Designation: D 1397 – 93 (Reapproved 1998)

Standard Test Method for Unsaponifiable Matter in Alkyd Resins and Resin Solutions[1]

This standard is issued under the fixed designation D 1397; 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 Department of Defense.

1. Scope

1.1 This test method covers the determination of unsaponifiable matter in alkyd resins and resin solutions. This test method is not applicable to alkyd resins containing modifying agents such as urea, melamine, phenols, rosin, and styrene.

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.* For a specific hazard statement, see Note 4.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

3. Significance and Use

3.1 The unsaponifiable matter in alkyd resins controls the properties of the final film.

4. Apparatus

4.1 *Aluminum Beaker*, having a capacity of 125 mL.[3]

4.2 *Flask and Condenser*—A 200-mL Erlenmeyer flask fitted with a water-cooled glass reflux condenser. The connection between the flask and condenser shall be a standard 24/40 taper ground-glass joint.

4.3 *Separatory Funnels*—Three 500-mL capacity fitted with standard-taper, ground-glass stoppers and stopcocks. Stopcocks should be lubricated sparingly with ether-insoluble stopcock grease. Alternatively, funnels fitted with tetrafluoroethylene (TFE-fluorocarbon) stopcocks may be used.

4.4 *Steam Bath*.

4.5 *Vacuum Drying Oven*—A small, laboratory-size vacuum oven, thermostatically controlled to operate at 80 ± 5°C. A water aspirator vacuum source is satisfactory.

5. Reagents and Materials

5.1 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 its use without lessening the accuracy of the determination.

5.2 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*.

5.4 *Benzene–Alcohol Mixture*—Mix equal volumes of benzene and ethyl alcohol, add 2 drops of phenolphthalein indicator solution, and neutralize with 0.02 *N* sodium hydroxide (NaOH) solution to a persistent faint pink color.

5.5 *Ethyl Alcohol* (95 volume %)—Pure ethyl alcohol or denatured alcohol conforming to Formula No. 2B of the U. S. Bureau of Internal Revenue.

5.6 *Ethyl Ether*.

5.7 *Phenolphthalein Indicator Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in ethyl alcohol (95 %) and dilute to 100 mL with ethyl alcohol.

5.8 *pH Indicator Paper*, universal type.

5.9 *Sodium Hydroxide Solution* (50 %)—Dissolve sodium hydroxide (NaOH) in an equal weight of water.

---

[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 D 1397 – 56 T. Last previous edition D 1397 – 88.

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

[3] Aluminum beakers, Catalog No. 2100, manufactured by the A. H. Thomas Co., W. Washington Square, Philadelphia, PA 19105, have been found satisfactory for this purpose.

[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.

5.10 *Sodium Hydroxide, Standard Solution* (0.02 *N*)—Prepare and accurately standardize a 0.02 *N* aqueous NaOH solution.

6. Procedure

6.1 Weigh by difference, from a closed container into the 200-mL Erlenmeyer flask, a portion of resin or resin solution containing from 0.05 to 0.2 g of unsaponifiable matter (Note 1) (8 to 10 g of resin solution usually is sufficient).

NOTE 1—The maximum specimen size is limited to 10 g of nonvolatile matter; otherwise saponification or separation difficulties may arise. The specimen should be weighed to the nearest milligram.

6.2 Add 10 mL of benzene, and warm to dissolve the sample. Add 50 mL of alcohol, swirl gently to mix, and then add slowly 5 mL of the NaOH solution (50 %), whileswirling gently. Add 5 mL of water, attach to the condenser, and allow to reflux gently on the steam bath for 2 h.

6.3 Remove from the heat source, cool to room temperature, and wash down the condenser and joint with a few millilitres of water from a wash bottle. Transfer the contents of the flask to a 500-mL separatory funnel with the aid of water from the wash bottle. Finally, rinse the flask with three 25-mL portions of ether, adding the ether washes to the sample in the separatory funnel. Add sufficient water to bring the volume of the lower aqueous layer to 300 mL, and add 10 mL of alcohol.

6.4 Stopper the separatory funnel, shake gently, and allow the layers to separate. Draw off the lower aqueous layer into the second separatory funnel (Note 2). Continue the extraction of the aqueous layer with successive 20-mL portions (not less than three) until a colorless ether extract is obtained, combining the ether extracts in the first funnel, and using the second and third funnels for the successive extractions.

NOTE 2—If the layers do not separate easily, carefully draw off the lower, clear, aqueous layer and add 2 to 3 mL of alcohol, by means of a pipet, to the ether-emulsion phases in the separatory funnel. Swirl gently to break the emulsion, and continue to draw off the lower layer. This procedure for breaking the emulsion may be repeated on subsequent extractions, if necessary.

6.5 Wash the final combined ether extracts with 25-mL portions of water until the washings are neutral when tested with the indicator paper or solution. Transfer the final ether extract portion-wise into the 125-mL beaker containing a small boiling stone and previously weighed to the nearest 1 mg, evaporating the ether from each portion on the steam bath (Note 3). (**Precaution—**See Note 4.) Finally, rinse the separatory funnel with a few successive millilitres of ether, adding these washes to the extract in the beaker.

NOTE 3—The metal top of the steam bath should be covered with clean aluminum foil to prevent corrosion of the aluminum beaker during the evaporation.

NOTE 4—**Precaution:** In addition to other precautions, be sure to use a hood.

6.6 Evaporate the final portion of ether; then transfer the beaker and its contents to the vacuum oven, previously heated to 80°C. Heat to constant weight, allowing to cool to room temperature in a desiccator before weighing.

6.7 After weighing, take up the residue in 50 mL of warm (approximately 50°C) benzene-alcohol mixture. Titrate with 0.02 *N* NaOH solution to the same persistent faint pink color as in the neutralization of the benzene-alcohol mixture (see 5.3).

7. Calculation and Report

7.1 Calculate the unsaponifiable matter as follows, and report the results to the nearest 0.1 %:

$$F = VN \times 0.280 \quad (1)$$

where:

F = fatty acids in extract, g,
V = NaOH solution required for titration of the residue, mL,
N = normality of the NaOH solution, and
0.280 = the factor used for normal 18-carbon atom fatty acids. If coconut, lauric, pelargonic, or other short chain fatty acids are suspected or known to be present, use the arbitrary factor 0.216 in the above equation.

$$U = [(R - F)/S] \times 100 \quad (2)$$

where:

U = unsaponifiable matter,% ,
R = residue, g, and
S = specimen, g.

8. Precision and Bias

8.1 On the basis of an interlaboratory study of this test method in which the within-laboratory standard deviation was found to be 0.08 % absolute and the between-laboratory standard deviation was found to be 0.11 % absolute the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

8.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator, should be considered suspect if they differ by more than 0.25 % absolute.

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 0.33 % absolute.

8.2 *Bias*—No bias can be determined for this test method since no standard alkyd resin exists.

9. Keywords

9.1 alcohol benzene solution; alkyd resin; alkyd resin solution; coconut acid; lauric acid; pelargonic acid