Designation: D126 – 87 (Reapproved 2012)

Standard Test Methods for Analysis of Yellow, Orange, and Green Pigments Containing Lead Chromate and Chromium Oxide Green[1]

This standard is issued under the fixed designation D126; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover procedures for the chemical analysis of yellow, orange, and green pigments containing lead chromate and chromium oxide green.

1.2 The analytical procedures appear in the following order:

	Sections
CHROME YELLOW, CHROME ORANGE, AND MOLYBDATE ORANGE	
Organic Colors and Lakes	7
Moisture and Other Volatile Matter	8
Matter Soluble in Water	9
Lead Chromate	10 and 11
Total Lead	12
Sulfate	13 and 14
Carbon Dioxide	15
Molybdenum	16 and 17
Extenders	18 – 22
Calculation of Substances Other than Insoluble Lead Compounds	23 and 24
PURE CHROME GREEN AND REDUCED CHROME GREEN	
Organic Colors and Lakes	25
Moisture and Other Volatile Matter	26
Matter Soluble in Water	27
Iron Blue	28
Lead Chromate	29 and 30
Barium Sulfate and Insoluble Siliceous Material	31
Total Lead	32
Sulfate	33
Calcium Oxide Soluble in Acid	34 and 35
Extenders	36
Calculation of Insoluble Lead Compounds	37
CHROMIUM OXIDE GREEN	
Organic Colors and Lakes	38
Moisture and Other Volatile Matter	39
Matter Soluble in Water	40
Total Chromium as Chromium Oxide	41

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety problems, 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.* Specific hazard statements are given in Note 3.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments

D521 Test Methods for Chemical Analysis of Zinc Dust (Metallic Zinc Powder)

D1013 Test Method for Determining Total Nitrogen in Resins and Plastics (Withdrawn 2007)[3]

D1193 Specification for Reagent Water

E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

3. Summary of Test Methods

3.1 *Chrome Yellow, Chrome Orange, and Molybdate Orange:*

3.1.1 Organic colors and lakes are determined qualitatively by boiling the sample in water, then ethyl alcohol, and finally chloroform.

3.1.2 Moisture and other volatile matter are determined in accordance with Test Method A of Test Methods D280.

3.1.3 Matter soluble in water is determined by boiling in water and filtering.

3.1.4 Lead chromate is determined by dissolving the sample in dilute HCl, filtering and titrating potentiometrically with $FeSO_4$ solution after addition of $HClO_4$.

3.1.5 Total lead is determined by precipitation as lead sulfide solution with H_2SO_4 and final precipitation as lead sulfate.

3.1.6 Sulfate is determined by dissolving the sample in acetic acid, neutralizing with sodium carbonate, plus addition

[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.31 on Pigment Specifications.

Current edition approved June 1, 2012. Published August 2012. Originally approved in 1922. Last previous edition approved in 2006 as D126 – 87 (2006). DOI: 10.1520/D0126-87R12.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

of HCl to an aliquot followed by addition of $BaCl_2$ to precipitate as barium sulfate.

3.1.7 Carbon dioxide is determined by evolution.

3.1.8 Molybdenum is determined by precipitation as the sulfide, solution in HNO_3 and H_2SO_4, addition of NH_4OH and H_2SO_4. The solution is reduced in a Jones reductor, collected under $Fe_2(SO_4)_3$ solution and titrated with $KMnO_4$ solution.

3.1.9 Extenders are either:

3.1.9.1 Calcium carbonate, calcium sulfate, magnesium carbonate or;

(a) The compounds in 3.1.9.1 are determined qualitatively by precipitation with ammonium solution.

(b) If chromium is present, it is reduced and the lead salts dissolved in dissolving solution. Hydroxides and hydrous oxides are precipitated by addition of HCl and NH_4OH and filtered. CaC_2O_4 is precipitated with calcium oxalate solution and filtered, ashed and weighed as CaO. Alternatively, the precipitate is dissolved in H_2SO_4 and titrated with $KMnO_4$. Magnesium is determined on the filtrate from calcium determination by precipitation as the phosphate with ammonium phosphate solution.

3.2 *Chromium Oxide Green:*

3.2.1 Organic colors and lakes are determined qualitatively by boiling the sample in water, then ethyl alcohol, and finally choloroform.

3.2.2 Moisture and other volatile matter are determined in accordance with Test Method A of Test Methods D280.

3.2.3 Matter soluble in water is determined by boiling in water and filtering.

3.2.4 Total chromium as chromium oxide is determined by dissolving the sample in dilute HCl, filtering and titrating potentiometrically with $FeSO_4$ solution after addition of $HClO_4$.

4. Significance and Use

4.1 These test methods are for analysis designed as an aid in quality of yellow, orange, and green pigments containing lead chromate and chromium oxide green. Some sections may be applicable to analysis of these pigments when extracted from whole paints.

5. Purity of Reagents and Water

5.1 *Reagents*—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.[4] 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.

5.2 *Water*—Unless otherwise indicated, references to water for use in the preparation of reagents and in analytical procedures shall be understood to mean reagent water conforming to Type II of Specification D1193.

6. Preparation of Sample

6.1 Mix the sample thoroughly and take a representative portion for analysis. Reduce any lumps or coarse particles to a fine powder by grinding. Grind extracted pigments to pass a No. 80 (180-μm) sieve (Note 1). Discard any skins that do not pass through the sieve. Thoroughly mix the finely ground pigment and preserve in stoppered and suitably identified bottles or containers.

NOTE 1—Detailed requirements for this sieve are given in Specification E11.

6.2 Moisten the weighed portions of extracted pigments with a small amount of suitable wetting agent (Note 1) before adding reagents for analysis.

NOTE 2—A 0.1 % solution of sodium dioctylsuccinosulfonate has been found satisfactory. (This material is sold under the trade name of Aerosol OT.) Wetting agents containing mineral salts, sulfates, or sulfonates which may be hydrolyzed to sulfates, should be avoided; the use of alcohol is also undesirable because of its tendency to reduce chromates.

NOTE 3—**Warning:** As the National Institute for Occupational Safety and Health has stated that hexavalent chromium compounds are hazardous to health, care should be exercised in preparation of the sample. The wearing of a respirator and rubber or synthetic gloves are recommended. If hexavalent chromium materials come in contact with the skin, wash thoroughly with soap and water.

[4] *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.

CHROME YELLOW, CHROME ORANGE, AND MOLYBDATE ORANGE

(Primrose, Lemon, and Medium Yellows; Chrome Oranges; Lead Molybdate or Basic Lead Chromate; Molybdate Orange)

ORGANIC COLORS AND LAKES

7. Procedure

7.1 Boil 2 g of the sample 2 min with 25 mL of water, let settle, and decant the supernatant liquid. Similarly, boil the residue with 25 mL of ethyl alcohol (absolute or 95 %) and decant as before. Likewise boil with 25 mL of chloroform and again decant. If any one of the above solutions is colored, organic colors are present. If all solutions remain colorless, organic colors are presumably absent. The presence of organic colors resistant to the above reagents is unlikely, but may be tested for by reference to procedures given in standard reference works.[5]

[5] Reference may be made to the following: Payne, H. F., "Organic Coatings Technology," Vol II, John Wiley & Sons, Inc., New York, NY, 1961.

MOISTURE AND OTHER VOLATILE MATTER

8. Procedure

8.1 Determine moisture and other volatile matter in accordance with Test Method A of Test Methods D280.

MATTER SOLUBLE IN WATER

9. Procedure

9.1 Place 2.5 g of the sample in a graduated 250-mL flask. Add 100 mL of water and boil for 5 min. Cool, dilute to exactly 250 mL, mix, and allow to settle. Filter the supernatant liquid through a dry paper and discard the first 20 mL. Evaporate 100 mL of the clear filtrate to dryness in a weighed dish, heat for 1 h at 105 to 110°C, cool, and weigh.

9.2 *Calculation*—Calculate the % of matter soluble in water as follows:

$$\text{Matter soluble in water, \%} = (R \times 2.5 \times 100)/S \quad (1)$$

where:

R = weight of residue, and
S = specimen weight, g.

LEAD CHROMATE[6]

10. Reagents

10.1 *Dissolving Solution*—Saturate 1 L of water with NaCl. Filter. Add to the filtered solution 150 mL of water and 100 mL of HCl (sp gr 1.19).

10.2 *Ferrous Sulfate, Standard Solution (0.3 N)*—Dissolve 86 g of $FeSO_4 \cdot 7H_2O$ in 500 mL of water to which 30 mL of H_2SO_4 (sp gr 1.84) has been added with constant stirring. Dilute to 1 L and standardize not more than 6 h before use by potentiometric titration against 0.7-g portions of $K_2Cr_2O_7$.

11. Procedure

11.1 Dissolve 1 g of the sample in 150 mL of the dissolving solution. Agitate for 10 to 15 min, keeping the solution cold until dissolution is complete (Note 4). If dissolution is not complete, filter through fine grade filter paper and wash with three 10-mL portions of cold dissolving solution. Add 10 mL of $HClO_4$ (70 %), dilute to 250 mL, and titrate potentiometrically with $FeSO_4$ solution.

NOTE 4—Incomplete solution of the pigment is evidence of the possible presence of barium sulfate, silica, silicates, or other acid-insoluble extenders (see Section 18). Some chrome yellows may contain organic addition agents and will give a turbid solution at this point.

Newer chemically resistant-type lead chromate type pigments (silica encapsulated) cannot be decomposed by the procedures described in this method. Pigments of this type may require treatment with strong alkali hydroxide or hydrofluoric acid.

Also, if trivalent antimony has been used in manufacturing the product, pentavalent antimony may be present which would interfere in the determination of lead chromate.

[6] Sections 23 and 24 under "Calculation of Substances Other than Insoluble Lead Compounds" should be read carefully before proceeding with the analyses described in Sections 10 to 22.

11.2 Alternatively, the solution may be reduced by a known excess of $FeSO_4$ solution and back-titrated with $KMnO_4$ solution in the presence of $MnSO_4$, or excess KI may be added and the liberated iodine titrated with $Na_2S_2O_3$ solution, using starch indicator. The iodine liberation method is not applicable in the presence of molybdenum.

TOTAL LEAD[6]

12. Procedure

12.1 Dissolve 0.5 g of sample as described in Section 11. Add 5 mL of ethyl alcohol (95 % or absolute) and boil until the chromium is reduced, as indicated by a green color. Filter if any insoluble residue is present, retaining the filtrate and washings for the determination. Add NH_4OH (sp gr 0.90) to this solution until a faint precipitate begins to form; then add 5 mL of HCl (sp gr 1.19) slowly, dilute to 500 mL, and pass a rapid current of H_2S into the solution until precipitation is complete. Settle, filter, and wash with water containing H_2S.

12.2 Rinse the precipitate from the filter (Note 5) into a beaker containing 25 mL of HNO_3 (1+3) and boil until all PbS has dissolved. Add 10 mL of H_2SO_4 (1+1) and evaporate to strong fumes of SO_3. Cool and add 50 mL of water and 50 mL of ethyl alcohol (95 %) (Note 6). Let stand 1 h; then filter on a tarred Gooch crucible. Wash with ethyl alcohol (95 %), dry, ignite at 500 to 600°C, and weigh as $PbSO_4$.

NOTE 5—If a trace of sulfide remains on the paper, the stained portion of the paper may be separately treated with bromine water, the paper filtered off, and the filtrate added to the body of the solution.

NOTE 6—Any sulfur remaining from decomposition of the sulfides may be mechanically removed as a globule of solidified sulfur at this point.

SULFATE[6]

13. Reagents

13.1 *Barium Chloride Solution*—Dissolve 117 g of $BaCl_2 \cdot 2H_2O$ in water and dilute to 1 L.

13.2 *Dissolving Solution*—See 10.1.

13.3 *Sodium Carbonate Solution (saturated)*—Prepare a solution containing excess Na_2CO_3 at laboratory temperature, and free of SO_4. Decant the clear solution for use as required.

14. Procedure

14.1 Digest 1.25 g of the sample with 100 mL of dissolving solution at 100°C for 5 min. Add 25 mL of glacial acetic acid and 15 mL of ethyl alcohol and heat gently for 10 min to reduce chromium, as indicated by the green color of the solution. Cool. Neutralize with saturated Na_2CO_3 solution and add a slight excess. Transfer to a 250-mL volumetric flask, dilute to the mark with distilled water, and mix. Filter without washing through a dry filter paper, discarding the first 10 to 15 mL.

14.2 Take a 200-mL aliquot of the filtrate, neutralize with HCl (1+1), and add 10 mL excess. Heat to boiling and boil for 5 min. To the gently boiling solution, add 15 mL of $BaCl_2$ solution dropwise with constant stirring. Digest on a steam bath for 2 h. Filter through an ignited tarred Gooch crucible,

wash with HCl (1+99), and finally with hot water. Dry at 105 to 110°C, ignite at 900°C, and weigh.

CARBON DIOXIDE[6]

15. Procedure

15.1 Determine CO_2 by the evolution method on 2.5 g of the sample, using dilute HNO_3 free of NO or NO_2 and absorbing the CO_2 in soda lime or in KOH solution.

MOLYBDENUM[6]

16. Reagents

16.1 *Ferric Sulfate Solution*—Dissolve 20 g of $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ in 200 mL of water to which has been added 50 mL of H_2SO_4 (sp gr 1.84) and 20 mL of H_3PO_4 (85 %), and dilute to 1 L.

16.2 *Jones Reductor*—The reductor shall contain at least a 35-cm column of amalgamated zinc, prepared by shaking 20 to 30-mesh zinc free of iron or carbon with $HgCl_2$ solution (20 g/L) in sufficient quantity to produce an amalgam containing 1 to 5 % of mercury, and supported by a suitable inert pad of asbestos, glass wool, or other inert material.

16.3 *Potassium Permanganate, Standard Solution (0.1 N)*—Dissolve 3.16 g of $KMnO_4$ in water and dilute to 1 L. Let stand 8 to 14 days, siphon off the clear solution (or filter through a medium porosity fritted disk), and standardize against the National Bureau of Standards standard sample No. 40 of sodium oxalate ($Na_2C_2O_4$) as follows: In a 400-mL beaker dissolve 0.2500 to 0.3000 g of the Bureau of Standards sodium oxalate in 250 mL of hot water (80 to 90°C) and add 15 mL of H_2SO_4 (1+1). Titrate at once with $KMnO_4$ 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 solution shall not be below 60°C by the time the end point has been reached. (More 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 (non-mercury type) as a stirring rod is most convenient.) Keep the $KMnO_4$ solution in a glass-stoppered bottle painted black to keep out light, or in a brown glass bottle stored in a dark place.

17. Procedure

17.1 Dissolve 1 g of the sample as described in Section 11. Add 5 mL of ethyl alcohol (95 % or absolute) and boil until chromium is reduced. Filter if any insoluble residue is present, retaining the filtrate and washings. Add NH_4OH (sp gr 0.90) cautiously until a faint precipitate begins to form, then add 15 mL of H_2SO_4 (sp gr 1.84) and dilute to 300 mL. Heat to boiling, pass in a rapid stream of H_2S for 15 min, and dilute with 300 mL of hot water. Pass in H_2S for 10 min, boil for 3 min, and cool. Pass in H_2S for 10 min, and let stand at room temperature for 1 h. Filter and wash with H_2SO_4 (1+99) saturated with H_2S.

17.2 Rinse the sulfide precipitate into the original beaker and add 20 mL of HNO_3 (sp gr 1.42) and 5 mL of H_2SO_4 (sp gr 1.84) (see Note 5). Cover and heat to fumes. Cool, add 10 mL of HNO_3 (sp gr 1.42), and again fume. Repeat this operation if necessary until a light-colored solution is obtained. Wash the cover and inside of the beaker and fume again to remove all HNO_3. Dilute to 200 mL and add NH_4OH (1+4) until neutral; then add 10 mL of H_2SO_4 (sp gr 1.84).

17.3 Cool the solution and reduce by passing through a Jones reductor at a rate not exceeding 100 mL/min, collecting the effluent under 200 mL of $Fe_2(SO_4)_3$ solution. Titrate with $KMnO_4$ solution. A blank determination should also be made.

EXTENDERS[6]

18. General Considerations

18.1 Extenders fall into two groups, depending on their solubility or insolubility in the dissolving solution described in Section 10, as follows:

A. Extenders Soluble in Dissolving Solution—Calcium sulfate (gypsum), calcium carbonate (whiting), and magnesium carbonate.

B. Extenders Insoluble in Dissolving Solution—Silica, magnesium silicate, and clay (Note 7).

18.2 Extenders of group *A* may be present if the analysis shows sulfates and carbonates to be in the pigment, and are absent if sulfate and carbonate are absent. Since the latter situation rarely exists, it is advisable to test for the presence of calcium and magnesium to determine if extenders are present. Extenders of group *B* are recognized as an insoluble residue following acid solution of the pigment, and may be determined quantitatively if desired, by the method described in Section 31. Extenders of group *A*, if present, may affect the calculation of insoluble lead compounds as given in Section 23. Their qualitative or quantitative estimation may be necessary.

NOTE 7—Some lead chromates may contain zirconium or titanium compounds, some of which are insoluble in the dissolving solution, but are not to be considered as extenders, since they have been added to improve the properties of the pigment.

Qualitative Detection of Extenders of Group A

19. Reagents

19.1 *Ammonium Phosphate Solution*—Dissolve 100 g of $(NH_4)_2HPO_4$ in water and dilute to 1 L.

20. Procedure

20.1 Dissolve 1 g of the sample as described in Section 11. Add 5 mL of ethyl alcohol (95 % or absolute) and boil until the chromium is reduced. An insoluble residue at this point denotes the presence of extenders of Group B. Filter if necessary and wash well.

20.2 To the filtrate, add NH_4OH (1+4) until just ammoniacal, boil 5 min, and allow to digest in a warm place until the precipitate has coagulated. Filter, washing well with hot water and reserving the filtrate. Dissolve the precipitate on the filter with HCl (1+1), washing back into the original beaker. Reprecipitate, filter, and wash as before.