Designation: D2351 – 90 (Reapproved 2015)

Standard Test Method for Sulfide in White Pigment Separated from Solvent-Reducible Paints[1]

This standard is issued under the fixed designation D2351; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of sulfide sulfur in white pigment separated from solvent-reducible paints.

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

1.3 *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:*[2]

D215 Practice for the Chemical Analysis of White Linseed Oil Paints (Withdrawn 2005)[3]

D1193 Specification for Reagent Water

D2371 Test Method for Pigment Content of Solvent-Reducible Paints

3. Summary of Test Method

3.1 The extracted pigment is placed in a flask with mossy zinc. The hydrogen sulfide generated by addition of HCl reacts with lead nitrate in an absorption flask forming lead sulfide. The lead sulfide is dissolved with nitric acid (HNO_3) and the lead determined as lead sulfate in accordance with Test Methods D215.

3.2 A rapid method is also described.

4. Significance and Use

4.1 Sulfide containing pigments such as lithopone have been used in paints in varying degrees in the past years. As such it is useful to formulators and users to be able to monitor the amount of this compound in whole paints.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent grade water conforming to Type II of Specification D1193.

5.3 *Ammoniacal Cadmium Chloride or Zinc Sulfate Solution*—Dissolve 8 g of cadmium chloride ($CdCl_2 \cdot 2H_2O$) in 200 mL of water and add 200 mL of ammonium hydroxide (NH_4OH, sp gr 0.90); or, dissolve 200 g of zinc sulfate ($ZnSO_4 \cdot 7H_2O$) in 1080 mL of water and 920 mL of NH_4OH (sp gr 0.90).

5.4 *Hydrochloric Acid* (sp gr 1.19)—Concentrated HCl.

5.5 *Lead Nitrate, Alkaline Solution*—Into 100 mL of potassium hydroxide (KOH) solution (56 g in 140 mL of water) pour a saturated solution of lead nitrate ($Pb(NO_3)_2$) (250 g in 500 mL of water) until the precipitate ceases to redissolve, stirring constantly while mixing. Let settle, filter through a glass filter, and dilute the clear filtrate with an equal volume of water. About 3 volumes of the $Pb(NO_3)_2$ solution will be required for 1 volume of the KOH solution.

5.6 *Mossy Zinc.*

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

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[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.

[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.

5.7 *Nitric Acid* (1+4)—Mix 1 volume of concentrated HNO_3, (sp gr 1.42) with 4 volumes of water.

5.8 *Potassium Iodate, Standard Solution*—Dissolve 3.6 g of potassium iodate (KIO_3) and 39 g of potassium iodide (KI) in 1 L of water. For general work the theoretical sulfur titer of this solution should be used; for special work the solution may be standardized against similar material, such as a lithopone of known sulfide sulfur content. The theoretical titer is based on standard sodium oxalate ($Na_2C_2O_4$) and is obtained as follows: To 300 mL of water in a 600-mL flask, preferably glass-stoppered, add 10 mL of HCl (sp gr 1.19) and 1 g of KI. Cool and add 10 mL of 0.1 *N* potassium permanganate ($KMnO_4$) solution which has been standardized against $Na_2C_2O_4$. Swirl gently, stopper, and let stand for 5 min. Titrate the liberated iodine with standard sodium thiosulfate ($Na_2S_2O_3$) solution until the color fades. Then add 10 mL of starch solution and continue the titration until the blue color is destroyed. Repeat the titration, except substitute 10 mL of the KIO_3 for the $KMnO_4$ solution. Calculate the normality of the KIO_3 solution as follows.

5.8.1 *Standardization Calculation for Theoretical Sulfur Titer:*

$$B = \frac{v_1 \times N}{V_2} \quad (1)$$

where:

B = normality of KIO_3,
V_1 = standard $Na_2S_2O_3$ solution, mL, required to titrate 10 mL of $KMnO_4$ solution,
N = normality of standardized $KMnO_4$ solution, and
V_2 = standard $Na_2S_2O_3$ solution, mL, required to titrate 10 mL of KIO_3 solution.

5.8.2 *Standardization Against Known Pigment:*

$$C = (A \times S)/(V \times 100) \quad (2)$$

where:

A = sulfur in known pigment, %
C = sulfide equivalent of the KIO_3 solution, g/mL,
S = pigment, g, and
V = KIO_3 solution required to titrate known pigment, mL.

5.9 *Starch Indicator* (for Sulfur Titration)—To 1 L of boiling water add a cold suspension of 6 g of starch in 100 mL of water and boil vigorously for 5 min. Cool the solution, add 6 g of zinc chloride ($ZnCl_2$) dissolved in 50 mL of cold water, thoroughly mix, and set aside for 24 h. Decant the clear supernatant liquid into a suitable container, add 3 g of KI, and mix thoroughly.

5.9.1 (*Optional*) Prepare an emulsion of 6 g of soluble starch in 25 mL of water, add a solution of 1 g of sodium hydroxide (NaOH) in 10 mL of water, and stir the solution until it gels. Dilute to 1 L with water, add 3 g of KI, and mix thoroughly.

6. Preparation of Sample

6.1 Separate and prepare the pigment for this determination in accordance with Test Method D2371.

7. Procedure

7.1 Place 0.5 to 1 g of the pigment in a flask with about 10 g of "feathered" or mossy zinc and add 50 mL of water; insert a stopper carrying a separatory funnel and an exit tube. Run in 50 mL of HCl (sp gr 1.19) from the funnel, having previously connected the exit tube to two absorption flasks in series; the first flask containing 100 mL of alkaline lead nitrate solution, the second flask, 50 mL of the same solution as a safety device. After all of the acid has run into the evolution flask, heat slowly, finally boiling until the first appearance of steam in the first absorption flask.

7.2 Disconnect, let the lead sulfide (PbS) settle, filter, and wash with cold water, then with hot water until neutral to litmus paper and until the washings give no test for lead. Dissolve the PbS precipitate in hot HNO_3 (1+4) and determine the lead as lead sulfate ($PbSO_4$) in accordance with Test Method D215.

7.3 For very rapid work, the evolved hydrogen sulfide (H_2S) may be absorbed in an ammoniacal $CdCl_2$ or $ZnSO_4$ solution (5.3) contained in two flasks connected in series, the contents of the absorption flasks washed into a vessel with cold water and diluted to about 1 L, acidified with HCl (sp gr 1.19), and titrated with standard KIO_3 solution using starch indicator (5.9).

8. Calculation

8.1 Calculate the percent of sulfide sulfur, *E*, as follows:

NOTE 1—The percent of sulfide sulfur can be calculated from the percent of total zinc and zinc soluble in acetic acid (2 to 3 %), assuming the sulfide to be zinc sulfide (ZnS). See section on Total Zinc of Test Method D215.

$$E = [(P \times 0.1054)/S] \times 10C \quad (3)$$

where:

P = $PbSO_4$ formed, g, and
S = sample used, g.

$$E = (AV/S) \times 100 \quad (4)$$

where:

A = sulfide equivalent of the KIO_3 solution, g/mL,
V = KIO_3 solution required for titration of specimen, mL, and
S = sample used, g.

9. Precision

9.1 Data are not available to determine the precision of this test method. There are no plans at present to obtain such data. This test method has been in use for several years and is considered acceptable.

10. Keywords

10.1 sulfide; white pigment