



## Standard Test Methods for Analysis of Yellow, Orange, and Green Pigments Containing Lead Chromate and Chromium Oxide Green<sup>1</sup>

This standard is issued under the fixed designation D 126; 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 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 *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:

- D 280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments<sup>2</sup>
- D 521 Test Methods for Chemical Analysis of Zinc Dust (Metallic Zinc Powder)<sup>2</sup>
- D 1013 Test Method for Determining Total Nitrogen in Resins and Plastics<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- E 11 Specification for Wire Cloth Sieves for Testing Purposes<sup>4</sup>

### 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 D 280.

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<sub>4</sub> solution after addition of HClO<sub>4</sub>.

3.1.5 Total lead is determined by precipitation as lead sulfide solution with H<sub>2</sub>SO<sub>4</sub> 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 of HCl to an aliquot followed by addition of BaCl<sub>2</sub> 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<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, addition of NH<sub>4</sub>OH and H<sub>2</sub>SO<sub>4</sub>. The solution is reduced in a Jones reductor, collected under Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution and titrated with KMnO<sub>4</sub> solution.

3.1.9 Extenders are either:

<sup>1</sup> 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 May 29, 1987. Published July 1987. Originally published as D 126 – 22. Last previous edition D 126 – 65 (1981)<sup>ε1</sup>.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 06.03.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.02.



3.1.9.1 Calcium carbonate, calcium sulfate, magnesium carbonate or;

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

(b) (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  $\text{NH}_4\text{OH}$  and filtered.  $\text{CaC}_2\text{O}_4$  is precipitated with calcium oxalate solution and filtered, ashed and weighed as CaO. Alternatively, the precipitate is dissolved in  $\text{H}_2\text{SO}_4$  and titrated with  $\text{KMnO}_4$ . 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 chloroform.

3.2.2 Moisture and other volatile matter are determined in accordance with Test Method A of Test Methods D 280.

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  $\text{FeSO}_4$  solution after addition of  $\text{HClO}_4$ .

## 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.<sup>5</sup> 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 D 1193.

## 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- $\mu\text{m}$ ) 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 E 11.

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.

<sup>5</sup> *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 *Anal. 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.<sup>6</sup>

## MOISTURE AND OTHER VOLATILE MATTER

## 8. Procedure

8.1 Determine moisture and other volatile matter in accordance with Test Method A of Test Methods D 280.

## MATTER SOLUBLE IN WATER

## 9. Procedure

9.1 Place 2.5 g of the sample in a graduated 250-mL flask.

<sup>6</sup> Reference may be made to the following: Payne, H. F., "Organic Coatings Technology," Vol II, John Wiley & Sons, Inc., New York, NY, 1961.

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<sup>7</sup>

### 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  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 500 mL of water to which 30 mL of  $\text{H}_2\text{SO}_4$  (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  $\text{K}_2\text{Cr}_2\text{O}_7$ .

### 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  $\text{HClO}_4$  (70 %), dilute to 250 mL, and titrate potentiometrically with  $\text{FeSO}_4$  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.

11.2 Alternatively, the solution may be reduced by a known excess of  $\text{FeSO}_4$  solution and back-titrated with  $\text{KMnO}_4$  solution in the presence of  $\text{MnSO}_4$ , or excess KI may be added and the liberated iodine titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  solution, using starch indicator. The iodine liberation method is not applicable in the presence of molybdenum.

## TOTAL LEAD<sup>7</sup>

### 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  $\text{NH}_4\text{OH}$  (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  $\text{H}_2\text{S}$  into the solution until precipitation is complete. Settle, filter, and wash with water containing  $\text{H}_2\text{S}$ .

12.2 Rinse the precipitate from the filter (Note 5) into a beaker containing 25 mL of  $\text{HNO}_3$ (1+3) and boil until all PbS has dissolved. Add 10 mL of  $\text{H}_2\text{SO}_4$ (1+1) and evaporate to strong fumes of  $\text{SO}_3$ . 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  $\text{PbSO}_4$ .

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<sup>7</sup>

### 13. Reagents

13.1 *Barium Chloride Solution*—Dissolve 117 g of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  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  $\text{Na}_2\text{CO}_3$  at laboratory temperature, and free of  $\text{SO}_4$ . 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  $\text{Na}_2\text{CO}_3$  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  $\text{BaCl}_2$  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<sup>7</sup>

### 15. Procedure

15.1 Determine  $\text{CO}_2$  by the evolution method on 2.5 g of the sample, using dilute  $\text{HNO}_3$  free of NO or  $\text{NO}_2$  and absorbing the  $\text{CO}_2$  in soda lime or in KOH solution.

## MOLYBDENUM<sup>7</sup>

### 16. Reagents

16.1 *Ferric Sulfate Solution*—Dissolve 20 g of  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$  in 200 mL of water to which has been

<sup>7</sup> 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.



added 50 mL of  $\text{H}_2\text{SO}_4$  (sp gr 1.84) and 20 mL of  $\text{H}_3\text{PO}_4$  (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  $\text{HgCl}_2$  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  $\text{KMnO}_4$  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 ( $\text{Na}_2\text{C}_2\text{O}_4$ ) 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  $\text{H}_2\text{SO}_4$  (1+1). Titrate at once with  $\text{KMnO}_4$  solution, stirring the liquid vigorously and continuously. The  $\text{KMnO}_4$  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  $\text{KMnO}_4$  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  $\text{NH}_4\text{OH}$  (sp gr 0.90) cautiously until a faint precipitate begins to form, then add 15 mL of  $\text{H}_2\text{SO}_4$  (sp gr 1.84) and dilute to 300 mL. Heat to boiling, pass in a rapid stream of  $\text{H}_2\text{S}$  for 15 min, and dilute with 300 mL of hot water. Pass in  $\text{H}_2\text{S}$  for 10 min, boil for 3 min, and cool. Pass in  $\text{H}_2\text{S}$  for 10 min, and let stand at room temperature for 1 h. Filter and wash with  $\text{H}_2\text{SO}_4$  (1+99) saturated with  $\text{H}_2\text{S}$ .

17.2 Rinse the sulfide precipitate into the original beaker and add 20 mL of  $\text{HNO}_3$  (sp gr 1.42) and 5 mL of  $\text{H}_2\text{SO}_4$  (sp gr 1.84) (see Note 5). Cover and heat to fumes. Cool, add 10 mL of  $\text{HNO}_3$  (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  $\text{HNO}_3$ . Dilute to 200 mL and add  $\text{NH}_4\text{OH}$  (1+4) until neutral; then add 10 mL of  $\text{H}_2\text{SO}_4$  (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  $\text{Fe}_2(\text{SO}_4)_3$  solution. Titrate with  $\text{KMnO}_4$  solution. A blank determination should also be made.

## EXTENDERS<sup>7</sup>

### 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  $(\text{NH}_4)_2\text{HPO}_4$  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  $\text{NH}_4\text{OH}$  (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  $\text{HCl}$  (1+1), washing back into the original beaker. Reprecipitate, filter, and wash as before.

20.3 Combine the washings, make just acid with  $\text{HCl}$  (1+1), and evaporate to a volume of about 250 mL. Add 50 mL of  $(\text{NH}_4)_2\text{HPO}_4$  solution, cool, and add 50 mL of  $\text{NH}_4\text{OH}$  (sp gr 0.90). Allow to stand overnight. A precipitate indicates the presence of extenders of Group A.

### Quantitative Determination of Extenders of Group A

## 21. Reagents

21.1 *Ammonium Oxalate Solution*—Dissolve 30 g of ammonium oxalate in water and dilute to 1 L.

21.2 *Ammonium Phosphate Solution*—See Section 19.

## 22. Procedure

22.1 If the sample is a chrome yellow or orange use the procedure given in Section 14 for dissolving and reducing chromium. For other chromium pigments heat gently 2 g of sample in a porcelain dish without ignition until iron blue, if



present, is just decomposed. Transfer to a beaker and dissolve the lead salts in 150 mL of dissolving solution as described in Section 11.

22.2 Add 20 mL of HCl (sp gr 1.19) and digest 1 h at 100°C. Dilute to 300 mL, filter and wash thoroughly. Add NH<sub>4</sub>OH (1+4) to the filtrate and washings until just ammoniacal, boil 5 min and allow to digest in a warm place until the hydroxides and hydrous oxides are coagulated. Filter, washing well with diluted water and reserve the filtrate. Redissolve the precipitate with HCl (1+1) washing back into the original beaker. Re-precipitate, filter and wash as before. Combine the washings with the original filtrate and add 50 mL of ammonium oxalate solution. Filter off the CaC<sub>2</sub>O<sub>4</sub> precipitate on quantitative paper. Transfer to a tarred crucible, ash, ignite at 1300°C, cool in a desiccator, and weigh as CaO. Alternatively, the washed precipitate may be dissolved in H<sub>2</sub>SO<sub>4</sub>(1+1) and the resulting solution titrated hot with 0.1 *N* KMnO<sub>4</sub> solution, as described in the Procedure section under Calcium in Test Methods D 521.

22.3 Make the filtrate from the calcium determination slightly acid with HCl (1+1) and evaporate to 250 mL volume. Add 50 mL of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> solution, cool, and add 50 mL of NH<sub>4</sub>OH (sp gr 0.90). Allow to stand overnight. Filter on suitable quantitative paper, wash with NH<sub>4</sub>OH (1+19), ignite in a platinum crucible at 1050°C for 1 h and weigh. Care must be taken to char the paper slowly before igniting.

22.4 *Calculation*—Calculate the percent of extenders (as oxides) as follows:

$$\text{Calcium oxide, \%} = \text{weight of CaO} \times 50 \quad (2)$$

$$\text{Magnesium oxide, \%} = \text{weight of Mg}_2\text{P}_2\text{O}_7 \times 18.11 \quad (3)$$

The calculation of the amount of extenders as carbonates or sulfates is described in Section 24.

## CALCULATION OF SUBSTANCES OTHER THAN INSOLUBLE LEAD COMPOUNDS

### 23. Calculations Where Extenders Are Absent

23.1 “Insoluble lead compounds” in chrome yellow and chrome orange may consist of PbCrO<sub>4</sub>, PbSO<sub>4</sub>, 2PbCO<sub>3</sub> · Pb(OH)<sub>2</sub>, PbO, or PbMoO<sub>4</sub>. The first two are characteristic of the chrome yellows, the first, third, and fourth of the basic chrome oranges, and the first, second, and last of molybdate oranges. For purpose of determining conformance with specification requirements, where “insoluble lead compounds” are defined as above, make the following calculations if extenders are absent:

23.2 If molybdenum is present, calculate the percent of PbMoO<sub>4</sub> from the titration of Section 17 as follows:

$$A = \text{PbMoO}_4, \% = \text{mL titration} \times \text{normality of KMnO}_4 \times 12.24 \quad (4)$$

23.3 Calculate the percent of PbCrO<sub>4</sub> from the titration of Section 11 as follows:

$$B = \text{PbCrO}_4, \% = \text{mL titration} \times \text{normality of FeSO}_4 \times 10.77 \quad (5)$$

23.4 Calculate the percent of total lead as oxide and the percent of excess PbO from the analysis of Section 12 as follows:

$$C = \text{PbO, \%} = \text{grams of PbSO}_4 \times 147.2 \quad (6)$$

$$D = \text{excess PbO, \%} = C - (0.6906 B + 0.6078 A) \quad (7)$$

23.5 Calculate the sulfate as SO<sub>3</sub> from the analysis of Section 14 as follows:

$$E = \text{SO}_3, \% = \text{grams of BaSO}_4 \times 34.3 \quad (8)$$

23.5.1 If *E* is equal to or greater than 0.3587 *D*, the % of PbSO<sub>4</sub> equals 1.3587 *D*, and the % total insoluble lead compounds equals *A* + *B* + 1.3587 *D*.

23.5.2 If *E* is less than 0.3587 *D*, the percentage of PbSO<sub>4</sub> equals 3.788 *E*, and a new excess of PbO is calculated as follows:

$$F = \text{Excess PbO, \%} = D - 2.788 E \quad (9)$$

23.6 Calculate the percent of CO<sub>2</sub> from the analysis of Section 15 as follows:

$$G = \text{CO}_2, \% = \text{grams of CO}_2 \times 40 \quad (10)$$

23.6.1 If *G* is equal to or greater than 0.1314 *F*, the percent of basic lead carbonate (2 PbCO<sub>3</sub> · Pb(OH)<sub>2</sub>) is 1.1584 *F* and the percent of total insoluble lead compounds is *A* + *B* + 3.788 *E* + 1.1584 *F*.

23.6.2 If *G* is appreciably in excess, extenders are probably present. If *G* is less than 0.1314 *F*, the percent of 2 PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> is 8.813 *G* and the excess PbO is:

$$H = \text{Excess PbO, \%} = F - 7.608 G \quad (11)$$

23.6.2.1 The percent of total insoluble lead compounds is *A* + *B* + 3.788 *E* + 8.813 *G* + *H*.

## 24. Calculations Where Extenders Are Present

24.1 If extenders are present, calculate the CO<sub>2</sub> equivalent as follows:

$$\begin{aligned} I &= \text{CO}_2 \text{ equivalent of extenders} \\ &= \text{CaO, \%} \times 0.786 + \text{MgO, \%} \times 1.100 \end{aligned} \quad (12)$$

24.2 If *I* is less than *G*, use *G* − *I* as the net CO<sub>2</sub> for purposes calculating the 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> content of the pigment.

$$\text{Total extenders} = \text{CaO, \%} + \text{MgO, \%} + I \quad (13)$$

24.3 If *I* is greater than *G*, some of the extender is present as CaSO<sub>4</sub>(Note 8). Calculate the total percent of extenders as follows:

$$J = \text{CO}_2 \text{ equivalent of MgO} = \text{MgO \%} \times 1.100 \quad (14)$$

$$K = \text{CO}_2 \text{ present as CaCO}_3 = G - J \quad (15)$$

$$\text{CaCO}_3, \% = 2.73 K \quad (16)$$

$$L = \text{CaO present as sulfate, \%} = \text{CaO, \%} \pm 1.27 K \quad (17)$$

$$\text{CaSO}_4, \% = 2.43 L \quad (18)$$

$$\text{SO}_3 \text{ combined as CaSO}_4, \% = 1.43 L \quad (19)$$

24.3.1 *E* − 1.43 *L* equals the net SO<sub>3</sub> to be used for calculating the PbSO<sub>4</sub> content of the pigment. If *I* is greater than *G*, no calculation of 2PbCO<sub>3</sub> · Pb(OH)<sub>2</sub> is necessary, and the excess PbO is given by *F*.

$$\text{Total extenders, \%} = 2.100 \times \text{MgO, \%} + 2.73 K + 2.43 L \quad (20)$$

NOTE 8—It is impractical to detect by chemical means whether a



pigment contains  $\text{CaCO}_3$  and  $\text{PbSO}_4$ , or  $\text{CaSO}_4$  and  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ . This calculation assumes the former as more probable.

## PURE CHROME GREEN AND REDUCED CHROME GREEN

### ORGANIC COLORS AND LAKES

#### 25. Procedure

25.1 Determine organic colors and lakes in accordance with Section 7.

### MOISTURE AND OTHER VOLATILE MATTER

#### 26. Procedure

26.1 Determine moisture and other volatile matter in accordance with Section 8.

### MATTER SOLUBLE IN WATER

#### 27. Procedure

27.1 Determine matter soluble in water in accordance with Section 9.

### IRON BLUE

#### 28. Procedure

28.1 Determine the total nitrogen (by the Kjeldahl-Gunning method) (Note 9) on 1 g of the sample, adding 2 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  before digestion for at least  $2\frac{1}{2}$  h.

NOTE 9—For further details refer to Test Method D 1013.

28.2 *Calculation*—Calculate the percent of iron blue as follows:

$$\text{Iron blue, \%} = \text{nitrogen, \%} \times 3.4 \quad (21)$$

NOTE 10—Qualitative tests may be made for other nitrogen-containing blue pigments.

### LEAD CHROMATE

#### 29. Reagents

29.1 *Ferrous Sulfate, Standard Solution* (0.3 N)—See 10.2.

29.2 *Potassium Permanganate Standard Solution* (0.1 N)—Prepare as described in 16.3. Standardization is unnecessary except for the alternative procedure given in Section 30.

#### 30. Procedure

30.1 Mix thoroughly 1 g of sample with at least 10 g of  $\text{Na}_2\text{O}_2$  in a 30-mL pure iron crucible. Heat gently until the fusion is complete; then heat strongly, rotating the crucible with iron tongs (not Nichrome or chromium plate) for a few minutes to ensure complete fusion. Allow to cool; then transfer the crucible and cover to a beaker containing 250 mL of water. When the action has ceased, rinse and remove the crucible and cover, and boil for at least 10 min to destroy excess peroxide. Make just acid with  $\text{H}_2\text{SO}_4$  (1+1) and add about 35 mL in excess. Add 2.5 mL of 0.1 N  $\text{KMnO}_4$  solution and heat to boiling. Add 10 mL of  $\text{HCl}$  (1+4) and boil to reduce manganese and lead as indicated by clearing of the solution. If the solution

is not clear after 5 min boiling, add 5 mL of additional  $\text{HCl}$  (1+4), and repeat until a clear solution is obtained. Cool and titrate with  $\text{FeSO}_4$  solution on a potentiometric apparatus; or alternatively, add a measured excess of  $\text{FeSO}_4$  and back-titrate with  $\text{KMnO}_4$  solution in the presence of  $\text{MnSO}_4$ .

### BARIUM SULFATE AND INSOLUBLE SILICEOUS MATERIAL<sup>8</sup>

#### 31. Procedure

31.1 Heat gently 1 g of sample in a porcelain dish without ignition until the iron blue is just decomposed. Transfer to a beaker and dissolve the lead salts as described in Section 11, warming if necessary. Filter through a tared Gooch crucible, wash thoroughly, ignite at 600 to 800°C, and weigh.

31.2 *Calculation*—Calculate the percent of  $\text{BaSO}_4$  and insoluble siliceous material as follows:

$$\begin{aligned} \text{BaSO}_4 \text{ and insoluble siliceous material, \%} & \quad (22) \\ &= \text{weight of precipitate} \times 100 \end{aligned}$$

### TOTAL LEAD

#### 32. Procedure

32.1 Determine total lead on the filtrate from the determination of  $\text{BaSO}_4$  and insoluble matter (Section 31) in accordance with the directions of Section 12.

### SULFATE

#### 33. Procedure

33.1 After decomposition of the iron blue in 1.25 g of sample as described in Section 31, digest the residue with 20 mL of  $\text{HCl}$  (sp gr 1.19) at 100°C until solution is complete. Add 300 mL of water and heat to boiling. Filter and wash thoroughly. Determine sulfate on the filtrate and washings as described in Section 14.

### CALCIUM OXIDE SOLUBLE IN ACID

#### 34. Reagents

34.1 *Ammonium Oxalate Solution*—See 21.1.

#### 35. Procedure

35.1 Decompose 2 g of sample as described in Section 31. Add 20 mL of  $\text{HCl}$  (sp gr 1.19) and proceed in accordance with 21.1 to the end of the calcium determination.

35.2 *Calculation*—Calculate the percent of  $\text{CaO}$  soluble in acid as follows:

$$\text{CaO soluble in acid, \%} = \text{grams CaO} \times 50 \quad (23)$$

<sup>8</sup> See Note 7 of Section 18.

## EXTENDERS

## CALCULATION OF INSOLUBLE LEAD COMPOUNDS

### 36. Procedure

36.1 The method described in Sections 31, 34, and 35 suffices for the detection and estimation of all common extenders except  $\text{MgCO}_3$ . This may be tested for the filtrate from the CaO determination by the method described in Section 22.

### 37. Procedure

37.1 The insoluble lead compounds may be calculated by the methods of Sections 23 and 24.

## CHROMIUM OXIDE GREEN

### ORGANIC COLORS AND LAKES

#### 38. Procedure

38.1 Determine organic colors and lakes in accordance with Section 7.

### MOISTURE AND OTHER VOLATILE MATTER

#### 39. Procedure

39.1 Determine in accordance with Section 8.

### MATTER SOLUBLE IN WATER

#### 40. Procedure

40.1 Determine in accordance with Section 9.

### TOTAL CHROMIUM AS CHROMIUM OXIDE

#### 41. Procedure

41.1 Using 0.4 g of the sample proceed as in Section 30.

41.2 *Calculation*—Calculate the percent of chromium as  $\text{Cr}_2\text{O}_3$  as follows:

$$\text{Cr}_2\text{O}_3, \% = \text{mL titration} \times \text{normality of FeSO}_4 \times 63.34 \quad (24)$$

#### 42. Precision and Bias

42.1 Data are not available to determine the precision and bias of these test methods. There are no plans at present to obtain such data.

#### 43. Keywords

43.1 chromium oxide green pigment; green pigment containing lead chromate and chromium oxide; lead chromate pigment; lead containing pigment; molybdate pigment; orange pigment containing lead chromate and chromium oxide; yellow pigment containing lead chromate and chromium oxide

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).*