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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Practice for the Chemical Analysis of White Linseed Oil Paints[1]

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 Pigments[2]

D 50 Test Methods of Chemical Analysis of Yellow, Orange, Red, and Brown Pigments Containing Iron and Manganese[2]

D 280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments[2]

D 717 Test Methods for Analysis of Magnesium Silicate Pigment[2]

D 1193 Specification for Reagent Water[3]

D 1208 Test Methods for Common Properties of Certain Pigments[2]

D 1301 Test Methods for Chemical Analysis of White Lead Pigments[2]

D 1394 Test Methods for Chemical Analysis of White Titanium Pigments[2]

D 1398 Test Method for Fatty Acid Content of Alkyd Resins and Alkyd Resin Solutions[2]

D 1469 Test Methods for Total Rosin Acids Content of Coating Vehicles[2]

D 1542 Test Method for Qualitative Detection of Rosin in Varnishes[2]

D 1959 Test Method for Iodine Value of Drying Oils and Fatty Acids[2]

D 2349 Test Method for Qualitative Determination of Nature of Thinner in Solvent-Reducible Paints[4]

D 2350 Test Method for Antimony Oxide in White Pigment Separated from Solvent-Reducible Paints[4]

D 2351 Test Method for Sulfide in White Pigment Separated from Solvent-Reducible Paints[4]

D 2352 Test Method for Sulfur Dioxide in White Pigment Separated from Solvent-Reducible Paints[4]

D 2369 Test Method for Volatile Content of Coatings[4]

D 2371 Test Method for Pigment Content of Solvent-Reducible Paints[4]

D 2372 Practice for of Separation of Vehicle from Solvent-Reducible Paints[4]

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

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

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

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[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.

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.

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 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 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 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 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)

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[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.

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* ($(NH_4)_2SO_4$).

16.1.6 *Barium Chloride* ($BaCl_2 \cdot 2H_2O$). (**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* ($K_2Cr_2O_7$).

16.1.11 *Potassium Ferrocyanide, Standard Solution*—Dissolve 22 g of pure potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) 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 $K_4Fe(CN)_6$ 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 $K_4Fe(CN)_6$ 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 $(NH_4)_2SO_4$. 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 $K_2Cr_2O_7$ 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 $K_4Fe(CN)_6$ 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.

21. Total Lead

21.1 *Reagents*:

21.1.1 *Acetic Acid:* **Precaution**—See 4.3.

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

21.1.3 *Ammonium Polysulfide*—See 16.1.4.

21.1.4 *Ammonium Sulfide* ($(NH_4)_2S$). **Precaution**—See 4.7.

21.1.5 *Ether*.

21.1.6 *Ethyl Alcohol* (*95%*).

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

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

21.1.9 "*Lead Acid*"—Mix 300 ml of concentrated H_2SO_4 (sp gr 1.84) and 1800 ml of water. Dissolve 1 g of lead acetate in 300 mL of water and add this to the hot solution while stirring. Let stand at least 24 h and siphon through a thick asbestos filter.

21.1.10 *Nitric Acid* (*1 + 1*)—Mix equal volumes of concentrated nitric acid (HNO_3, sp gr 1.19) (**Precaution**—See 4.4) and water.

21.1.11 *Nitric Acid* (*1 + 3*)—Mix 1 volume of concentrated HNO_3 (sp gr 1.19) (**Precaution**—See 4.4) with 3 volumes of water.

21.1.12 *Potassium Dichromate Solution* (*100 g/L*)—Dissolve 100 g of potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 1 L.

21.1.13 *Sodium Sulfide Solution* (*20 to 30 g/L*)—Dissolve 20 to 30 g of sodium sulfide (Na_2S) in water and dilute to 1 L.

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

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

21.2 *Procedure*:

21.2.1 Unite the filtrate and washings (total volume 150 to 200 mL) from the total insoluble matter (see Section 20), pass H_2S into the solution until it is saturated, add an equal volume of water, and again saturate with H_2S. Filter, wash with water containing a little H_2S, dissolve in hot HNO_3 (1 + 3), washing the paper with hot water. Add 10 to 20 mL of H_2SO_4 (1 + 1), evaporate until copious fumes of H_2SO_4 are evolved. Cool, add about 75 ml of water and then about 75 mL of ethyl alcohol (95%). Stir, let settle, filter on a Gooch crucible, wash with diluted alcohol, and dry in an oven at 105 to 110°C; or, ignite gently in a radiator[6] or muffle, cool, and weigh as lead sulfate ($PbSO_4$). Calculate to lead oxide (PbO).

NOTE 7—It is not possible to determine the amount of basic lead carbonate and lead sulfate when carbonates or soluble sulfates of other metals, such as calcium, are present. Also, neither basic lead carbonate nor basic lead sulfate are definite compounds.

21.2.2 If the pigment contains antimony, filter and wash the sulfide precipitate as described in 21.2.1. Wash the precipitate with a fine jet of water from the paper into a porcelain dish or casserole, add 25 mL of ammonium polysulfide, cover the vessel, and warm the mixture at 40 to 60°C for 10 to 15 min while stirring frequently. Wash the cover, filter through the same paper, and wash with Na_2S (20 to 30 g/L) or $(NH_4)_2S$ solution. Discard the filtrate. Dissolve the residue in hot HNO_3 (1 + 3), and determine the lead as lead sulfate ($PbSO_4$) as described in 20.2.1; or, the original sulfide precipitate may be discarded and the lead determined on a separate portion of the pigment as follows: to 1 g of the sample in a covered beaker, add 40 mL of HCl (1 + 1) and boil gently for 5 to 10 min. Wash off the cover and evaporate to dryness. To the residue add sufficient HCl (sp gr 1.19) to dissolve the $PbSO_4$ (with pigments containing considerable amounts of $PbSO_4$, it may be necessary to add 15 to 20 ml of HCl (sp gr 1.19)), add about 50 mL of hot water, boil a few minutes, filter hot through paper, and wash with hot water until the washings give no test for lead. (If the sample contains no insoluble matter, omit the filtration.)

21.2.3 To the filtrate add 20 mL of H_2SO_4 (sp gr 1.84) and evaporate until dense white fumes of sulfur trioxide (SO_3) are copiously evolved. Allow to cool, but not below 60°C, and then add slowly 50 mL of water while agitating the solution. Heat to boiling for several minutes in order to ensure complete solution of antimony sulfate. Allow the $PbSO_4$ to settle out until the supernatant liquid is clear, not letting the temperature fall below 60°C. If the liquid does not clear quickly it must be heated longer. When clear, pour the solution through a weighed porcelain Gooch crucible with asbestos mat, decanting the solution as completely as possible without allowing more than a very small amount of $PbSO_4$ to go over into the crucible. Add 10 mL more of concentrated H_2SO_4 (sp gr 1.84) to the $PbSO_4$ in the original beaker and boil for several minutes. Cool, add slowly 30 mL of water, and again heat to boiling for a few minutes. Allow the solution to cool to about 60°C and completely transfer the $PbSO_4$ to the Gooch crucible. Wash with "lead acid" (see 21.1.9) to remove soluble sulfates and finally wash free of acid with diluted alcohol (equal parts of ethyl alcohol or denatured alcohol and water). Dry in an oven at 105 to 110°C, or ignite gently in a radiator or muffle. Calculate to PbO, or determine as lead chromate ($PbCrO_4$) as described in 21.2.6.

21.2.4 If soluble compounds of barium or calcium are present, barium sulfate ($BaSO_4$) and calcium sulfate ($CaSO_4$) will be included with the $PbSO_4$. If soluble silica (SiO_2) is present, it will also be included with the $PbSO_4$. In such cases, the $PbSO_4$ precipitate after washing with diluted alcohol may be dissolved in acid ammonium acetate and the lead determined as $PbCrO_4$ as described in 21.2.6. For ordinary work, the amount of $BaSO_4$ dissolved by the acetate treatment may be disregarded.

21.2.5 If the pigment contains no soluble antimony, barium, or calcium compounds, the lead may be determined directly on the original pigment as follows: to 1 g of the sample in a covered beaker, add 25 mL of HNO_3 (1 + 1) and boil gently a few minutes. Wash off the cover, evaporate to dryness on a steam bath, moisten with HNO_3, add hot water, and heat a few minutes. Filter and wash with hot water until washings are lead-free. Add 10 to 20 ml of H_2SO_4 (1 + 1) to the clear solution, evaporate, and determine lead as $PbSO_4$ as described in 21.2.1.

21.2.6 In the absence of soluble compounds of antimony, iron, aluminum, and barium, the following procedure may be used: treat 1 g of the original pigment with 25 mL of HNO_3 (1 + 1) and proceed as described in 20.2.1. To the clear solution, diluted to 200 mL, add NH_4OH in slight excess, acidify with acetic acid, and add 4 to 6 mL more of acetic acid. Heat to boiling and add 10 to 15 mL of a solution of $K_2Cr_2O_7$ (100 g/L). Heat until the yellow precipitate assumes an orange color, let settle, and filter on a weighed Gooch crucible. Wash by decantation until the washings are colorless, finally transferring all of the precipitate. Wash with ethyl alcohol (95 %) and then with ether. Dry to constant weight at 110°C, cool, and

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[6] U. S. Geological Survey, *Bulletin 700* (1919), p. 33.

weigh as $PbCrO_4$. Calculate to PbO.

22. Antimony Oxide

22.1 Determine antimony oxide in accordance with Test Method D 2350.

23. Soluble Barium

23.1 Boil the combined filtrate and washings, reduced to volume by evaporation if need be, from the lead sulfate (PbS) precipitate (see 21.2) to expel hydrogen sulfide (H_2S). Add a slight excess of H_2SO_4 (1 + 4) over the amount required to precipitate the barium, heat to boiling, let stand on a steam bath about 1 h, filter on a weighed Gooch crucible, wash with hot water, dry, ignite, cool, and weigh as barium sulfate ($BaSO_4$) (Note 2 and Note 8). Calculate to barium oxide (BaO).

NOTE 8—The precipitate will include any $BaSO_4$ that may have been dissolved as such. The weighed precipitate should be tested for $CaSO_4$, and if present, it should be removed by treating with hot HCl (1 + 3), filtering, washing, igniting, and again weighing.

24. Aluminum Oxide (Fe_3O_2, TiO_2, P_2O_5)

24.1 *Reagents*:

24.1.1 *Ammonium Chloride Solution* (*25 g/L*)—Dissolve at least 25 g of ammonium chloride (NH_4Cl) in water and dilute to 1 L.

24.1.2 *Ammonium Hydroxide* (*1 + 5*)—Mix 1 volume of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90) (**Precaution**—See 4.1) with 1 volume of water.

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

24.1.4 *Methyl Red Indicator, Alcoholic Solution* (*2 g/L*)—Dissolve 0.2 g of methyl red in alcohol and dilute to 100 mL.

24.1.5 *Nitric Acid* (*sp gr 1.42*)—Concentrated nitric acid (HNO_3). **Precaution**—See 4.4.

24.2 *Procedure*:

24.2.1 Boil the filtrate from the lead sulfide (PbS) precipitate (see 21.2) to expel hydrogen sulfide (H_2S), add a few drops of HNO_3, and continue the boiling a few minutes to oxidize any iron that may be present. In case soluble barium was present, use the filtrate from 23.1. To the solution containing at least 25 g of NH_4Cl/L of solution, or an equivalent amount of HCl, add a few drops of methyl red indicator, alcoholic solution and heat just to boiling. Carefully add NH_4OH (1 + 5) dropwise until the color of the solution changes to a distinct yellow. Boil the solution for 1 to 2 min and filter at once. Wash the precipitate thoroughly with hot NH_4Cl solution (Note 9). Ignite the precipitate, cool, and weigh as aluminum oxide (Al_2O_3) (Note 10).

NOTE 9—For very accurate work, or when the precipitate is large, the precipitate should be dissolved in HCl (1 + 1) and the precipitation repeated.

NOTE 10—This precipitate may also contain ferric oxide (Fe_2O_3), titanium dioxide (TiO_2), and phosphorus pentoxide (P_2O_5).

25. Total Zinc

25.1 *Reagents*:

25.1.1 *Acetic Acid* (*1 + 49*)—Mix 1 volume of concentrated acetic acid (sp gr 1.05) (**Precaution**—see 4.3) with 49 volumes of water.

25.1.2 *Ammonium Acetate*.

25.1.3 *Ammonium Chloride* (NH_4Cl).

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

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

25.1.6 *Hydrochloric Acid* (*1 + 2*)—Mix 1 volume of concentrated HCl (sp gr 1.19) (**Precaution**—See 4.2) with 2 volumes of water.

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

25.1.8 *Potassium Ferrocyanide, Standard Solution*—See 16.1.11.

25.1.9 *Uranyl Indicator*—Dissolve 5 g of uranyl nitrate in water and dilute to 100 mL, or dissolve 5 g of uranyl acetate in water made slightly acid with acetic acid and dilute to 100 mL.

25.2 *Procedure*:

25.2.1 To the combined filtrate and washings from the alumina determination (see 24.2.1), add sufficient NH_4Cl to give 5 g/100 mL of solution, and then add 1 g of ammonium acetate.[7] Make slightly acid with acetic acid and pass in a current of H_2S to saturation. Allow the precipitate to settle completely, filter on paper, and wash with a solution of acetic acid (1 + 49) saturated with H_2S. Transfer the precipitate and filter to the vessel in which the precipitation was effected, add 30 mL of water and 10 mL of concentrated HCl (sp gr 1.19), heat until all zinc is in solution, add 200 mL of water and a small piece of litmus paper; add NH_4OH (sp gr 0.90) until slightly alkaline, make just acid with HCl, then add 3 mL of concentrated HCl (sp gr 1.19), heat nearly to boiling, and titrate with standard $K_4Fe(CN)_6$ solution as described in 16.1.11 using uranyl indicator solution.

25.2.2 Zinc may be determined directly on the original sample as follows (Note 11): weigh accurately about 1 g (or an amount that will give a buret reading approximately equal to that obtained in the standardization) of the pigment, transfer to a 400-mL beaker, add 30 ml of HCl (1 + 2), boil a few minutes, add 200 mL of water, and a small piece of litmus paper; add concentrated NH_4OH until slightly alkaline, render just acid with HCl, then add 3 mL of HCl (sp gr 1.19), heat nearly to boiling, and titrate with standard $K_4Fe(CN)_6$ solution as described in 16.1.11 using uranyl indicator solution.

NOTE 11—If the sample contains antimony, it should be precipitated by H_2S in the hot acid solution, filtered off, washed, and the filtrate neutralized, etc., for zinc. The H_2S precipitate may also contain lead sulfide (PbS). If no sulfide separation is made, any cadmium present will be counted as zinc.

25.2.3 When iron is present, total zinc may be determined directly on the original sample as follows (Note 11). Weigh accurately about 1 g (or an amount that will give a buret reading approximately equal to that obtained in the standardization) of the pigment, transfer to a 250-ml beaker, moisten with alcohol, add 30 ml of HCl (1 + 2), boil for 2 or 3 min, and add about 100 ml of water. Add about 2 g of NH_4Cl make slightly alkaline with NH_4OH, heat to boiling, let settle on a steam bath, filter into a 400-ml beaker, and wash the residue

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[7] Gooch, F. A., *Representative Procedures in Quantitative Chemical Analysis*, 1st Ed. (1916), p. 107.

once with hot water. Remove the 400-mL beaker and pour HCl (1 + 2) on the residue, catching the filtrate therefrom in the 250-ml beaker; wash a few times with hot water. Add to this filtrate 1 g of NH_4Cl and make slightly alkaline with NH_4OH, boil, let settle, filter on paper used for first filtration, and wash thoroughly with hot water, catching the filtrate and washings in the 400-mL beaker containing the first filtrate. Add a small piece of litmus paper, acidify with HCl, add 3 mL of HCl (sp gr 1.19), heat nearly to boiling, and titrate with standard $K_4Fe(CN)_6$ solution as described in 16.1.11.

25.2.4 With pigments containing zinc oxide (ZnO) and zinc sulfide (ZnS), the ZnO may be determined as follows: weigh accurately 1 g of the pigment, transfer to a 250-mL beaker, moisten with alcohol, add about 100 mL of acetic acid (1 + 49), stir vigorously but do not heat, cover and let stand for 18 h, stirring once every 5 min for the first 30 min. Filter, wash with acetic acid (1 + 49) followed by water until the washings give no test for zinc with $K_4Fe(CN)_6$ solution. Dilute the clear filtrate to about 200 mL with water, add 30 mL of HCl (1 + 2), and a small piece of litmus paper; add NH_4OH (sp gr 0.90) until slightly alkaline, render just acid with HCl, then add 3 mL of concentrated HCl (sp gr 1.19), heat nearly to boiling, and titrate with $K_4Fe(CN)_6$ solution as described in 25.2.4. Calculate this result to zinc, subtract from total zinc, and calculate the difference to zinc sulfide (ZnS). (Any zinc carbonate ($ZnCO_3$) or zinc sulfate ($ZnSO_4$) is included in the ZnO.)

26. Soluble Calcium

26.1 *Reagents*:

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

26.1.2 *Ammonium Oxalate, Saturated Solution* $(NH_4)_2\cdot C_2O_4)$.

26.1.3 *Potassium Permanganate, Standard Solution* (*0.1 N*)—Dissolve 3.2 g of pure potassium permanganate ($KMnO_4$) in water and dilute to 1 L. Let stand 8 to 14 days, siphon off the clear solution (or filter through an asbestos filter), and standardize against NIST's standard sample 40c of sodium oxalate as follows: in a 400-mL beaker, dissolve 0.25 to 0.30 g (accurately weighed) of sodium oxalate in 250 mL of hot water (80 to 90°C) and add 15 mL of sulfuric acid (H_2SO_4, 1 + 1). Titrate at once with the $KMnO_4$ solution, stirring the liquid vigorously and continuously. The $KMnO_4$ must not be added more rapidly than 10 to 15 mL/min, and the last 0.5 to 1 mL must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The temperature of the solution should not be below 60°C by the time the end point is reached. (Too rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot plate during the titration. The use of a small thermometer as a stirring rod is most convenient.) The weight of sodium oxalate used multiplied by 0.833 gives its iron equivalent. The $KMnO_4$ solution should be kept in a glass-stoppered bottle painted black to keep out light.

26.1.4 *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.

26.2 *Procedure*:

26.2.1 Heat to boiling the united filtrate and washings, reduced in volume if need be, from the ZnS determination (see 25.2.2), add 1 mL of NH_4OH and an excess of a hot saturated $(NH_4)_2C_2O_4$ solution. Continue the boiling until the precipitate becomes granular; let stand about 1 h, filter, and wash with hot water. Ignite, cool, and weigh as calcium oxide (CaO) (Note 2, Note 12, and Note 13). Alternatively, place the beaker in which the precipitation was made under the funnel, pierce the apex of the filter with a stirring rod, and wash the precipitate into the beaker with hot water. Pour warm H_2SO_4 (1 + 4) through the paper and wash a few times. Add about 30 mL of H_2SO_4 (1 + 4), dilute to about 250 mL, heat to 90°C, and titrate at once with 0.1 *N* $KMnO_4$ solution (the temperature of the solution should not be below 60°C when the end point is reached, see 25.1.3). Calculate to CaO (Note 2, Note 12, and Note 13). (The iron equivalent of $KMnO_4 \times 0.502 = CaO$ value.)

NOTE 12—Care must be exercised in this washing, as 1 L of boiling water will dissolve over 0.01 g of calcium oxalate (CaC_2O_4).

NOTE 13—For more accurate work, the CaC_2O_4 precipitate should be ignited, cooled, cautiously moistened with water, redissolved in HCl, and the solution diluted to 100 mL. Add NH_4OH in slight excess, boil the liquid, and filter and wash if a precipitate appears. Reprecipitate the calcium with NH_4OH and $(NH_4)_2C_2O_4$, as described in 25.2.1, filter, wash, ignite, cool, and weigh; or, titrate as described.

27. Soluble Magnesium

27.1 *Reagents*:

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

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

27.1.3 *Hydrochloric Acid* (*1 + 3*)—Mix 1 volume of concentrated HCl (sp gr 1.19) (**Precaution**—See 4.2) with 3 volumes of water.

27.1.4 *Sodium Ammonium Phosphate, Saturated Solution* ($NaNH_4HPO_4$).

27.2 *Procedure*:

27.2.1 Acidify the filtrate from the calcium determination (see 26.2.1) with HCl, add 10 mL of a saturated solution of $Na(NH_4)HPO_4$ and NH_4OH dropwise, with constant stirring. When the crystalline magnesium ammonium phosphate $(Mg(NH_4)PO_4$ has formed, add 5 mL excess of NH_4OH. Allow the solution to stand in a cool place for not less than 4 h, preferably overnight (Note 14). Filter and wash with water containing 2.5 % ammonia. Dissolve the precipitate in a small quantity of hot HCl (1 + 3), dilute the solution to about 100 mL with water, add 1 mL of a saturated solution of $Na(NH_4)HPO_4$ and NH_4OH dropwise, with constant stirring, until the precipitate is again formed, and then add 5 mL excess of NH_4OH. Let the precipitate stand in a cool place for not less than 2 h, filter on a Gooch crucible, wash with water containing 2.5 % of ammonia, ignite, cool, and weigh as magnesium pyrophosphate (MgP_2O_7) (Note 15). Calculate to magnesium oxide (MgO).

NOTE 14—The smaller the amount of magnesium present, the longer the precipitate must be allowed to settle.

NOTE 15—If the sample contained manganese, it will be caught in large part with the $Mg_2P_2O_7$. If desired, manganese may be determined by dissolving the $Mg_2P_2O_7$. If desired, manganese may be determined by dissolving the $Mg_2P_2O_7$ in nitric acid (**Precaution**—See 4.4) and applying the bismuthate method.

28. Carbon Dioxide

28.1 Determine carbon dioxide in accordance with Test Methods D 1301.

29. Total Soluble Sulfur Compounds (Note 2)

29.1 Determine total soluble sulfur in accordance with Methods D 34. This determination includes soluble sulfates, sulfur trioxide (SO_3) formed from sulfur dioxide, (SO_2), and the SO_3 that is formed from sulfide sulfur.

30. Soluble Sulfate (Note 2)

30.1 Determine soluble sulfates in accordance with Test Methods D 50.

31. Sulfide Sulfur

31.1 Determine sulfide sulfur in accordance with Test Method D 2351.

32. Sulfur Dioxide

32.1 Determine sulfur dioxide in accordance with Test Method D 2352.

33. Matter Soluble in Water

33.1 Determine matter soluble in water in accordance with Test Methods D 1208.

NOTE 16—The nature of the water-soluble matter may be determined by further examination, as the percentages of sulfur trioxide (SO_3) and calcium oxide (CaO) may be indicative.

NOTE 17—The water-soluble content of composite pigmentation, as determined in accordance with this method, is frequently higher than the sum of the water-soluble matter in the individual pigments. Possibly this is due to reaction in water between the individual pigments.

34. Calculation

34.1 The calculation of the component pigments of a mixed or combination pigment may be a somewhat difficult matter. Certain assumptions must be made, depending upon the complexity of the mixed pigment, as to the composition or formulas of component pigments and as to the manner in which the acidic and basic radicals are combined. Add any $Al_2O_3(Fe_2O_3)$ found in the soluble portion to the siliceous matter and report the sum as“ insoluble siliceous matter’’ unless the soluble aluminum is high; in this case, an aluminate is probably present, and the Al_2O_3 should be reported as Al_2O_3. If a small amount of soluble magnesium is found, it should also be added to the siliceous matter. If the soluble magnesium is high, the presence of $MgCO_3$ is indicated, and the MgO is calculated to $MgCO_3$ as described in 34.3. The insoluble siliceous matter reported should be based on the weight obtained on drying the total insoluble matter at 105°C if the combined water contained therein is to be considered.

34.2 Report TiO_2 as TiO_2, ZnS as ZnS, and $BaSO_4$ as $BaSO_4$. If $CaCO_3$, $CaSO_4$, $BaCO_3$, and $MgCO_3$ are absent, calculate CO_2 to basic carbonate white lead ($Pb(CO_3)_2 \cdot Pb(OH)_2$), and soluble SO_3 to $PbSO_4$. Calculate any excess of lead to PbO, add it to the $PbSO_4$, and report the sum as basic lead sulfate. Alternatively, multiply the sum of $PbSO_4$ + PbO by 0.058 to obtain the ZnO; add this result to the $PbSO_4$ + PbO and report as basic sulfate white lead. (The ZnO factor is based on the assumption that the average composition of commercial basic sulfate white lead is 78.5 % $PbSO_4$, 16.0 % PbO, and 5.5 % ZnO.) Lead oxide (PbO) should not be reported except in the presence of $PbSO_4$ unless the entire analysis is reported in the elementary or oxide form.

34.3 If the sample contains CO_2 but not soluble SO_3, calculate total lead to basic carbonate white lead ($Pb(CO_3)_2 \cdot Pb(OH)_2$); calculate residual CO_2 to $CaCO_3$, then to $BaCO_3$ and $MgCO_3$ if soluble barium and magnesium should be present in sufficient amounts to indicate the presence of these carbonates. The CO_2 result will be an index of this. A small amount of residual CaO is probably from the siliceous matter and should be added to the insoluble siliceous matter.

34.4 A small amount of soluble barium may be from the $CaCO_3$ used or may be due to the solubility of $BaSO_4$, if this compound is present in the original pigment. This barium may be calculated to $BaSO_4$ and added to the $BaSO_4$ found in the insoluble matter.

34.5 If the sample contains soluble SO_3 but no CO_2, calculate CaO to $CaSO_4$ or $CaSO_4 \cdot 2H_2O$; residual SO_3 to $PbSO_4$; add residual PbO to $PbSO_4$ and report the sum as basic lead sulfate. Alternatively, multiply $PbSO_4$ + PbO by 0.058 and add the result to the $PbSO_4$ + PbO, and report the total as basic sulfate white lead.

34.6 If the sample contains $CaCO_3$ ($MgCO_3$, $BaCO_3$) and also basic sulfate white lead, or $CaSO_4$ and basic carbonate white lead, or a mixture of these, it is not possible to determine or calculate the amount of $PbCO_3$ or $PbSO_4$ with any degree of certainty (see Note 2 and Note 3). The presence of appreciable amounts of CaO and SO_3 in the water-soluble matter indicates the probable presence of $CaSO_4$ in the original pigment. The following arbitrary calculations may be made: calculate water-soluble SO_3 to $CaSO_4$ or $CaSO_4 \cdot 2H_2O$, subtract this SO_3 from total soluble SO_3, and calculate the remainder to $PbSO_4$; calculate residual CaO to $CaCO_3$, and then residual CO_2 to $(PbCO_3)_2 \cdot Pb(OH)_2$. If there is an excess of CO_2, calculate to $MgCO_3$ or $BaCO_3$, if the amounts of soluble magnesium and barium indicate the probable presence of these carbonates. Add residual PbO to $PbSO_4$ and calculate as described in 34.5 to basic sulfate white lead.

34.7 Report total antimony as Sb_2O_3.

34.8 Calculate sulfide sulfur to ZnS. Subtract the zinc equivalent to the sulfur from the total zinc, then subtract the zinc required for the basic sulfate white lead, and report the remainder as ZnO.

34.9 Report directly the following: moisture and other volatile matter, loss on ignition, SO_2 and matter soluble in water.

35. Keywords

35.1 analysis of paint; white oil; analysis of pigment; white oil; lead analysis; white linseed oil paints; chemical analysis