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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Guide for Determining Constituents Classified as Hazardous Contained in Protective Coatings[1]

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1. Scope

1.1 This guide applies to liquid protective coatings, related products, and their dried films. It is a guide for the selection of analytical procedures for the determination of the presence and quantity of selected materials that may present potential physiological hazards.

1.2 Various levels of government have established laws and regulations that limit the quantity or prohibit the presence of certain materials classified as hazardous in protective coatings. Materials subject to such regulations are within the scope of this guide.

1.3 A hazardous material within the scope of this guide is one that exhibits harmful physiological effects through ingestion, inhalation, absorption, or skin or eye contact. Hazards associated with combustion are not within its scope.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 49 Test Methods of Chemical Analysis of Red Lead[2]
D 126 Test Methods for Analysis of Yellow, Orange, and Green Pigments Containing Lead Chromate and Chromium Oxide Green[2]
D 215 Practice for Chemical Analysis of White Linseed Oil Paints[3]
D 283 Test Methods of Chemical Analysis of Cuprous Oxide and Copper Pigments[2]
D 444 Test Methods for Chemical Analysis of Zinc Yellow Pigment (Zinc Chromate Yellow)[2]
D 564 Test Methods for Liquid Paint Driers[3]
D 715 Test Methods for Analysis of Barium Sulfate Pigment[2]
D 1301 Test Methods for Chemical Analysis of White Lead Pigments[2]
D 1844 Test Methods for Chemical Analysis of Basic Lead Silicochromate[2]
D 1845 Test Methods for Chemical Analysis of Strontium Chromate Pigment[2]
D 2348 Test Method for Arsenic in Paint[3]
D 2349 Test Method of Qualitative Determination of Nature of Thinner in Solvent-Reducible Paints[3]
D 2350 Test Method for Antimony Oxide in White Pigment Separated From Solvent-Reducible Paints[3]
D 2371 Test Method for Pigment Content of Solvent-Reducible Paints[3]
D 2372 Practice for Separation of Vehicle From Solvent-Reducible Paints[3]
D 2374 Test Method for Lead in Paint Driers by EDTA Method[3]
D 2621 Test Method for Infrared Identification of Vehicle Solids From Solvent-Reducible Paints[3]
D 2698 Test Method for Determination of the Pigment Content of Solvent-Reducible Paints by High-Speed Centrifuging[3]
D 2742 Methods for Chemical Analysis of Tribasic Lead Phosphosilicate[4]
D 3257 Test Methods for Aromatics in Mineral Spirits by Gas Chromatography[5]
D 3271 Practice for Direct Injection of Solvent-Reducible Paints Into a Gas Chromatograph for Solvent Analysis[2]
D 3272 Practice for Vacuum Distillation of Solvents From Solvent-Reducible Paints For Analysis[3]
D 3280 Test Methods for Analysis of White Zinc Pigments[2]
D 3329 Test Method for Purity of Methyl Isobutyl Ketone by Gas Chromatography[5]
D 3335 Test Method for Low Concentrations of Lead, Cadmium, and Cobalt in Paint by Atomic Absorption Spectroscopy[3]
D 3432 Test Method for Free Toluene Diisocyanates in Urethane Prepolymers and Coating Solutions by Gas Chromatography[2]
D 3618 Test Method for Detection of Lead in Paint and Dried Paint Films[3]

[1] This guide is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.22 on Health and Safety.

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[2] *Annual Book of ASTM Standards,* Vol 06.03.

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

[4] Discontinued; see *1989 Annual Book of ASTM Standards,* Vol 06.02.

[5] *Annual Book of ASTM Standards,* Vol 06.04.

D 3624 Test Method for Low Concentrations of Mercury in Paint by Atomic Absorption Spectroscopy[3]
D 3717 Test Method for Low Concentrations of Antimony in Paint by Atomic Absorption Spectroscopy[3]
D 3718 Test Method for Low Concentrations of Chromium in Paint by Atomic Absorption Spectroscopy[3]
E 202 Test Methods for Analysis of Ethylene Glycols and Propylene Glycols[6]
E 260 Practice for Packed Column Gas Chromatography[7]

2.2 *ANSI Standard:*

Z66.1 Specification for Paints and Coatings Accessible to Children to Minimize Dry Film Toxicity[8]

2.3 *Federal Standards:*[9]

U.S. Federal Test Method Standard No. 141:
4021.1 Pigment Content (Ordinary Centrifuge)
4032 Vehicle Isolation (Super Centrifuge)
7041 Analysis of Basic Carbonate White Lead Pigment
7051 Analysis of Basic Sulfate White Lead Pigment
7071 Red Lead Pigments
7106 Analysis of Antimony Oxide Pigment
7111 Analysis of Chrome Green Pigment
7131 Analysis of Chrome Yellow and Chrome Orange Pigments
7135 Analysis of Cadmium Pigment
7231 Metal Content of Driers
7271 Analysis of Pigments Extracted from Chrome Yellow and Chrome Orange Paints
7281 Analysis of Pigment Extracted from Chrome Green Paints

2.4 *Canadian Standards Association Standards:*[10]

CAN2-1.500 Method of Test for Toxic Trace Elements in Protective Coatings:
1-GP-500.1 Determination of Lead in Low Concentration
1-GP-500.2 Determination of Leachable Cadmium in Low Concentration
1-GP-500.3 Determination of Leachable Barium in Low Concentration
1-GP-500.4 Determination of Leachable Antimony in Low Concentration
1-GP-500.5 Determination of Leachable Selenium in Low Concentration
1-GP-500.6 Determination of Leachable Mercury in Low Concentration

3. Summary of Guide

3.1 This guide covers each material separately, discussing the methods available, the advantages and drawbacks of each, including the range, the equipment needed, and when information is available, the precision. Methods discussed are:

3.1.1 ASTM methods adopted by Committee D-1,

3.1.2 Other ASTM methods believed to be applicable to paint and related products,

3.1.3 Methods adopted as standard by other scientific and technical or governmental organizations, and

3.1.4 Widely used methods reported in the literature.

4. Significance and Use

4.1 Protective coatings and related products containing materials classified as hazardous may be regulated or controlled in various ways as follows:

4.1.1 *Precautionary Labeling Required*:

4.1.1.1 Under the U.S. Federal Hazardous Substances Act and corresponding state laws, "consumer" paint products must carry precautionary labeling as specified in the laws, or implementing regulations, or both.

NOTE 1—Under the Federal Hazardous Substances Act lead, ethylene and diethylene glycol, petroleum distillates, and turpentine are classed as hazardous through ingestion. Methyl alcohol, benzene, xylene, and toluene are classed as hazardous through ingestion and inhalation. Ethylene diamine, diethylene triamine, and diglycidyl ethers are classed as strong sensitizers.

4.1.1.2 In certain states, coatings and related materials packaged and sold for industrial application are subject to precautionary labeling laws and regulations.

4.1.2 *Use Prohibited in Certain Areas*:

4.1.2.1 Under the U.S. Federal Hazardous Substances Act and the Lead Paint Poisoning Prevention Act, and the laws of certain states and municipalities, coatings and related products containing more than a specified quantity of lead are banned for use in and around a household or other areas where children might be exposed.

4.1.2.2 Under certain local ordinances, coatings and related products containing more than a specified quantity of "other toxic heavy metals" are also subject to control.

NOTE 2—The amount of lead, antimony, arsenic, cadmium, mercury, selenium, and soluble barium that may be present in coatings for use on children's furniture and toys and areas that might be chewed by children is restricted under ANSI Standard Z 66.1 and under various U.S. municipal ordinances.

4.1.3 *Subject to Approval for Certain Uses*:

4.1.3.1 The U.S. Food and Drug Administration permits only approved ingredients to be used in coatings for food and beverage containers or processing equipment that comes into contact with the product.

4.1.3.2 The U.S. Department of Agriculture authorizes for use on structural surfaces in federally inspected meat and poultry processing plants only coatings accepted as nonhazardous.

4.1.3.3 The U.S. Environmental Protection Agency regulations control the distribution of paints that claim special fungicidal or pesticidal characteristics, and the use in shipbottom paints of materials that have the potential for harming the aquatic environment.

NOTE 3—Cuprous oxide, bis(tributyltin oxide), arsenic, and mercury are classed as hazardous materials by the U.S. Environmental Protection Agency when used in antifouling paints.

4.1.4 *Environmental Controls During Use and Corrective Measures in the Event of Accidents or Misuse Required*:

[6] *Annual Book of ASTM Standards*, Vol 15.05.
[7] *Annual Book of ASTM Standards*, Vol 14.02.
[8] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.
[9] Available from Standardization Documents Order Desk, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094.
[10] Available from Canadian Standards Association, 178 Rexdale Blvd., Rexdale, Ontario, Canada M9W 1R3.

4.1.4.1 Under U.S. Occupational Safety and Health Act regulations, airborne concentrations of certain vapors, fumes, and dusts are limited in the work-place atmosphere. Coatings, when applied, may emit solvent vapors that are subject to these limits.

4.1.4.2 Under Occupational Safety and Health Act regulations, skin or eye contact with liquid paint containing specified potentially hazardous materials must be avoided and protective apparel may be required. In the event of hazardous skin or eye contact, corrective action to ameliorate physiological injury is prescribed.

NOTE 4—Over 400 materials have been classified by the Occupational Safety and Health Administration as being potentially hazardous. Of this number approximately 80 may be found in varying amounts as components of coatings and related products.[11]

4.1.4.3 To achieve air quality standards under the Clean Air Act, regulations of various states and regions control emissions of volatile organic compounds resulting from the application of surface coatings.

5. Pigment, Vehicle Separations (Centrifugal)

5.1 The methods listed in this section cover centrifugal separation of pigment from vehicle. The pigment may then be analyzed as described in subsequent sections. More recent methods utilizing analysis of the whole paint by atomic absorption spectroscopy may be preferred due to greater speed and accuracy.

5.2 Separation of the vehicle from the pigment is generally the first step in coatings analysis. There are three ASTM methods covering the use of centrifuges:

5.2.1 Test Method D 2371 describes the use of the normal laboratory centrifuge that develops 2000 *g*. It should be used where a quantitative determination of the amount of pigment in the coating is required.

5.2.2 Practice D 2372 covers use of a high-speed centrifuge that develops 10 000 *g* and is used when analysis of the vehicle is of main interest.

5.2.3 Test Method D 2698 covers use of a centrifuge that develops at least 32 000 *g*. Determination of the pigment content is the main objective of the method although the separated pigment may be solvent-extracted to remove residual vehicle.

NOTE 5—Centrifuge methods do not generally give good separations of pigments that bleed (partially dissolve) or have low densities and fine particle sizes (such as carbon black).

5.3 U.S. Federal Test Method Standard 141 contains two centrifuge methods. Federal Method 4021.1 is similar to Test Method D 2371 except that additional extraction mixtures are listed for difficult pigments and for cellulosic and vinyl lacquers. Federal Method 4032 is similar to Method D 2698 but has the same extraction solvents as in Federal Method 4021.1.

6. Solvent Separation

6.1 Practice D 3272 covers a vacuum distillation procedure that separates the solvents from the nonvolatile portion of paints so they may be analyzed.

6.2 Practice D 3271 covers analysis of the solvents by injection of the liquid coating into a gas chromatograph. Prior separation is not required.

ANALYTICAL METHODS

7. Heavy Metals Analysis, ASTM Methods

7.1 Methods for the analysis of pigments apply to dry pigment or to pigment separated from the vehicle in accordance with Section 5.

7.2 *Lead*:

7.2.1 *Pigment Analysis*—In all the following methods except for Methods D 2742, the concentration range for which the method is applicable is not given.

7.2.1.1 Test Methods D 49 cover procedures for the chemical analysis of dry red lead having the approximate formula Pb_3O_4 (probably $PbO_2 \cdot 2PbO$). Total lead is determined gravimetrically as lead sulfate.

7.2.1.2 Test Methods D 126—Total lead is determined gravimetrically as lead sulfate. The comparable Fed. Test Methods Std. 141 methods are 7271 and 7281.

7.2.1.3 Practice D 215—Two methods are described for the gravimetric determination of total lead, one as the sulfate and the other as the chromate. The choice of method may be dictated by potential interferences discussed in the text.

7.2.1.4 Test Methods D 1301 cover procedures for the chemical analysis of basic carbonate white lead and basic sulfate white lead. Total lead is determined gravimetrically as lead chromate. The comparable Fed. Test Method Std. 141 method is 7041.

7.2.1.5 Test Methods D 1844—Total lead is determined gravimetrically as lead chromate.

7.2.1.6 Methods D 2742—Silicon is removed by filtration and total lead determined gravimetrically as lead sulfate. The methods are designed for the analysis of essentially pure pigment.

7.2.1.7 Methods D 3280 cover procedures for the analysis of white zinc pigments, including leaded zinc oxide. Total lead is determined gravimetrically as lead sulfate.

7.2.2 *Analysis of Liquid Material or Dried Film*:

7.2.2.1 Test Methods D 564 cover the determination of percent lead in liquid driers (see Section 9). Total lead is determined gravimetrically as lead sulfate. The comparable Fed. Test Method Std. No. 141 method is 7231.

7.2.2.2 Test Method D 2374 covers a titrimetric determination of lead in paint driers that can be dissolved in a suitable solvent and utilizes excess EDTA (ethylene diamine tetraacetic acid) to react with lead and cupric sulfate to back titrate. The drier is dissolved in glacial acetic acid, diluted with isopropyl alcohol and water, and treated with an excess of standard EDTA solution. The excess is titrated with standard cupric sulfate solution using an indicator. The method includes a precision statement but the applicable concentration range is not given.

7.2.2.3 Test Method D 3335 covers the determination of lead contents between 0.01 and 5 % present in the solids of liquid coatings or in dried films. A specimen of liquid paint or dried film is prepared for analysis by dry ashing. The lead

[11] Occupational Safety and Health Reporter, Section 1910.1000 Table Z.1.

content of an acid extract of the ash is determined by atomic absorption spectroscopy. The precision statement is based on a relative scale.

7.2.2.4 Test Method D 3618 is intended as a screening test to determine if a sample of paint solids contains more than 0.5 % lead. The test will barely detect the presence of 0.4 % and will give a definite test at the 0.5 % level. The specimen is dry ashed and extracted. Lead present is oxidized to lead peroxide and spotted with "tetrabase" to develop a blue coloration. Higher or lower concentrations may be detected by this test method by making appropriate changes in the specimen size and reagent quantities.

7.3 *Chromium*:

7.3.1 *Pigment Analysis*:

7.3.1.1 *Test Methods D 126*—In these test methods the chromium content of pigments is only calculated as Cr_2O_3 for chromium oxide green. For chrome oranges, yellows, and greens the chromium is calculated as lead chromate.

7.3.1.2 Test Methods D 444 cover procedures for the chemical analysis of the pigment known commercially as" zinc yellow" or "zinc chromate yellow." Total chromium in the pigment is determined by titration using either the dichromate method or the thiosulfate method and calculated as CrO_3.

7.3.1.3 *Test Methods D 1844*—Total chromium in the pigment is determined as chromium trioxide by titration using the thiosulfate method.

7.3.1.4 *Test Methods D 1845*—Total chromium in the pigment is determined as chromium trioxide by titration using the thiosulfate method.

7.3.2 *Analysis of Liquid Paint or Dried Film*:

7.3.2.1 Test Method D 3718 covers the determination of chromium or chromium compounds (including chromium oxide) when present in the solids of liquid coatings or in dried films in the concentration range from 0.005 to 1.0 % (50 to 10 000 ppm) expressed as chromium. A specimen of liquid paint or dried film is prepared for analysis by dry ashing. A weighed quantity of the ash is digested with potassium permanganate and sulfuric acid. Chromium is determined on the filtered digestion mixture by atomic absorption spectroscopy.

7.4 *Barium*:

7.4.1 *Pigment Analysis*:

7.4.1.1 *Practices D 215*—Soluble barium is determined gravimetrically as the sulfate.

7.4.1.2 *Test Methods D 715*—Applicablility to mixed pigments when barium is a minor component is not indicated.

7.4.1.3 Methods D 3280 cover procedures for the analysis of white zinc pigments. Determination of total barium sulfate content is described in Section 20 of Methods D 3280.

7.4.2 *Analysis of Liquid Paint or Dried Film*—Current legislation restricts the quantity of "soluble" barium in coatings used in areas accessible to children, but the conditions of solubility are not usually defined. There is no ASTM method for soluble barium; see Section 10.

7.5 *Mercury*:

7.5.1 *Analysis of Liquid Paint or Dried Film*—Test Method D 3624 covers the determination of mercury contents between 10 and 1000 ppm in liquid coatings and dried films. The specimen of whole paint, paint vehicle, or dried film is digested using sulfuric and nitric acids, and the concentration of mercury determined using cold-vapor atomic absorption.

7.6 *Arsenic*:

7.6.1 *Analysis of Liquid Paint or Dried Film*—Test Method D 2348 covers the determination of less than 0.5 % arsenic in liquid coatings or dried films. Whole paint or dried film is digested in nitric and sulfuric acid. Sodium chloride is added and the arsenic trichloride distilled. Total arsenic is determined by titration with potassium bromate.

7.7 *Antimony*:

7.7.1 *Pigment Analysis: Test Method D 2350*—Total antimony is calculated from the antimony oxide content determined by titration with potassium permanganate. The concentration range for which the method is applicable is not given. The comparable Federal Method is 7106.

7.7.2 *Analysis of Liquid Paint or Dried Film*—Test Method D 3717 covers the determination of antimony contents between 50 and 200 ppm present in the solids of liquid coatings in dried films. The specimen of liquid paint or dried film is prepared for analysis by dry ashing at 500°C followed by refluxing with hydrochloric acid and stannous chloride. The antimony content of the acid extract is determined by atomic absorption spectroscopy.

7.8 *Cadmium*:

7.8.1 *Analysis of Whole Paint or Dried Film*—Test Method D 3335 covers the determination of cadmium contents between 50 and 150 ppm present in the solids of liquid coatings or in dried films. The sample of liquid paint or dried film is prepared for analysis by dry ashing. The content of cadmium is determined by atomic absorption spectroscopy.

8. Other Regulated Metallic Components

8.1 *Copper*:

8.1.1 *Pigment Analysis*—Methods for the analysis of the pigment portion of the coating after separation.

8.1.2 Methods D 283 cover analysis for total copper in copper-based pigments.

9. U.S. Federal Test Method Standard No. 141

9.1 *Lead*:

9.1.1 Method 7041 is comparable to Test Methods D 1301.

9.1.2 Method 7051 is comparable to Test Methods D 1301.

9.1.3 Method 7071.1 is for the quantitative measure of red lead in paint pigments.

9.1.4 Method 7111 is comparable to Test Methods D 126.

9.1.5 Method 7131 is comparable to Test Methods D 126.

9.1.6 Method 7231 is comparable to Test Methods D 564.

9.1.7 Method 7271 is comparable to Test Methods D 126.

9.1.8 Method 7281 is comparable to Test Methods D 126.

9.2 *Antimony*:

9.2.1 Method 7106 is comparable to Test Method D 2350.

9.3 *Cadmium*:

9.3.1 Method 7135.

10. Other Analytical Methods for Materials Classed as Hazardous Within the Scope of This Practice

10.1 National Standard of Canada CAN2-1.500 describes test methods for determining toxic elements in low concentrations in protective coatings, employing wet chemical and

atomic absorption and visible-ultraviolet spectrophotometric techniques. Determination of leachable elements are made on a dilute hydrochloric acid extract of the dried film that has first been ground to a specific fineness.

10.1.1 1-GP-500.1 is used for determining total lead in liquid and applied coatings by atomic absorption spectroscopy.

10.1.2 1-GP-500.2 is used for determining soluble cadmium in applied coatings by atomic absorption spectroscopy.

10.1.3 1-GP-500.3 is used for determining soluble barium in applied coatings by atomic absorption spectroscopy.

10.1.4 1-GP-500.4 is used for determining soluble antimony in applied coatings by visible-ultraviolet spectroscopy.

10.1.5 1-GP-500.5 is used for determining soluble selenium in applied coatings by visible-ultraviolet spectroscopy.

10.1.6 1-GP-500.6 is used for the detection of, and the quantitative determination of, soluble mercury in applied coatings by visible-ultraviolet spectroscopy.

11. Nonvolatile Vehicle Components, ASTM Methods

11.1 Test Method D 2621 covers the qualitative characterization or identification of separated paint vehicle solids by infrared spectroscopy within the limitations of this procedure.

12. Volatile Components

12.1 The volatile components of protective coatings must be identified to determine compliance with regulations covering labeling, work place concentrations, and air quality standards.

12.2 Gas chromatography is widely used for this purpose. However, owing to the empirical nature of the technique, chemical or instrumental confirmatory tests may be necessary as supplementary procedures.

12.3 Identification of the components of an unknown solvent blend would in many cases be expedited by means of a combination of gas chromatography and infrared spectroscopy or mass spectrometry.

12.4 Interconnected chromatographic, infrared analyzers are available that separate multicomponent mixtures into their pure components for infrared analysis.

12.5 Analysis of the volatile component of whole paint has been covered in Section 6.

12.6 The following ASTM methods cover the analysis of some of the volatile components of protective coatings currently subject to regulation as potentially hazardous materials:

12.6.1 Test Method D 2349 covers the determination of the nature of thinner in solvent-reducible house paints containing only hydrocarbon solvents.

12.6.2 Test Method D 3432 covers low molecular weight urethane products containing (*a*) 0.1 to 1.0 % and (*b*) 1.0 to 10 % of free toluene diisocyanate (TDI) content.

12.6.3 Test Methods D 3257 cover the determination of ethylbenzene and total eight-carbon (C_8) and heavier aromatics in the concentration range from 0.1 to 30 % in mineral spirits having a distillation range from 300 to 410°F (150 to 210°C). Oxygenated compounds, if present, may interfere and cause erroneous results.

12.6.4 Method D 3329 covers the determination of the purity of methyl isobutyl ketone by gas chromatography.

12.6.5 *Test Methods E 202*—See Sections 26 to 35 (Gas Chromatographic Techniques).

12.6.6 Practice E 260.

13. Keywords

13.1 antimony; aromatics; barium; cadmium; Canadian methods; chromium; copper; government regulations; hazardous substances; heavy metals; lead; mercury; pigments; selenium; solvents; zinc