Designation: D 2455 – 89 (Reapproved 1996)$^{\epsilon 1}$

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Method for Identification of Carboxylic Acids in Alkyd Resins[1]

This standard is issued under the fixed designation D 2455; 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—Editorial changes were made throughout in November 1996.

1. Scope

1.1 This test method covers the qualitative determination of the carboxylic acids 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 three laboratories. It is apparent that quantities as low as 1 % can readily be detected.

1.3 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *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]

D 2245 Test Method for Identification of Oils and Oil Acids in Solvent-Reducible Paints[3]

3. Summary of Test Method

3.1 The resin specimen is subjected to rapid transesterification with lithium methoxide to form methyl esters that are separated by programmed temperature gas-liquid chromatography on polar and nonpolar columns, then identified by their retention relative to a standard. If the presence of maleic or fumaric acids is indicated, an alternative transesterification with boron trifluoride is necessary.

4. Significance and Use

4.1 The presence of carboxylic acids in alkyd resins has a direct effect on the crosslinking capability of the resin. This test method helps the user 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 hot-wire type of detector 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	85
Programmed temperature details:	
Approximate column heating rate,°/ min	4.0
Starting column temperature, °C:	
Polyester-Carbowax 20M	125
Silicone grease, DC-11	75
Finishing column temperature,° C:	
Polyester-Carbowax 20M	225
Silicone grease, DC-11	250

5.2 *Columns*:

5.2.1 *Polar*—Bend a 6-ft (1.8-m) length of ¼-in. (6.4-mm) copper tubing into a U-shape and fill one side with 20 % polyethylene glycol 20M[4] on acid-washed 60 to 80-mesh white, flux-calcined diatomite, (USP code S1A)[5] and fill the other side with 20 % diethylene glycol succinate on the same solid support. Maintain constant vibration during the filling and add small amounts of the packing material alternately to each side. Condition at 225°C until "bleeding" reaches a minimum. Mount this column so that the sample passes first through the polyester section. Two 3-ft (0.9-m) sections, packed separately and joined together may be used if preferred.

5.2.2 *Nonpolar*—Pack a 6-ft (1.8-m) length of ¼-in. (6.4-mm) copper tubing with 20 % silicone grease on acid-washed 60 to 80-mesh Chromosorb W.[5] Condition at 250°C until "bleeding" reaches a minimum.

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

5.4 *Separatory Funnel*, 250 mL.

---

[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 28, 1989. Published June 1989. Originally published as D 2455 – 66. Last previous edition D 2455 – 69 (1981)$^{\epsilon 1}$.

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

[3] *Annual Book of ASTM Standards*, Vol 06.01.

[4] The sole source of supply of the polyethylene glycol, 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] The sole source of supply of white, flux-calcined diatomite, Chromosorb W known to the committee at this time is Celite Corp., P.O. Box 5108, Denver, CO 80217-5108. 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.

5.5 *Steam Bath*.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests (see Section 7). 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 as defined by Type IV of Specification D 1193.

6.3 *Boron Trifluoride Gas*.

6.4 *Lithium Methoxide in Methanol*—Add small pieces of metallic lithium, about the size of a small pea, one at a time to a flask containing absolute methanol which is chilled in an ice bath. Periodically titrate a few millilitres with standardized acid until the normality reaches 0.5 or more. If the normality exceeds 0.5, add a calculated amount of absolute methanol to adjust the reagent to 0.5*N*. Filter before each use. Keep tightly stoppered; it may be necessary to discard after one month.

6.5 *Methanol*, absolute.

6.6 *Methylene Chloride*.

6.7 *Sulfuric Acid* (1+5)—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 5 volumes of water.

6.8 *Triacetin*.

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 procedures and all applicable OSHA regulations are to be followed.

8. Procedure

8.1 Pour into a 125-mL flask, a specimen of resin containing approximately 0.3 g of nonvolatile material (Note 1) and add 15 mL of the 0.5*N* lithium methoxide reagent. Add an antibumping stone, attach a short air condenser, and place on a steam bath. Swirl constantly until solution is effected; then boil for 2 min. Remove the flask from the bath promptly at the end of the timed 2-min period, remove the condenser, and add 5 mL of H_2SO_4 (1+5) at once. Transfer the contents of the flask to a separatory funnel and dilute to 50 mL with water. Add 35 mL of methylene chloride and shake vigorously. Separate and wash the solvent layer with 15-mL portions of water until all sulfuric acid is removed; then withdraw the solvent into a small beaker. Place the beaker in a warm water bath and remove as soon as all of the solvent has been expelled. If solid methyl esters are present, add tetrahydrofuran dropwise with warming until all or most of the specimen has dissolved.

NOTE 1—Drying of the resin solutions 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 re-drying about three times.

8.2 Mount the 6-ft (1.8-m) polyester-polyethylene glycol[4] column in position so that the specimen will pass first through the polyester side and heat the column to starting temperature. Pick up about 5 µL of specimen in the syringe followed by approximately 0.2 µL of triacetin and introduce onto the column. Engage the mechanism for increasing column temperature immediately. When maximum column temperature is reached, maintain the temperature until all components emerge. Obtain a chromatogram in like manner with only the triacetin.

8.3 Repeat the chromatographic separation with the 6-ft (1.8-m) silicone grease column following the operating conditions described for this column in 5.1 and obtain a separate chromatogram with only the triacetin.

9. Identification

9.1 Calibration is always recommended and can be made directly with known methyl esters or by treating known esters as described in 8.1 (Note 2). In most cases, the peaks can be identified by their relative position on the chromatograms from the data given in Table 1, in which relative retention is calculated from the position of triacetin which should emerge between 20 and 25 min from the air peak under the conditions described.

NOTE 2—The acids maleic, fumaric, and itaconic do not form true methyl esters when treated as described in 8.1 so that their esters cannot

TABLE 1 Relative Retention Data for Methyl Esters of Some Carboxylic Acids (Formed by Lithium Methoxide Transesterification)

	Triacetin = 1	
Methyl Ester of Acid	6-ft (1.8-m) Polyester-Carbowax	6-ft (1.8-m) Silicone Grease
Pelargonic	0.29	0.83
Succinic	0.44	0.49
Benzoic	0.47	0.62
Orthotoluic	0.49	0.76
Fumaric	0.63 (0.38)[A]	0.69 (0.49)[A]
Maleic	0.64 (0.52)[A]	0.68 (0.47)[A]
Lauric	0.66	1.29
Adipic	0.71	0.83
Itaconic	0.74	0.83
Diglycolic	0.79	0.70
p-tertiary butyl benzoic	0.83	1.16
Myristic	0.90	1.55
Tetrahydrophthalic	0.97	1.07
Azelaic	1.08	1.31
Palmitic	1.14	1.79
Sebacic	1.19	1.43
Terephthalic	1.22	1.23
Orthophthalic	1.26	1.17
Isophthalic	1.26	1.26
Stearic	1.36	2.02
Oleic	1.41	1.98
Linoleic	1.49	1.98
Linolenic	1.60	1.98

[A] When transesterified with boron trifluoride in methanol.

---

[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.

be used directly for calibration; treatment with boron trifluoride will be necessary. Adducts of maleic and fumaric acid will not be detectable under any conditions.

9.2 Since maleic and fumaric acids have the same relative retention, distinction can be made only by repeating the transesterification and substituting concentrated boron trifluoride in methanol as the catalyst, using 5 mL of reagent and boiling for 5 min. Prepare the catalyst by bubbling the gas into a flask containing chilled absolute methanol until the titration of 1 mL of the reagent, when diluted with 25 mL of methanol, uses 11 to 12 mL of 0.5*N* KOH in methanol, titrating to the yellow end point with thymol blue indicator solution. At the end of the 5-min reflux, transfer the specimen to a separatory funnel with 50 mL of water and 35 mL of methylene chloride and shake vigorously. Filter the methylene chloride layer (no washing is necessary) and evaporate. Obtain a chromatogram of the resultant mixed esters as before and calculate their retention relative to triacetin. Identify from Table 1.

9.3 Since fatty acid methyl esters are eluted, it may sometimes be possible to identify the drying oil present in the sample, but a more precise method, Test Method D 2245, based on quantitative calculation of the fatty acid composition is recommended.

10. Precision and Bias

10.1 No statement is made about either the precision or bias since the results of this test method are qualitative rather than quantitative.

11. Keywords

11.1 alkyd resins; carboxylic acids; gas chromatographic; methylation; monomers; polyester; transesterification