Designation: D1726 – 11

Standard Test Methods for Hydrolyzable Chloride Content of Liquid Epoxy Resins[1]

This standard is issued under the fixed designation D1726; 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 These test methods cover the determination of the easily hydrolyzable chloride content of liquid epoxy resins which are defined as the reaction product of a chlorohydrin and a di- or polyfunctional phenolic compound.

NOTE 1—There is no known ISO equivalent to this standard.

1.1.1 In Test Method A, the easily hydrolyzable chloride is saponified with potassium hydroxide and directly titrated with hydrochloric acid. This test method can be used for concentrations of 1 weight % and below.

1.1.2 In Test Method B, the easily hydrolyzable chloride is again saponified with potassium hydroxide, then titrated potentiometrically with silver nitrate. This test method can be used for concentrations of 5 to 2500 ppm hydrolyzable chloride.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.* For specific hazard statements see Sections 10 and 16.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D329 Specification for Acetone
D841 Specification for Nitration Grade Toluene
D1193 Specification for Reagent Water
D3620 Specification for Glacial Acetic Acid
D6440 Terminology Relating to Hydrocarbon Resins
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 The terminology in these test methods follows the standard terminology defined in Terminology D6440.

3.2 *Definitions:*

3.3 *hydrolyzable chloride, n*—the low level chlorine-containing components of the liquid epoxy resin, typically residual chlorohydrin ethers, which react with water or alcohol to form hydrochloric acid (HCl).

4. Summary of Test Method

4.1 The sample is refluxed in the presence of a known amount of 0.1 *N* alcoholic potassium hydroxide to saponify the hydrolyzable chlorides.

4.2 *Test Method A*—The amount of potassium hydroxide consumed in the hydrolysis is a measure of the hydrolyzable chloride content of the resin.

4.3 *Test Method B*—The amount of potassium chloride detected by direct titration with standard silver nitrate solution is a measure of the hydrolyzable chloride content of the resin.

5. Significance and Use

5.1 The hydrolyzable chloride content of liquid epoxy resins is an important variable in determining their reactivity and the properties of coatings made from them. These test methods may be used to determine the hydrolyzable chloride content of manufactured epoxy resins and confirm the stated hydrolyzable chloride content of purchased epoxy resins.

6. Interferences

6.1 Unless stated otherwise, the following interferences apply to both test methods:

6.1.1 Test Method A—Alkaline substances easily titratable by HCl, can impact the analysis resulting in lower than expected results. Likewise, acidic species, that may behave as the HCl titrant can impact the analysis resulting in higher than expected results. Liquid epoxy resin samples should be neutral when analyzed by this test method.

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[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 D01.33 on Polymers and Resins.

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[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.

6.1.2 Test Method B—Thiocyanate, cyanide, sulfide, bromide, iodide, or other substances capable of reacting with silver ion, as well as substances capable of reducing silver ion in acidic solutions will impact the analysis resulting in higher than expected results.

6.1.3 Test Methods A and B (using a visual indicator) may not be applicable to samples containing heat sensitive impurities, leading to high color in the reacted solution.

7. Purity of Reagents

7.1 *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,[3] where such specifications are available. 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D1193.

TEST METHOD A – 1 Weight % and Below of Hydrolyzable Chloride

8. Apparatus

8.1 *Reflux Apparatus,* consisting of a 250-mL Erlenmeyer flask attached to a reflux condenser.

8.2 *Hot Plate,* with variable heat control.

8.3 *Magnetic Stirrer,* with polytetrafluorethylene (PTFE)-coated stirring bar.

8.4 *Buret.*

9. Reagents and Materials

9.1 *Hydrochloric Acid, Standard* (0.1 *N*)—Dilute 9 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1 L with water. Standardize against 0.25 g of sodium carbonate (Na_2CO_3) accurately weighed and dissolved in 75 to 100 mL of water.

9.2 *Methyl Ethyl Ketone (MEK).*

9.3 *Phenolphthalein Indicator Solution*—Dissolve 1 g of phenolphthalein in 100 mL of methanol, ethanol, or isopropanol.

9.4 *Potassium Hydroxide, Alcohol Solution* (0.1 *N*)—Dissolve 5.6 g of potassium hydroxide (KOH) in 1 L of methanol (99 %). No standardization of the solution is necessary.

9.5 *Toluene* (**Warning**—See Section 10.), conforming to Specification D841.

9.6 *Boiling Chips.*

10. Hazards

10.1 Consult the latest regulations and supplier's Material Safety Data Sheets regarding all materials used in this method.

10.2 Hydrochloric acid and potassium hydroxide are corrosive. Toluene and methyl ethyl ketone are flammable and their vapors can be harmful. Precautions should be taken to avoid inhalation and skin or eye contact with these chemicals. All sample preparations should be done in a well ventilated area, such as a fume hood.

11. Procedure

11.1 Weigh to the nearest 0.001 g, 6 to 8 g of neutral specimen into a 250-mL glass-stoppered Erlenmeyer flask. By means of a pipette, transfer 50.0 mL of 0.1 *N* alcoholic KOH solution into the flask and add 15 mL of toluene. Stopper the flask and swirl to mix.

11.2 Prepare a blank in a separate 250-Erlenmeyer flask, adding 15 mL of toluene and 50 mL of 0.1 *N* alcoholic KOH. Swirl to mix.

11.3 Add a few boiling chips and attach each flask to a reflux condensers on the hot plate.

11.4 Allow each solution to reflux gently for 15 ± 1 min on a hot plate. At the end of the reflux period, remove each flask from the hot plate and cool to room temperature with the condenser in place.

11.5 Rinse down each condenser with 20 mL of toulene then remove the condensers from the flasks.

11.6 Add 3 drops of phenolphthalein indicator solution to each flask, and titrate with 0.1 *N* HCl. The end point is detected when 1 drop of 0.1 *N* HCl changes the solution from pink to colorless.

NOTE 2—Add 100 mL of MEK to the specimen if required to ensure a homogeneous solution during titration of the excess KOH solution.

12. Calculation

12.1 Calculate the weight percent hydrolyzable chloride content of the specimen as follows:

$$H = \frac{[(B - V)N \times 3.545]}{W} \quad (1)$$

where:

H = weight percent hydrolyzable chloride,
B = HCl required for titration of the blank, mL,
V = HCl required for titration of the hydrolyzed specimen, mL,
N = normality of the HCl,
3.545 = grams of chlorine per milliequivalent multiplied by the percentage factor of 100, and
W = specimen weight, g.

13. Precision

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

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[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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

13.1.1 *Repeatability*—Two results obtained by the same operator should be considered suspect if they differ by more than 0.02 % absolute.

13.1.2 *Reproducibility*—Two results obtained by operators in different laboratories should be considered suspect if they differ by more than 0.05 weight %.

TEST METHOD B – 5-2500 PPM Hydrolyzable Chloride

14. Apparatus

14.1 *Reflux Apparatus,* consisting of a 250-mL Erlenmeyer flask attached to a reflux condenser.

14.2 *Hot Plate,* with variable heat control.

14.3 *Magnetic Stirrer,* with polytetrafluoroethylene (PTFE)-coated stirring bar.

14.4 *Glass Buret or Automatic Potentiometric Titrator.*

14.5 *Silver Titrode* or equivalent.

14.6 *Boiling Chips.*

14.7 *Analytical Balance,* capable of weighing to 0.001 g.

15. Reagents and Material

15.1 *Acetone,* (**Warning**—See Section 16.) conforming to Specification D329.

15.2 *Bromcresol Green Indicator Solution (0.1 %)*—Dissolve 0.1 g of bromcresol green in 100 mL of water.

15.3 *Nitric acid,* (HNO_3) (1 + 1) diluted with water.

15.4 *Potassium Hydroxide,* alcohol solution (0.1 *N*)—Dissolve 5.6 g of potassium hydroxide (KOH) in 1 L of methanol (99 %). No standardization of the solution is necessary.

15.5 *Silver Nitrate,* alcohol solution (0.0025 *N*)—Dissolve 0.425 g of silver nitrate ($AgNO_3$), weighed to the nearest 0.001 g, in L of methanol (99 %). Standardize against hydrochloric acid or sodium chloride (NaCl) solution either gravimetrically or potentiometrically, frequently enough to detect changes of 0.0005 *N*.

15.6 *Toluene,* (**Warning**—See Section 16.) conforming to Specification D841.

15.7 *Glacial Acetic Acid,* (**Warning**—See Section 16.) conforming to Specification D3620.

16. Hazards

16.1 Consult the latest regulations and supplier's Material Safety Data Sheets regarding all materials used in this method.

16.2 Nitric acid, glacial acetic acid, potassium hydroxide, and silver nitrate are corrosive. Acetone and toluene are flammable and their vapors can be harmful. Precautions should be taken to avoid inhalation and skin or eye contact with these chemicals. All sample preparations should be done in a well ventilated area, such as a fume hood.

17. Procedure

17.1 Weigh 2 to 3 g of specimen, to the nearest 0.005 g, into a 250-mL Erlenmeyer flask. Add 20 mL of toluene, 20 mL of acetone, and 50 mL of 0.1 *N* alcoholic KOH. Swirl or mix until dissolution is complete.

17.2 Prepare a blank in a separate 250–mL Erlenmeyer flask, adding 20 mL of toluene, 20 mL of acetone, and 50 mL of 0.1 *N* alcoholic KOH. Swirl to mix.

17.3 Add several boiling chips, connect the flasks to separate reflux condensers, and gently reflux each for 15 ± 1 min on a hot plate.

17.4 Remove the hot plate from under the flask and allow the flask and contents to cool to room temperature. Rinse down the condenser with approximately 20 mL of acetone then remove from the flasks.

17.5 Quantitatively transfer the contents of each flask to separate 250-mL titration vessels using acetone as wash solution. Dilute each solution to about 125 mL with acetone.

17.6 For manual titrations, insert a stirring bar into each flask, and place on a magnetic stirrer.

17.6.1 Add five drops of bromcresol green indicator.

17.6.2 While stirring add 50 mL of glacial acetic acid. Alternatively, 1 + 1 nitric acid can be added dropwise just until the permanent color changes from blue to yellow instead of adding the acetic acid. (**Warning**—If using nitric acid, do not add any excess. Do not acidify the solution until ready to begin the titration. Make certain that the solution is at room temperature before acidifying. These cautions are necessary to prevent the chloride results from being low due to recombination with the resin.)

17.6.3 Titrate with 0.0025 *N* silver nitrate to the first blue endpoint, stable for 20 seconds.

17.7 For automated potentiometric titrations, insert a stirring bar and place on a magnetic stirrer or attach to the titration device equipped with a stirrer.

17.7.1 While stirring add 50 mL of glacial acetic acid. Alternatively, 1 + 1 nitric acid can be added dropwise just until the permanent color changes from blue to yellow instead of adding the acetic acid. (**Warning**—If using nitric acid, do not add any excess. Do not acidify the solution until ready to begin the titration. Make certain that the solution is at room temperature before acidifying. These cautions are necessary to prevent the chloride results from being low due to recombination with the resin.)

17.7.2 Titrate with 0.0025 **N** silver nitrate to the inflection point using the combination silver electrode and the automatic titrator or buret.

18. Calculation

18.1 Calculate the parts per million hydrolyzable chloride content of the specimen as follows:

$$H = [(V - B)N \times 35.45 \times 10^3]/W \qquad (2)$$

where:

H = parts per million hydrolyzable chloride,
B = $AgNO_3$ required for the titration of the blank, mL,
V = $AgNO_3$ required for the titration of the hydrolyzed specimen, mL,

N = Normality of the $AgNO_3$,
35.45×10^{3} = grams of chlorine per milliequivalent multiplied by the ppm conversion of 1×10^6, and
W = specimen weight, g.

19. Precision

19.1 A liquid epoxy resin of approximately 150 ppm hydrolyzable chloride was sampled and analyzed at five laboratories and seven analysts obtained the following results.

19.1.1 *Repeatability*—The difference between two results obtained by the same analyst should not vary by more than 8.32 % at the 95 % confidence level.

19.1.2 *Reproducibility*—The difference between two results, each the mean of two determinations, obtained by analysts in different laboratories should not vary by more than 15.88 % relative at the 95 % confidence level.

20. Keywords

20.1 hydrolyzable chloride; liquid epoxy resin; saponifiable chloride

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