



Designation: D 215 – 91 (Reapproved 2002)

Standard Practice for the Chemical Analysis of White Linseed Oil Paints¹

This standard is issued under the fixed designation D 215; 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 covers the chemical analysis of the usual white linseed oil paints. The methods included are listed in Table 1.

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 34 Guide for Chemical Analysis of White Pigments²
- D 50 Test Methods of Chemical Analysis of Yellow, Orange, Red, and Brown Pigments Containing Iron and Manganese²
- D 280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments²
- D 717 Test Methods for Analysis of Magnesium Silicate Pigment²
- D 1193 Specification for Reagent Water³
- D 1208 Test Methods for Common Properties of Certain Pigments²
- D 1301 Test Methods for Chemical Analysis of White Lead Pigments²
- D 1394 Test Methods for Chemical Analysis of White Titanium Pigments²
- D 1397 Test Method for Unsaponifiable Matter in Alkyd Resins and Resin Solutions²
- D 1398 Test Method for Fatty Acid Content of Alkyd Resins and Alkyd Resin Solutions²
- D 1469 Test Method for Total Rosin Acids Content of Coating Vehicles²
- D 1542 Test Method for Qualitative Detection of Rosin in Varnishes²
- D 1959 Test Method for Iodine Value of Drying Oils and Fatty Acids²

TABLE 1 List of Test Methods

| Test Method | Section | ASTM Method |
|--|---------|-------------|
| Preparation of Sample | 4 | ... |
| Water | 5 | D 1208 |
| Volatile Thinner | 6 | D 2369 |
| Nature of Thinner | 7 | D 2349 |
| Percentage of Pigment | 8 | D 2371 |
| Percentage of Nonvolatile Vehicle | 9 | ... |
| Separation of Vehicle | 10 | D 2372 |
| Unsaponifiable Matter | 11 | D 1397 |
| Fatty Acids | 12 | D 1398 |
| Iodine Number of Fatty Acids | 13 | D 1959 |
| Resin | 14 | D 1542 |
| Qualitative Analysis, Single, Mixed, or Composite Pigments | 15 | ... |
| Quantitative Analysis, Single Pigment | 16 | D 34 |
| Quantitative Analysis, Mixed or Composite Pigments: | | |
| Moisture and Other Volatile Matter | 17 | D 280 |
| Loss on Ignition | 18 | D 1208 |
| Insoluble Matter | 19 | ... |
| Total Lead (Antimony) | 20 | ... |
| Antimony Oxide | 21 | D 2350 |
| Soluble Barium | 22 | ... |
| Aluminum Oxide | 23 | ... |
| Total Zinc | 24 | ... |
| Soluble Calcium | 25 | ... |
| Soluble Magnesium | 26 | ... |
| Carbon Dioxide | 27 | D 1301 |
| Total Soluble Sulfur Compounds | 28 | D 34 |
| Soluble Sulfate | 29 | D 50 |
| Sulfide Sulfur | 30 | D 2351 |
| Sulfur Dioxide | 31 | D 2352 |
| Matter Soluble in Water | 32 | D 1208 |

- D 2349 Test Method for Qualitative Determination of Nature of Solvent Composition in Solvent-Reducible Paints⁴
- D 2350 Test Method for Antimony Oxide in White Pigment Separated from Solvent-Reducible Paints⁴
- D 2351 Test Method for Sulfide in White Pigment Separated from Solvent-Reducible Paints⁴
- D 2352 Test Method for Sulfur Dioxide in White Pigment Separated from Solvent-Reducible Paints⁴
- D 2369 Test Method for Volatile Content of Coatings⁴
- D 2371 Test Method for Pigment Content of Solvent-Reducible Paints⁴
- D 2372 Practice for of Separation of Vehicle from Solvent-Reducible Paints⁴

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

Current edition approved May 15, 1991. Published July 1991. Originally published as D 215 – 25 T. Last previous edition D 215 – 73 (1979)^{ε1}.

² Annual Book of ASTM Standards, Vol 06.03.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 06.01.



3. Purity of Reagents

3.1 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.

3.2 Unless otherwise indicated, references to water shall be understood to mean Type II reagent grade water conforming to Specification D 1193.

4. Hazards

4.1 *Ammonium Hydroxide* causes severe burns and may be fatal if swallowed. Read the appropriate Material Safety Data Sheets (MSDS) before using.

4.2 *Hydrochloric and Sulfuric Acids* cause severe burns and may be fatal if swallowed. Read the appropriate MSDS before using.

4.3 *Acetic Acid* causes severe burns and may be fatal if swallowed. Read the appropriate MSDS before using.

4.4 *Nitric Acid* causes burns and may be fatal if swallowed. Vapor is extremely hazardous and may cause nitrogen oxide poisoning. Read the appropriate MSDS before using.

4.5 *Toluene* is flammable. Vapors are harmful. Use with adequate ventilation. Read the appropriate MSDS before using.

4.6 *Hydrogen Sulfide* is both an irritant and an asphyxiant. Read the appropriate MSDS before using.

4.7 *Ammonium Sulfide* evolves hydrogen sulfide on contact with acid or acid fumes. See 4.6. Read the appropriate MSDS before using.

4.8 *Barium Chloride*—Soluble barium salts are poisonous when taken by mouth. Read the appropriate MSDS before using.

5. Preparation of Sample

5.1 On receipt of a sample, make a record of the label noting especially the brand, the name of the manufacturer, and any statement as to the composition of the paint and the net contents. Weigh the unbroken package, open, note odor and condition of the contents, pour into a clean container, and mix thoroughly by pouring from one container to the other, finally leaving the well-mixed sample in the second container which shall be tightly closed. The well-mixed sample shall be used at once for the analysis. The original can and cover may be cleaned with a suitable solvent, wiped dry, and then weighed. This weight subtracted from the original weight will give the net weight of the contents. If desired, the specific gravity of the paint may be determined, the weight per gallon calculated, and the volume of paint and the capacity of the container may be measured.

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.

ANALYSIS OF PAINT

6. Water

6.1 Determine water in accordance with Test Methods D 1208.

7. Volatile Thinner

7.1 Determine the volatile matter in accordance with Test Method D 2369. Calculate the loss in weight as the percentage of water and volatile thinner. Subtract from this the percentage of water as determined in accordance with Section 6. Report the remainder as percent volatile thinner.

8. Nature of Thinner

8.1 Determine the nature of the thinner in accordance with Test Method D 2349.

9. Percentage of Pigment

9.1 Determine the percentage of pigment in accordance with Test Method D 2371. Preserve the pigment as prepared in a stoppered bottle for use in Sections 16 and 17.

10. Percentage of Nonvolatile Vehicle

10.1 Add together the percentages of water, volatile thinner, and pigment, and subtract the sum from 100. Report the remainder as nonvolatile vehicle.

TESTING NONVOLATILE VEHICLE

11. Separation of Vehicle

11.1 Separate the vehicle from the pigment in accordance with Test Method D 2372. Retain the vehicle so obtained for use in the unsaponifiable matter (see 12.1) and fatty acids (see 13.1) determinations.

12. Unsaponifiable Matter

12.1 Determine the unsaponifiable content of the vehicle in accordance with Test Method D 1398.

13. Fatty Acids

13.1 Determine the fatty acids in accordance with Test Method D 1398.

14. Iodine Number of Fatty Acids

14.1 Determine the iodine number of fatty acids (see 13.1) in accordance with Test Method D 1959.

NOTE 1—If appreciable amounts of rosin or of unsaponifiable matter are found to be absent in the vehicle of a paint, the iodine number of the fatty acids gives the best indication (though not proof) of the presence of linseed oil. An iodine number of less than 175 (Wijs) for the fatty acids is an indication that the nonvolatile vehicle was not pure linseed oil.

15. Rosin

15.1 Determine the presence of rosin in the fatty acids (see 13.1) in accordance with Test Method D 1542.

15.2 If desired, determine the amount of rosin quantitatively in accordance with Test Method D 1469.



ANALYSIS OF PIGMENT

Qualitative Analysis, Total Pigments—Single, Mixed, or Composite

16. Qualitative Analysis

16.1 Reagents:

16.1.1 *Acetic Acid*. (**Precaution**—See 4.3)

16.1.2 *Acid Ammonium Acetate Solution*—Mix 150 ml of acetic acid (8 + 2) 100 ml of water, and 95 ml of NH_4OH (sp gr 0.90).

16.1.3 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH). (**Precaution**—See 4.1)

16.1.4 *Ammonium Polysulfide*—Pass H_2S gas into 200 ml of NH_4OH (sp gr 0.90) in a bottle immersed in running water or in iced water until the gas is no longer absorbed; then add 200 mL of NH_4OH (sp gr 0.90) and dilute with water to 1 litre. Digest this solution with 25 g of flowers of sulfur for several hours and filter.

16.1.5 *Ammonium Sulfate* ($(\text{NH}_4)_2\text{SO}_4$).

16.1.6 *Barium Chloride* ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$). (**Precaution**—See 4.8)

16.1.7 *Hydrochloric Acid* (1 + 1)—Mix equal volumes of concentrated hydrochloric acid (HCl , sp gr 1.19) (**Precaution**—See 4.2) and water.

16.1.8 *Hydrogen Peroxide* (H_2O_2), 3%.

16.1.9 *Hydrogen Sulfide* (H_2S). (**Precaution**—See 4.6)

16.1.10 *Potassium Dichromate* ($\text{K}_2\text{Cr}_2\text{O}_7$).

16.1.11 *Potassium Ferrocyanide, Standard Solution*—Dissolve 22 g of pure potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) in water and dilute to 1 L. To standardize, transfer about 0.2 g (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400-mL beaker. Dissolve in 10 mL of HCl (sp gr 1.19) and 20 ml of water. Drop in a small piece of litmus paper, add NH_4OH until slightly alkaline, add HCl until just acid, and then 3 mL of HCl (sp gr 1.19). Dilute to about 250 mL with hot water and heat nearly to boiling. Run in the $\text{K}_4\text{Fe}(\text{CN})_6$ solution slowly from a buret, while stirring constantly, until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing 1 min. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of $\text{K}_4\text{Fe}(\text{CN})_6$ solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume, and acidity as obtained when the sample is titrated.

16.1.12 *Potassium Iodide* (KI).

16.1.13 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4). (**Precaution**—See 4.2)

16.1.14 *Sulfuric Acid* (1 + 19)—Carefully mix 1 volume of concentrated H_2SO_4 (sp gr 1.84) (**Precaution**—See 4.2) with 19 volumes of water.

16.2 Procedure:

16.2.1 The following qualitative analysis should be made and the quantitative scheme modified as required. Add acetic acid slowly to the pigment until all carbonate is decomposed (noting whether any H_2S is evolved), then add a large excess of acid ammonium acetate solution. Boil, filter, and test the filtrate for metals other than lead and zinc (especially calcium and

barium). The absence of calcium in this filtrate indicates that the extending pigments contain no calcium carbonate (CaCO_3) or calcium sulfate (CaSO_4); the absence of barium indicates that the extending pigments contain no barium carbonate (BaCO_3).

NOTE 2—If the original sample contained BaCO_3 , and lead sulfate (PbSO_4), CaSO_4 , or other soluble sulfate, the soluble barium will form with the soluble sulfate a precipitate of BaSO_4 which will be determined as “insoluble matter.” If the sample contained strontium sulfate (SrSO_4) or strontium carbonate (SrCO_3), some SrSO_4 may be counted as BaSO_4 , some strontium will count as soluble barium, and some may be counted as calcium oxide (CaO). Strontium is not separated, as it probably will not be encountered, or will be present as an impurity in the barium and calcium compounds.

16.2.2 Wash the matter insoluble in acid ammonium acetate solution with another portion of this solution, and finally with hot water. This insoluble matter shall be dried, ignited, and tested for siliceous matter, BaSO_4 , and titanium compounds. To test for the latter, place a small amount of the insoluble matter, or of the original sample (about 0.5 g) in a 250-mL resistant glass beaker; add 20 mL of concentrated H_2SO_4 (sp gr 1.84) and 7 to 8 g of $(\text{NH}_4)_2\text{SO}_4$. Mix well, and boil for a few minutes. A residue denotes the presence of silica or siliceous matter. Cool the solution, dilute with 100 mL of water, heat to boiling, settle, filter, and wash with hot H_2SO_4 (1 + 19) until free from titanium. The residue may be tested for lead, barium, and silica.

16.2.3 Add H_2O_2 to a small portion of the filtrate; a clear yellow-orange color indicates the presence of titanium. Boil another portion of the filtrate with metallic tin or zinc; a pale blue to violet coloration indicates titanium.

16.2.4 Treat another portion (about 1 g) of the pigment with 20 ml of HCl (1 + 1) and note whether any H_2S is evolved; boil the solution for about 5 min, add about 25 ml of hot water, filter, and wash with hot water. Render a small portion of the filtrate alkaline with NH_4OH , acidify with HCl , and add a little BaCl_2 solution; a white precipitate (BaSO_4) indicates the presence of a soluble sulfate. To another portion of the filtrate add a little H_2SO_4 ; a white precipitate indicates the presence of lead, soluble barium, or both (some CaSO_4 may also separate). Filter, wash to remove free acid, and treat the precipitate with a few drops of KI solution; the formation of yellow lead iodide (PbI_2) indicates the presence of lead. The white precipitate may also be treated with H_2S water; the formation of black lead sulfide (PbS) indicates the presence of lead.

16.2.5 To another portion of the original filtrate (see 16.2.1) add NH_4OH until alkaline, render slightly acid with acetic acid, heat to boiling, and add a little $\text{K}_2\text{Cr}_2\text{O}_7$ solution; a yellow or orange-yellow precipitate indicates the presence of lead, soluble barium, or both. To another portion of the original filtrate add a few drops of $\text{K}_4\text{Fe}(\text{CN})_6$ solution; a white precipitate with a bluish tinge indicates the presence of zinc. Pass into the remaining portion of the original filtrate a current of H_2S for 5 to 10 min, add an equal volume of water, and pass H_2S into the solution for about 5 min. Filter and wash with H_2S water. Digest the precipitate with ammonium polysulfide, filter, acidify the filtrate with HCl , and warm; the presence of antimony is indicated by the separation of an orange-colored precipitate. The filtrate from the H_2S precipitate may be tested



for barium, calcium, and magnesium in the usual manner.

Quantitative Analysis, Single Pigment

17. Quantitative Analysis

17.1 If the sample is a single pigment, proceed in accordance with Guide D 34, for the particular pigment to be tested.

Quantitative Analysis, Mixed or Composite Pigments

18. Moisture and Other Volatile Matter

NOTE 3—On an extracted and dried pigment, this determination is of little value. If the original paint contained gypsum, a part of the combined water of the latter will be driven off in the drying of the extracted pigment and in the “moisture” determination.

18.1 Determine the moisture and other volatile matter in accordance with Test Methods D 280.

19. Loss on Ignition

NOTE 4—This determination may serve as a rough or approximate check in many cases on the carbon dioxide, water, etc.

19.1 Determine loss on ignition in accordance with Test Methods D 1208.

20. Insoluble Matter

20.1 Reagents:

20.1.1 Alcohol.

20.1.2 Hydrochloric Acid (sp gr 1.19)—Concentrated hydrochloric acid (HCl). (**Precaution**—See 4.2)

20.1.3 Hydrochloric Acid (1 + 1)—Mix equal volumes of concentrated HCl (sp gr 1.19) (**Precaution**—See 4.2) and water.

20.1.4 Sodium Carbonate (Na_2CO_3), anhydrous.

20.1.5 Sodium Carbonate (10 g/L)—Mix 10 g of Na_2CO_3 with water and dilute to 1 L.

20.1.6 Sulfuric Acid (1 + 4)—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) (**Precaution**—See 4.2) with 4 volumes of water.

20.2 Procedure:

20.2.1 Moisten 1 g of the pigment with a few drops of alcohol, cover, add 40 ml of HCl (1 + 1) and boil gently for 5 to 10 min. Wash the cover, evaporate to dryness, and heat at about 150°C for 30 min to 1 h to dehydrate the residue. Moisten the residue with 4 ml of concentrated HCl (sp gr 1.19), allow to stand a few minutes, dilute with 100 ml of hot water, boil a few minutes, filter hot through paper, and wash with hot water (until washings give no test for lead and chlorine).

20.2.2 Ignite the paper and residue in a platinum or porcelain crucible, cool, and weigh the total insoluble matter (Note 2). (The insoluble matter may be filtered off on a Gooch crucible, washed with hot water, dried at 105°C, cooled, and weighed; it shall then be ignited, cooled, and weighed, when it is desired to get the loss on ignition (combined water, organic matter, etc.) of the same, or if the insoluble matter is not to be further examined.) If the sample contains titanium pigment, practically all of the titanium dioxide (TiO_2) will be found in

the insoluble matter along with barium sulfate (BaSO_4) and siliceous matter. Should an examination of the insoluble matter be necessary, it is advisable to remove the TiO_2 before proceeding further. The TiO_2 may be removed (or determined on a separate portion) in accordance with Test Methods D 1394.

20.2.3 After removing the TiO_2 , the residue containing siliceous matter and BaSO_4 may be ignited to remove the filter. To determine BaSO_4 , mix the ignited insoluble matter with about ten times its weight of anhydrous Na_2CO_3 (grinding the mixture in an agate mortar if necessary) and fuse in a covered platinum crucible, heating about 1 h. Let cool, place the crucible and the cover in a 200-mL glazed porcelain casserole (Note 5), add about 100 mL of water, and heat until the mass is disintegrated. Filter on paper into a 300-mL glazed porcelain casserole (leaving the crucible and the cover in the original casserole) and wash the casserole and filter thoroughly with a hot solution of Na_2CO_3 (10 g/L). Place the casserole containing the crucible and cover under the funnel, pierce the filter with a glass rod, and wash the residue into the original casserole by means of a jet of hot water. Wash the paper with hot HCl (1 + 1) and then with hot water. Remove the crucible and the cover. Evaporate the HCl solution to dryness, and heat at about 150°C for 30 min to 1 h. Moisten the residue with about 10 mL of concentrated HCl (sp gr 1.19), dilute with 100 mL of hot water, boil a few minutes, filter hot through paper, and wash thoroughly with hot water. Dilute the filtrate to a volume of 300 mL, bring to boiling, and add, dropwise, 5 mL of H_2SO_4 (1 + 4). Allow to stand in a warm place for 1 h or so, filter on a weighed Gooch crucible, wash with hot water, ignite, cool, and weigh as BaSO_4 . Subtract the sum of the percentages of BaSO_4 and TiO_2 from the percentage of total insoluble matter and report the result as the percentage of insoluble siliceous matter (Note 6).

NOTE 5—A casserole is preferable to a beaker, as silica is dissolved from glass when in long contact with a strong sodium carbonate solution.

NOTE 6—Any soluble aluminum oxide (Al_2O_3) (or iron oxide (Fe_2O_3)) and in most cases magnesium oxide (MgO), and sometimes some calcium oxide (CaO), come from the siliceous pigment used. Magnesium oxide generally denotes the presence of asbestine.

20.2.4 To determine silica, acidify the filtrate from the barium carbonate (BaCO_3) filtration (20.2.3) with HCl, boil to expel the CO_2 , evaporate to dryness, bake to dehydrate the silica, moisten with HCl, dilute with 100 mL of hot water, and boil and filter through the same paper as was used to recover silica from the BaCO_3 portion. Wash thoroughly with hot water and proceed in accordance with Test Methods D 717.

20.2.5 If it is desired to look for magnesium, combine the filtrate obtained in accordance with 20.2.4 with the filtrate from the final BaSO_4 separation (20.2.3) and test for Al_2O_3 and MgO in the usual way. To recover MgO that may have dissolved in the procedure for the elimination of the TiO_2 , make the filtrate containing the TiO_2 just alkaline with NH_4OH , bring to boiling, filter, and wash. The filtrate may be tested for MgO. Any Al_2O_3 present will be precipitated along with the TiO_2 . To recover this, ignite and weigh as TiO_2 and Al_2O_3 . Deduct for TiO_2 present in the sample; the difference is Al_2O_3 .