Designation: D 2456 – 91 (Reapproved 1997)$^{\epsilon 1}$

Standard Test Method for
Identification of Polyhydric Alcohols in Alkyd Resins[1]

This standard is issued under the fixed designation D 2456; 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.

ϵ^1 NOTE—Footnotes were changed editorially in September 1997.

1. Scope

1.1 This test method covers the qualitative determination of the polyols in alkyd resins, including resin-modified alkyds. It may be used for analyzing polyesters, but additional peaks may appear from monomers such as styrene.

1.2 The constituents of three resin samples have been correctly identified in collaborative work by five laboratories. Quantities as low as 1 %, obtained by blending samples of known composition, were readily detected.

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 a specific hazard statement, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

3. Summary of Test Method

3.1 The resin specimen is subjected to aminolysis to form amides of the carboxylic acids and to release the polyols present, followed by direct acetylation with acetic anhydride. The acetates are extracted and then separated by application of programmed temperature gas chromatography.

4. Significance and Use

4.1 The types of polyhydric alcohols used in the synthesis of alkyd resins has a direct effect on crosslinking capabilities of the resin. This test method helps determine the reactivity of the resin.

5. Apparatus

5.1 *Linear Programmed Temperature Gas Chromatograph*—Any instrument with programming features should be suitable if equipped with a thermal conductivity detector (TCD)[3] and adaptable to the following operating conditions:

Detector cell temperature, °C	300
Detector cell current, mA	150
Injection port temperature, °C	330
Helium flow at exit, cm^3/min	60
Programmed temperature details:	
Approximate column heating rate, deg/min	7.9
Starting column temperature, °C	50
Finishing column temperature,° C	225

5.2 *Columns (Note 1)*—A 4-ft (1.2-m) length of ¼-in. (6.4-mm) outside diameter copper tubing packed with 10 weight % of polyethylene glycol, 20M[4] on 60 to 80 mesh acid washed, white flux-calcined diatomite (UPS Code S1A), and conditioned at 240°C until“ bleeding” reaches a minimum.

NOTE 1—Commercially available columns may be selected and used provided they are capable of performing operations equivalent to the columns specified in this test method.

5.3 *Syringe*, having a fixed needle, 10-µL capacity.

6. Reagents

6.1 *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.[5] 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 as defined by Type IV of Specification D 1193.

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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 D01.33 on Polymers and Resins.

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

[3] Thermal conductivity detector is adequate within the scope of this test method. However, a flame ionization detector (FID) may be used if desired without compromising results of the analysis.

[4] The sole source of supply of the Carbowax 20M known to the committee at this time is Union Carbide Corp., 39 Old Ridgebury Rd., Danbury, CT 06817. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[5] *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.

6.3 *Acetic Anhydride*.

6.4 *n-Butylamine*, boiling point 76 to 78°C.

6.5 *Chloroform*.

7. Hazards

7.1 The reagents and samples used in this test method may, under some conditions, be hazardous. Refer to the manufacturer's Material Safety Data Sheets for specific handling and safety precautions. Safe laboratory handling procedures and all applicable OSHA regulations are to be followed.

8. Procedure

8.1 Weigh a sample of resin containing not less than 1.0 g of nonvolatile material into a 125-mL flask (Note 1) and add 6 mL of *n*-butylamine. Reflux under a water-cooled condenser for 1 h. Cool and add 25 mL of acetic anhydride slowly and cautiously through the top of the condenser and reflux the mixture for 90 min. Cool, add 35 mL of water, boil for 5 to 10 min, and cool. Transfer to a separatory funnel, filtering if necessary, using water sparingly for the transfer. Extract twice with 25-mL portions of chloroform, shaking vigorously for each extraction. Combine the chloroform extracts and wash with 50-mL portions of water until acid-free. Filter through rapid paper freshly dampened with chloroform, collecting the filtrate in a 250-mL beaker. Reduce the volume to 5 or 10 mL by evaporating the solvent with a current of air in a warm water bath (Note 3).

NOTE 2—Drying of the resin solution is not usually necessary but interference may come from a few high-boiling mineral solvents. They can be removed by dissolving the specimen in 3 mL of chloroform or acetone, drying the specimen with a current of air in a warm water bath, redissolving, and redrying about three times.

NOTE 3—If all the chloroform is expelled, there is a danger of losing some of the lower-boiling polyol acetates.

8.2 Inject approximately 5 µL of the remaining specimen into the chromatograph, using the operating conditions tabulated in 5.1 and holding the temperature at 225°C at the completion of the program until all the volatile components have emerged.

9. Identification

9.1 Calibration is always recommended and can be made with polyol acetates or by treating known polyols in accordance with 8.1. In most cases, the peaks can be identified by their relative position on the chromatogram from the data given in Table 1, in which the relative retention is calculated from the second of the two peaks that are produced by the reagents which appear between 14 and 16 min under the programming conditions described in 5.1.

NOTE 4—With many alkyd resin specimens, a peak will appear with relative retention of 1.54 due to the presence of *ortho*-phthalic anhydride in the resin.

10. Precision and Bias

10.1 The precision and bias for this test method has not been determined.

11. Keywords

11.1 alkyd resin; aminolysis; gas chromatography; polyester resin; polyhydric alcohol; polyol; polyol acetates

TABLE 1 Relative Retention Data for Polyol Acetates

Acetate of Polyol	Relative Retention Time (Second Reagent Peak = 1)
2,3-Butylene glycol	0.70
Propylene glycol	0.72
Ethylene glycol	0.76
1,3-butylene glycol	0.82
Neopentyl glycol	0.84
1,4-Butanediol	0.98
Dipropylene glycol	1.05
Diethylene glycol	1.16
Glycerol	1.24
Trimethylol ethane	1.33
Trimethylol propane	1.37
Triethylene glycol	1.43
(*o*-Phthalic acid derivative)	(1.54)
Pentaerythritol	1.81
Mannitol	3.08
Sorbitol	3.24