Designation: D 1957 – 86 (Reapproved 2001)

Standard Test Method for Hydroxyl Value of Fatty Oils and Acids[1]

This standard is issued under the fixed designation D 1957; 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 the hydroxyl content of castor oil, dehydrated castor oil, and their derivatives. This test method may also be used for other fatty products such as fatty alcohols, mono- and diglycerides, and hydroxystearic acid, but the precision will not necessarily be as indicated.

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 whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

3. Significance and Use

3.1 Hydroxyl value is important in establishing reactivity with acids and isocyanates. It is also a measure of the degree of dehydration of castor oil.

3.2 This test method determines the total amount of residual hydroxyl groups present in oils and other fatty acid-containing materials, reported as hydroxyl value.

3.3 This test method involves the acetylation of hydroxyl-containing fatty oils and acids using pyridine as solvent. Other groups that will react with acetic anhydride such as primary and secondary amines under the conditions of the method will be reported as hydroxyl. The hydroxyl value is expressed as milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of the oil. A correction is applied for acid groups present.

4. Apparatus

4.1 *Erlenmeyer Flask*, 250-mL, standard ground-glass-stoppered.

4.2 *Condensers*, straight-tube, Liebig type, having standard ground-glass joints.

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.[3] 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I of Specification D 1193.

5.3 *Acetic Anhydride*, (**Warning**—See 6.5) fresh.

5.4 *n-Butyl Alcohol* (**Warning**—See 6.1), neutralized with 0.5 *N* alcoholic potassium hydroxide (KOH) solution to a faint pink phenolphthalein end point.

5.5 *Ethyl Alcohol or Denatured Alcohol*, conforming to Formula No. 3A or 30 of the U. S. Bureau of Alcohol, Tobacco, and Firearms. Formula No. 3A is a mixture of 100 parts by volume of ethanol to 5 parts by volume of methanol. Formula 30 is 100 parts by volume of ethanol and 10 parts by volume of methanol.

5.6 *Phenolphthalein Indicator Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in methanol, ethanol, or isopropanol, and dilute to 100 mL.

5.7 *Potassium Hydroxide, Alcoholic Solution* (0.5 N) (**Warning**—See 6.3)—Prepare and standardize a 0.5 *N* solution of potassium hydroxide (KOH) in ethanol. The strength

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

[3] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

should be not less than 0.5 *N* in order that the blank titrations will take less than 50 mL to avoid refilling the buret.

5.8 *Pyridine* (**Warning**—See 6.4), distilled at 114 to 115°C.

5.9 *Pyridine-Acetic Anhydride Solution* (3 + 1)—Mix 3 volumes of pyridine with 1 volume of acetic anhydride. Prepare fresh before using.

6. Hazards

6.1 *n-Butyl Alcohol* is a flammable liquid. The liquid and vapor are irritants to the eyes, skin and mucous membranes. Use with adequate ventilation (hood), (TLV-100 PPM). See supplier's Material Safety Data Sheet.

6.2 *Ethyl Alcohol* (*denatured*) is a flammable liquid. Liquid and vapor are harmful, the severity depending upon the concentration of the alcohol and the nature and concentration of the denaturant. Do not use denatured alcohol containing benzene. Do not swallow. Avoid breathing vapor and contact with skin and eyes. See supplier's Material Safety Data Sheet.

6.3 *Potassium Hydroxide* and its strong solutions are caustic to the skin and eyes. Avoid all contact with skin and eyes. Remove contaminated clothing and wash before reuse. See supplier's Material Safety Data Sheet.

6.4 *Pyridine* is a flammable liquid and hazardous by inhalation. It is an eye, skin, and respiratory irritant (TLV-5 PPM). May cause liver and kidney damage. Use with adequate ventilation; perform all operations in a hood. See supplier's Material Safety Data Sheet.

6.5 *Acetic Anhydride* is corrosive and may cause burns to the skin and eyes; the vapor is irritating to mucous membranes. Use in a hood. Remove contaminated clothing and wash before reuse. See supplier's Material Safety Data Sheet.

7. Procedure

7.1 Weigh, to 0.1 mg into a 250-mL Erlenmeyer flask, the correct amount of sample for acetylation determined as follows:

Hydroxyl Value	Specimen Weight, g
0 to 20	10
20 to 50	5
50 to 100	3
100 to 200	2

7.2 Weigh 9.0 to 11.0 g of the sample into another flask for the acid value. If the test method is being used for fatty acids, such as hydroxystearic acid, the weight should be 0.9 to 1.1 g.

7.3 Pipet 5.0 mL of the pyridine-acetic anhydride solution into the flask containing the specimen for acetylation. For samples having 0 to 20 hydroxyl value, add an additional 5 mL of pyridine to the flask. Thoroughly mix the contents by gentle swirling. Pipet another 5.0 mL of pyridine-acetic anhydride solution into an empty flask for the reagent. Add 10 mL of pyridine, neutralized to phenolphthalein, to the specimen for the acid value blank. Thoroughly mix the contents by gentle swirling.

7.4 Insert reflux condensers into the Erlenmeyer flasks. Place the flasks on an opening of a steam bath and heat for 1 h. By this method of heating only slight, if any, refluxing will occur.

7.5 Add 10 mL of water through the condensers to the flasks. Heat on the steam bath for an additional 10 min with reflux condensers attached. Allow the flasks to cool to room temperature with condensers still attached.

7.6 Add 25 mL of neutralized *n*-butyl alcohol to each flask in the following manner. About half should be added through the condenser, the condenser removed, and the remaining alcohol used to wash down the sides of the flasks. Add 1 mL of phenolphthalein indicator solution to each flask and titrate to a faint pink end point with 0.5 *N* alcoholic KOH solution.

8. Calculation and Report

8.1 Calculate the hydroxyl value as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of sample as follows:

$$\text{Hydroxyl value} = \frac{B + (SA/C) - V}{S} N \times 56.1$$

where:

- A = KOH solution required for titration of the acid value, mL,
- B = KOH solution required for titration of the reagent blank, mL,
- C = sample used for the acid value, g,
- V = KOH solution required for titration of the acetylated specimen, mL, and
- S = sample used for acetylation, g.

8.2 Report the results to the first decimal place.

NOTE 1—For routine analysis, the ethanol acid value may be substituted in most cases for the pyridine acid value, and the calculation altered accordingly.

9. Precision and Bias

9.1 The following criteria should be used for judging the acceptability of results at the 95 % confidence level:

9.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than 2.4.

9.1.2 *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 3.0.

9.2 *Bias*—Bias has not been determined.

10. Keywords

10.1 drying oils; hydroxyl value; fatty acids; hydroxyl value