



Designation: D 3168 – 85 (Reapproved 1999)

Standard Practice for Qualitative Identification of Polymers in Emulsion Paints¹

This standard is issued under the fixed designation D 3168; 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.

1. Scope

1.1 This practice describes a procedure for the qualitative identification in emulsion paints of most types of polymers present as major components of the paint vehicle. Limitations are discussed in Sections 5 and 10.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 16 Terminology for Paint, Related Coatings, Materials, and Applications²

D 1193 Specification for Reagent Water³

D 2621 Test Method for Infrared Identification of Vehicle Solids from Solvent-Reducible Paints²

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers⁴

3. Terminology

3.1 *Definitions*—For definitions of terms, refer to Terminology D 16.

4. Summary of Practice

4.1 The vehicle is extracted from the dried paint and after filtering is cast on a salt plate. The infrared spectrum is obtained and compared with reference spectra for identification of major components.

4.2 The paint is applied to a filament and pyrolyzed to depolymerize the vehicle. An internal standard is added and the

pyrolyzate is separated into its components by gas-liquid chromatography. Monomers are identified by comparison of relative retention times.

5. Significance and Use

5.1 Identification of specific acrylic polymers in emulsion paints is often difficult or impossible by infrared alone. This is particularly true when the acrylic is present in a small amount as a comonomer with vinyl acetate, or when blended with alkyds or other ester systems. If identification of an acrylic component is required in such a system, it may often be accomplished by gas-liquid chromatographic analysis of the pyrolyzed paint film. The presence of a number of other polymers may often also be confirmed by pyrolysis since they produce characteristic and reproducible pyrograms.

5.2 The pyrograms obtained from unknown samples vary in complexity according to the sample composition. It is necessary to establish the presence or absence of as many components as possible from a study of the infrared spectra obtained in the first part of this practice. The gas-liquid chromatography results may then be used to help identify any unknown components present and to confirm identifications made by infrared.

6. Interferences

6.1 Dibutyl maleate and dibutyl fumarate monomers are not successfully recovered by this procedure. If their presence is suspected as comonomer in a vinyl acetate copolymer system, *n*-butyl alcohol should be found in the pyrolyzate. This evidence, together with the absence of butyl acrylate or butyl methacrylate monomer peaks, is an indirect indication of the presence of one or both of these monomers.

6.2 The presence of relatively low quantities of copolymerized acids may not be successfully established by this procedure, due to some unavoidable decomposition of acrylate and methacrylate esters to acrylic or methacrylic acid and the corresponding alcohols during the pyrolysis. The infrared spectrum and an acid number determination, both run on the polymer solids, may usually be relied upon to establish the presence or absence of acid groups in the polymer.

¹ This practice is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials.

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² *Annual Book of ASTM Standards*, Vol 06.01.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

6.3 In the case where the polymer being analyzed is simple (such as a vinyl acetate-alkyl ester copolymer, or a single acrylate-methacrylate copolymer), it might be advantageous to examine the total pyrolyzate directly by infrared (as a solution in carbon disulfide).

7. Apparatus

7.1 *Spectrophotometer*, recording, double-beam, infrared, with a range from at least 2.5 μm to 15 μm and a spectral resolution of at least 0.04 μm over that range. For checking the performance of the infrared spectrophotometer, see Practice E 275.

7.2 *Cell Mount*, demountable.

7.3 *Halide Salt Crystals*, for use with demountable cell mount.

7.4 *Oven*, gravity or forced-draft, maintained at $105 \pm 2^\circ\text{C}$.

7.5 *Linear Programmed Temperature Gas Chromatograph*, equipped with a thermal conductivity detector.

7.6 *Pyrolysis Accessory*—Any suitable apparatus for achieving pyrolysis external to the chromatograph, that results in the recovery of sufficient pyrolyzate for identification purposes. The apparatus described in the Annex has been found to meet these requirements.

7.7 *Gas Chromatographic Column*, 10 ft (3 m) in length, $\frac{1}{4}$ in. (6.4 mm) in outside diameter copper tubing packed with 10 % silicone resin⁵ on 80 to 100-mesh acid-washed, dimethyl-dichlorosilane treated calcined diatomaceous earth.⁶

7.8 *Steam Bath or Low-Temperature Hot Plate*.

7.9 *Flask*, small Dewar.

8. Reagents

8.1 *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.⁷ 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.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

⁵ The sole source of supply of silicone resin SE-30, known to the committee at this time is General Electric Co. 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.

⁶ The sole source of supply of Chromosorb W, known to the committee at this time is Manville Sales Corp., Filtration and Minerals, 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.

⁷ *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.

8.3 *Extraction Solvent Mixture*—Equal volumes of *o*-dichlorobenzene, dimethylformamide, and tetrahydrofuran.

8.4 *Liquid Nitrogen*.

8.5 *Petroleum Ether* (30 to 60°C boiling range) or heptane.

9. Procedure—Infrared Analysis

9.1 Transfer 1 to 2 g of emulsion paint to a 100-mL borosilicate glass beaker. Add approximately 2 mL of water and swirl or use a clean glass rod to spread the paint uniformly over the bottom of the beaker.

9.2 Place the beaker in an oven at 105 to $\pm 2^\circ\text{C}$ for at least 2 h, breaking up any skins that form so that complete drying is ensured.

9.3 Add 50 mL of water, cover with a watchglass, and place on a steam bath or low-temperature hotplate for 1 h. This process removes emulsifiers, protective colloids, and other water-soluble components that might interfere with interpretation of the infrared spectrum. Decant off the clear water layer and discard. If the addition of the distilled water to the dried paint film produces a milky dispersion, the drying step in 9.2 was not complete and should be repeated.

NOTE 1—If there is an interest in characterization of the emulsifier system used, the water should be filtered through a fine-texture filter paper and taken to dryness. The solids may then be examined by infrared.

9.4 Dry for 15 to 20 min in an oven at 105 to $\pm 2^\circ\text{C}$. Add 50 mL of petroleum ether or heptane, cover with a watchglass, and bring to a slow boil for approximately 5 min. This process removes most emulsified plasticizers, oils, and other water insoluble, nonpolymeric organic materials, which might also interfere with the interpretation of the infrared spectrum. Decant off the solvent and discard.

NOTE 2—If there is an interest in characterizing the water-insoluble petroleum ether-soluble fraction, it should also be filtered through fine-texture paper, taken to dryness, and examined by infrared.

9.5 Add 10 mL of the extraction solvent mixture (8.3) and place on a steam bath or low-temperature hotplate for approximately 1 h. Filter, while still hot, through a fine-texture filter paper. If the polymer solution is viscous, it may be diluted further with extraction solvent mixture and warmed prior to filtration. Alternatively, the pigment may be removed from the polymer solution by centrifuging. Evaporate the solution on the steam bath or hotplate to a volume of 1 mL or less.

9.6 Place the concentrated polymer solution on a halide salt crystal and spread to form a uniform film. The thickness of the film should be such that when the infrared spectrum is recorded, the transmittance of the strongest band falls between 5 and 15 %. Dry the film in an oven at $105 \pm 2^\circ\text{C}$ for 1 h and cool in a desiccator.

9.7 Record the infrared spectrum from 2.5 to 15 μm so that a spectral resolution of 0.04 μm is maintained throughout that range. (Methods for achieving this resolution will vary according to the directions of the manufacturer of the instrument used.)

9.8 Compare the spectrum obtained with reference spectra prepared in a similar manner from emulsion paints of known