in 50 mL of warm (about 50°C) ethyl alcohol (95 %) containing approximately 1 mL of indicator solution and previously neutralized to a faint pink color. Titrate with 0.02 *N* NaOH solution to the same color.

9. Calculation

9.1 Calculate the percent of unsaponifiable matter, *M*, as follows:

$$A = VN \times 0.282 \tag{1}$$

$$M, \% = [(R - A)/S] \times 100 \tag{2}$$

where:
A = fatty acids in the extract, g,
V = volume of NaOH solution required for titration of the fatty acids (see 8.8), mL,
N = normality of the NaOH solution,
R = residue (see 8.7), g, and
S = specimen weight, g.

10. Precision and Bias

10.1 Precision and bias were not established at the time this test method was written. An effort is being made to assemble this information and if obtainable it will be published in future revisions. This test method has been in use for many years and its usefulness has been well established.

11. Keywords

11.1 drying oils; fatty acids; unsaponifiable matter