Doc: CHD 21 (24871)WC February 2024 IS 44 : XXXX

BUREAU OF INDIAN STANDARDS

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Draft Indian Standard

IRON OXIDE PIGMENTS FOR PAINTS — SPECIFICATION

(Third Revision of IS 44)

(ICS 87.060.10)

| Raw materials for Paints, Varnishes and | Last Date for Comments: 20 April 2024 |
|---|---------------------------------------|
| Related Product Sectional Committee, CHD 21 | |

Raw materials for Paints, Varnishes and Related Product Sectional Committee, CHD 21

FOREWORD

(Formal Clause shall be added later)

The initial set of standards, including IS 44 : 1950 for black oxide of iron, IS 45 : 1950 for manufactured red oxide of iron, IS 46 : 1950 for natural red oxide of iron, IS 47 : 1950 for ochre, IS 48 : 1950 for natural sienna (raw and burnt), and IS 49 : 1950 for natural umber (raw and burnt), were first issued in 1950. These standards were developed through collaborative efforts involving representatives from manufacturers and various government departments and authorities.

In 1969, all these standards underwent amalgamation into a revised version IS 44 : 1969, titled 'Specification for iron oxide pigments for paints (first revision)'. This updated specification categorized the material into six classes, aligning with the materials covered in the original set of standards. Notable changes included more stringent requirements for sulphur and sulphur compounds in class 2 material (manufactured red oxide), modified and unified requirements for volatile matter and water-soluble matter in class 3 to 6, a revised method for determining carbonates as carbon dioxide, and the introduction of new limits for ferrous iron, calcium compounds, and manganese content for specific classes.

In the second revision in 1991, classes were designated as grades. Requirements for in additional grade, namely, iron oxide yellow, were added. Requirements for total iron (as Fe_2O_3) for the Grades 2, 3 and 4; volatile matter for Grade 4 and matter soluble in water for Grade 1 were

modified. Three new requirements (a) sum of water soluble chloride and sulphate, (b) pH of aqueous extract, and (c) loss on ignition were added. The requirements for sulphur and compounds of sulphur were deleted.

This third revision has been undertaken to align the product standards with current market demands, enhancing its acceptance and relevance. Notable changes include:

- a) The material classification has been restructured into groups based on colours, categories reflecting iron content (expressed as iron (III) oxide), types based on water-soluble matter content and total water-soluble chlorides and sulfates (expressed as Cl⁻ and SO₄²⁻ ions), grades reflecting residue on sieve, and classes based on the origin of the material. This adjustment replaced the existing seven grades, bringing the standards in line with current market practices.
- b) Additionally, the requirements for each classification and their corresponding test methods have been updated. For instance, the test method for color measurement, staining power, and undertone have been revised, accompanied by updated requirements.
- c) To address health and safety concerns, restrictions have been introduced for lead and toxic heavy metals.
- d) Lastly, various editorial corrections and references have been updated to ensure accuracy and relevance in the revised standards

During this revision assistance has been drawn from ISO 1248 : 2006 "Iron oxide pigments-specification and method of test."

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'. The number of significant places retained in the rounded-off value should be the same as that of the specified value in this standard.

Draft Indian Standard

IRON OXIDE PIGMENTS FOR PAINTS — SPECIFICATION

(Third Revision)

1 SCOPE

This standard prescribes requirements and methods of sampling and test for natural and synthetic iron oxide pigments for paints.

2 REFERENCES

The standards listed below contain provisions which, through reference in this text constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

| IS No. | Title |
|--------------------------|--|
| IS 33 : 1992 | Inorganic pigments and extenders for paints — Methods of sampling and test (<i>third ravision</i>) |
| | |
| IS 101 (Part 4/ Sec 2) : | |
| | |
| IS 1070 : 2023 | Reagent grade water — Specification (fourth revision) |
| IS 1303 : 1983 | Glossary of terms relating to paints (second revision) |
| IS 2263 : 1979 | Methods of preparation of indicator solutions (first revision) |
| IS 2316 : 1990 | Methods of preparation of standard solutions for colorimetric and volumetric analysis (<i>second revision</i>) |

3 TERMINOLOGY

For the purpose of this standard, definitions given in IS 33 and IS 1303 shall apply.

4 CLASSIFICATION

4.1 General

Iron oxide pigments are classified as follows:

- a) by groups depending on their colour;
- b) by categories depending on their iron content, expressed as iron (III) oxide;
- c) by types depending on their content of water-soluble matter and their total content of water-soluble chlorides and sulfates, expressed as the ions Cl⁻ and SO₄²⁻;
- d) by grades depending on their residue on sieve;
- e) by classes depending on their origin.

4.2 Criteria for Classification

4.2.1 Groups

Depending on their colour, iron oxide pigments are divided into four groups:

- a) reds;
- b) yellows;
- c) browns;
- d) blacks.

4.2.2 Categories

Depending on their minimum iron content, expressed as iron (III) oxide, iron oxide pigments are divided into the categories (A, B and C) shown in Table 1.

| Group | Category | Minimum iron oxide content, expressed as Fe ₂ O ₃ % (by mass) | Colour Index No |
|---------|----------|--|--|
| Ded | А | 95 | Pigment red 101 77491 |
| Keu | В | 70 | Pigment red 102 |
| | С | 50 | 77491 |
| Vallow | A 83 | | Pigment yellow 42 77492 |
| Yellow | В | 70 | Pigment yellow 43 |
| | С | 50 | 77492 |
| | А | 87 | Pigment brown 6 77491, 77492 or 77499 |
| Brown | В | 70 | Pigment brown 7 |
| | С | 30 | 77491, 77492 and/or 77499 |
| Plack A | | 95 | Pigment black 11 |
| DIACK | В | 70 | 77499 |

Table 1 — Categories of iron oxide pigments

(*Clause* 4.2.2)

4.2.3 Types

Depending on their content of water-soluble matter and their total content of water-soluble chlorides and sulfates, iron oxide pigments are divided into the types shown in Table 2.

 Table 2 — Types of iron oxide pigments

(*Clause* 4.2.3)

| Characteristics | Type 1 | Тур | | |
|---------------------------|------------|-----------------------|------------|----------------|
| | Red and | Red and | Yellow and | Method of test |
| | brown only | brown only | black only | |
| Matter soluble in | | | | |
| water | | | | |
| (determined | < 0.2 | > 0.2 and < 1.0 | < 1.0 | 10.22 |
| after drying at | ≥ 0.5 | > 0.5 and ≥ 1.0 | ≥ 1.0 | 15 55 |
| 105 °C), % (by | | | | |
| mass) | | | | |
| Sum of water- | | | | |
| soluble chlorides | | | | |
| and sulfates, | | | | |
| expressed as the | ≤ 0.1 | - | - | Annex B |
| ions Cl^- and | | | | |
| SO4 ²⁻ , % (by | | | | |
| mass) | | | | |

4.2.4 Grades

Depending on their residue on sieve, iron oxide pigments are divided into the grades shown in Table 3.

Table 3 — Grades of iron oxide pigments

(*Clause* 4.2.4)

| Charactaristic | Grade 1 | Grade 2 | Grade 3 | Mothod of tost |
|--|---------|-----------------|---------------|----------------|
| Characteristic | Red, ye | Wiethou of test | | |
| Residue on sieve (45 µm), % (by mass) | ≤ 0.01 | > 0.01 - ≤ 0.1 | > 0.1 - ≤ 1.0 | IS 33 |

4.2.5 Classes

Depending on their origin, iron oxide pigments are divided into four classes:

- a) Class A manufactured pigment without extenders;
- b) Class B natural pigments without extenders;
- c) Class C mixtures of natural and manufactured pigments without extenders.

5 REQUIREMENTS

5.1 Composition

The iron oxide pigments covered by this standard consist mainly of iron oxides and hydrated iron oxides. Their colours are usually red, yellow, brown or black. The colour shall be entirely due to inorganic compounds of iron.

5.2 Designation

The designation of an iron oxide pigment shall include the following.

- a) An indication of the colour group to which it belongs, to which may be added a more precise indication of the actual colour (preferably by means of Colour Index No).
- b) A reference to this standard, that is, IS 44.
- c) The category of the iron oxide pigment.
- d) Its type.
- e) Its grade.
- f) Its class.

5.3 Form and Condition

The material shall be supplied in the form of dry powder or in such a condition that it may be reduced to powder form by crushing, without grinding action, under palette knife.

5.4 Lead Restriction

The material shall be tested for restriction from lead in accordance with ICP-OES or AAS method of IS 101 (Part 8/Sec 5). When thus tested the material shall not contain lead or compounds of lead or mixtures of both, calculated as metallic lead exceeding 90 ppm.

NOTE — When no lead is used during production, the product is considered lead free.

5.5 Heavy Metal Restriction

Product shall not be manufactured using mercury and mercury compounds, cadmium, chromium VI, arsenic, antimony, and their oxides. The material shall not contain more than 0.1 percent by weight in total of above toxic heavy metals in the form of natural impurities or impurities entailed by the production process which are contained in the raw material when tested by the relevant Atomic Absorption Spectroscopic methods.

5.6 All groups and category of the material shall conform to the requirements given in Table 4.

| <u>e</u> 1 | | Requirement Depending on Group and Category | | | | | | | | | | Method | |
|------------|---|---|-----|----|----|--------|----|----|-------|----|-----|--------|---------|
| SI No | Characteristics | | Red | | | Yellow | V |] | Brown | 1 | Bla | ıck | of Test |
| 140. | | | В | С | Α | В | С | Α | B | С | Α | В | Ref to. |
| i) | Total iron, expressed as iron(III) oxide (Fe ₂ O ₃), | 05 | 70 | 50 | 83 | 70 | 50 | 87 | 70 | 30 | 05 | 70 | Annex A |
| 1) | determined on the pigment after drying at 105 | 95 | 70 | 50 | 05 | 70 | 50 | 07 | 70 | 50 | 75 | 70 | |

Table 4 Requirement for Iron Oxide Pigment for Paints (Clause 5.6)

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| | °C, % (by mass) min | | | | | | | | | | | | | | |
|-------|---|---------|--|---------------------------|------|-------------------------------|------------|---------|-------|------------|------|----------|-----|---------|--|
| ii) | Volatile matter, percent by mass, Max | r | 1.0 | 1.5 | 2.5 | 1.0 | 2.5 | 2.5 | 1.0 | 2.5 | 2.5 | 1.0 | 2.5 | IS 33 | |
| :::) | Matter soluble in water, percent by | Type I | | ≤ 0.3 - ≤ 0.3 - | | | 16.22 | | | | | | | | |
| 111) | mass | Type II | > 0.3 | 3 and <u>s</u> | ≤1.0 | | ≤ 1.0 | | > 0. | 3 and : | ≤1.0 | ≤ 1 | 1.0 | 15 55 | |
| | Sum of water-soluble chloride and | | | | | | | | | | | | | | |
| iv) | sulphate expressed as Cl ⁻ and SO4 ²⁻ , | Type 1 | | ≤ 0.1 | | | - | | | ≤ 0.1 | | - | - | Annex B | |
| | percent by mass, Max | | | | | | | | | | | | | | |
| | Pasidua an siava (15 um) % by | Grade 1 | ≤ 0.01 | | | | | | | | | | | | |
| v) | mass | Grade 2 | > 0.01 and ≤ 0.1 | | | | | | IS 33 | | | | | | |
| | mass | Grade 3 | > 0.1 and ≤ 1.0 | | | | | | | | | | | | |
| vi) | Oil absorption | | | | | $\pm 10\%$ of approved sample | | | | | | | | IS 33 | |
| vii) | <i>p</i> H of aqueous extract | | Within $\pm 1 pH$ scale unit of approved sample | | | | | | | IS 33 | | | | | |
| viii) | Loss on ignition, percent by mass, Ma | ıx | | - | | | 13 | | | - | | - | - | Annex C | |
| iv) | Colour | | ΔE (mass tone and reduced tone) ≤ 1.0 | | | | | | | | | | | | |
| IX) | Colour | | | | ١ | with re | spect | to app | roved | sampl | e | | | Annex D | |
| x) | Strength percentage | | 100 ± 5 with respect to approved sample | | | | | | | | | | | | |
| | Total calcium, expressed as calcium | Class a | 0.2 | | | | | | | | | | | | |
| | oxide, determined on the pigment | Class a | 0.3 | | | | | Annor E | | | | | | | |
| XI) | after drying at 105 °C, percentage | Class b | | | | | | 5.0 | | | | | | Annex E | |
| | by mass, <i>Max</i> | & c | | | | | | 5.0 | | | | | | | |

6 PACKING AND MARKING

6.1 Packing

The material shall be suitably packed as agreed to between the purchaser and the supplier.

6.2 Marking

6.2.1 The containers shall be marked with the following information:

- a) Name of the material;
- b) Group, Category, Type, Grade and Class of the material;
- c) Indication of the source of manufacture;
- d) Net mass of the material;
- e) Batch No. or Lot No. in code or otherwise; and
- f) Month and year of manufacture
- g) Expiry date/shelf life/best before
- h) Lead content (Maximum);
- i) Toxic heavy metals content
- j) A cautionary note as below:
 - a. Keep out of reach of children; or
 - b. This product may be harmful if swallowed or inhaled

6.2.2 The packages may also be marked with the BIS Certification Mark.

6.2.3 BIS Certification Marking

The product(s) conforming to the requirements of this standard may be certified as per the conformity assessment schemes under the provisions of the Bureau of Indian Standards Act, 2016 and the Rules and Regulations framed there under, and the products may be marked with the Standard Mark.

7 TEST METHODS

7.1 Quality of Reagents

Unless specified otherwise, pure chemicals and distilled water (see IS 1070) shall be employed for tests.

NOTE – 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

8 SAMPLING

Representative samples of the material shall be drawn as prescribed under IS 33.

ANNEX A

[*Table* 4, *Sl No*. (i)]

DETERMINATION OF TOTAL IRON

A-1 GENERAL

Three methods of determination, Method 1 — External indicator method, Method 2 — Internal indicator method and Method 3 – Aluminum reduction method; have been prescribed, in case of dispute, Method 1 shall be used.

A-2 METHOD 1 — EXTERNAL INDICATOR METHOD

A-2.1 Outline of the Method

The ferric iron is reduced to ferrous state by stannous chloride and solution titrated against standard potassium dichromate solution using potassium ferricyanide as external indicator.

A-2.2 Reagents

A-2.1.1 *Hydrochloric Acid* — concentrated.

A-2.1.2 Standard Potassium Dichromate Solution — 0.1 N (see IS 2316).

A-2.1.3 Stannous Chloride Solution

Dissolve by heating 60 g of pure stannous chloride in a mixture of 400 ml of concentrated hydrochloric acid and 600 ml of water until the solution is complete. Cool, add a few pieces of

granulated tin and preserve the solution in an air-tight amber-coloured bottle to prevent oxidation.

A-2.1.4 Mercuric Chloride Solution — saturated.

A-2.1.5 Potassium Ferricyanide Indicator — (see IS 2263).

A-2.2 Procedure

A-2.2.1 Weigh accurately 0.25 g to 0.40 g of the material, dried as prescribed under IS 33 and transfer to a 500 ml conical flask. Add 25 ml of the hydrochloric acid and warm gently until clear solution is obtained. The addition of a few drops of stannous chloride solution after adding the acid gently assists dissolution of iron. If the solution of the sample is still not clear, digest the solution on a hot-plate, a evaporate to dryness and redissolve in hydrochloric acid as above. Filter into a long necked flask and dilute the solution to about 50 ml. Bring the solution to boil and keeping the solution hot, add stannous chloride solution in drops until the solution is colourless. It is best to keep a watch-glass on the flask while adding the stannous chloride is added by mistake, add potassium permanganate to the solution until a yellow colour appears, then adding one or two drops in excess.

NOTE — Only a very slight excess of stannous chloride solution should be added to form a slight silky white precipitate with mercuric chloride solution added subsequently. Reduction should be repeated if a black or grey precipitate is obtained.

Cool the solution rapidly and dilute to 150 ml to 200 ml with water. Add a slight excess of mercuric chloride solution (normally 5 ml) when a silky white precipitate will be formed.

A-2.2.2 Mix thoroughly and wash down the sides of the flask with cold water. Titrate the contents of the flask against standard potassium dichromate solution using potassium ferricyanide as external indicator.

A-2.2.3 Calculation

Total iron (as Fe₂O₃), percent by mass = $\frac{7.984 \times N \times V}{M}$

where,

N = normality of standard potassium dichromate solution;

V = volume, in ml, of standard potassium dichromate solution used; and

M =mass, in g, of material taken.

A-3 METHOD 2 — INTERNAL INDICATOR METHOD

A-3.1 Outline of the Method

The ferric iron is reduced by stannous chloride to ferrous state titrated against standard potassium dichromate solution using sodium diphenylamine sulphonate solution as indicator.

A-3.2 Reagents

A-3.2.1 Standard Potassium Dichromate — 0.1 N (see IS 2316).

A-3.2.2 Stannous Chloride Solution — Same as A-2.1.3.

A-3.2.3 Mercuric Chloride Solution — saturated.

A-3.2.4 Sulphuric Acid – Phosphoric Acid Mixture

Add slowly 150 ml of concentrated sulphuric acid to 700 ml of water with continuous stirring. Add to this 150 ml of phosphoric acid (85 percent w/w).

A-3.2.5 Sodium Diphenylamine Sulphonate Indicator Solution

Dissolve 0.2 to 0.3 g of sodium diphenylamine sulphonate in 100 ml of hot water. Cool and store in amber-coloured bottle.

A-3.3 Procedure

A-3.3.1 Proceed exactly as given in A-2.2.1.

A-3.3.2 Add 15 ml of sulphuric acid-phosphoric acid mixture and dilute to 100 ml. Add 5 drops of sodium diphenylamine sulphonate indicator solution and titrate with standard dichromate solution with constant stirring until the solution begins to darken. Complete the titration by adding the dichromate solution in drops until a permanent violet colouration is obtained. Carry out a blank determination with the reagents alone using the same procedure.

A-2.2.3 Calculation

Total iron (Fe₂O₃), percent by mass =
$$\frac{(V_1 - V_2) \times N \times 7.984}{M}$$

where

 V_1 = volume, in ml, of the standard potassium dichromate solution required to titrate test solution;

 V_2 = volume, in ml, of the standard potassium dichromate solution required for blank;

N = normality of standard potassium dichromate solution; and

M = mass, in g, of the material taken for determination.

A-3 METHOD 3 — ALUMINIUM REDUCTION METHOD

A-3.1 Outline of the Method

The ferric iron is reduced by aluminum to ferrous state titrated against standard potassium dichromate solution using sodium diphenylamine sulphonate solution as indicator.

A-3.2 Reagents

A-3.2.1 Potassium Dichromate (K₂Cr₂O₇)

A-3.2.1.1 Preparation of 250 ml (N/10) K₂Cr₂O₇ solution

Weigh out accurately 1.2 g-1.6 g (w_1) of K₂Cr₂O₇ into a 250 ml volumetric flask. Shake to dissolve the salt. Make up the volume with distilled water and shake well to mix uniformly.

A-3.2.1.2 Strength of $K_2Cr_2O_7$ solution $-\frac{w_1}{1.2258} \times \frac{N}{10}$

A-3.2.2 Concentrated HCl

A-3.2.3 Al-foil (A. R. Grade)

A-3.2.4 NH₄HF₂ / Syrupy H₃PO₄ (85%)

A-3.2.5 *Barium Diphenylaminesulphonate (BDS) Indicator Solution* — saturated aqueous solution (dissolve 0.2 g of the drystuff in 100 ml distilled water).

A-3.3 Procedure

Accurately weigh 0.4 g to 0.6 g of the sample (say, W g) in a 500 ml conical flask add 25 ml of conc. HCl, cover with a funnel and heat gently till dissolution. Cool and add 25 ml of distilled water, heat just to boiling and add a few pieces of Al-foils to the solution, heat carefully and shake by swirling the flask till yellow colour of Fe (III) solution is discharge (add 1 to 2 more pieces of Al-foils). Note that the foils are completely disintegrated to give a clear solution. Cool the solution under tap water to room temperature. Dilute the solution with 100 ml of distilled water. Add 2-3 g of NH₄HF₂ (or, 5 ml syrupy H₃PO₄) and add 4 to 5 drops of BDS indicator. Titrate with the standard (N/10) K₂Cr₂O₇ solution to violet end point. Record the titre value (V ml).

A-3.4 Calculation

| Amount of Fe ₂ O ₃ present in the sample | ≡ | K ₂ Cr ₂ O ₇ solution consumed |
|--|---|---|
| | ≡ | V ml of ($\frac{W1}{1.225 8}$) (N/10) K ₂ Cr ₂ O ₇ solution. |
| | ≡ | $(\frac{V X W 1}{1.225 8 X 10})$ ml (N) K ₂ Cr ₂ O ₇ solution. |
| 1000 ml of (N) $Cr_2O_7^{2-}$ solution | ≡ | 79.846 g of Fe ₂ O ₃ |
| $(\frac{V X W 1}{1.2258 X 10}) ml (N) Cr_2O_7^{2-}$ solution | ≡ | 79.846 X V X W1 1 000 X 1.225 8 X 10 |
| | = | 6.513 78 X V X W1 1000 |
| % of Fe ₂ O ₃ | = | 6.513 78 X V X W1 X 100 1000 X W |
| | = | 0.651 378 X V X W1 W |

Where,

V = Volume of standard (N/10) K₂Cr₂O₇ solution required for experimental solution.

 W_1 = Weight of K₂Cr₂O₇ crystal taken in g for the preparation of 250 ml (N/10) K₂Cr₂O₇ solution, and

W = Weight of the sample taken in g.

ANNEX B

[*Table* 4, *Sl No*. (iv)]

DETERMINATION OF WATER SOLUBLE CHLORIDE AND SULPHATE

B-1 PREPARATION OF AQUEOUS EXTRACT

Weigh about 5 g of pigment in a beaker. Add 200 ml of water and stir and boil for 5 minutes. Cool rapidly to room temperature and transfer to 250 ml volumetric flask and dilute to mark with water. Mix thoroughly by shaking and inversion. Filter it through filter paper and preserve the solution for determination of sulphate and chloride.

B-2 DETERMINATION OF SULPHATE

B-2.1 Outline of Method

The solution is heated and barium chloride is added to the solution. The barium sulphate precipitate, thus obtained, is dried and weighed.

B-2.2 Reagents

B-2.2.1 *Hydrochloric Acid* — concentrated.

B-2.2.2 Barium Chloride Solution — 5 percent. Weigh about 25 g of barium chloride into a beaker. Add about 200 ml of water and stir and boil for 5 minutes. Cool to room temperature and transfer to 500 ml volumetric flask and dilute to mark with water. Mix thoroughly by shaking and inversion.

B-2.3 Procedure

Take 50 ml of the clear aqueous extract obtained in **B-1**, in a beaker, acidify with 3 ml of the hydrochloric acid and boil the solution vigorously, taking care to avoid loss of solution by splashing. Add 5 percent barium chloride solution drop by drop, to the hot solution until in slight excess, and allow the solution to stand overnight. Decant the supernatant liquid through a tared sintered crucible (P 10 or P 16). Wash it free from chloride. Ignite it gently, and then at red heat. Cool it in a desiccator and weigh to the nearest 1 mg.

B-2.4 Calculation

Calculate the water soluble sulphate content (as SO₄) percentage by mass, as given below:

Water soluble sulphate content, percent by mass = $\frac{206 \times M_1}{M_2}$

where

 M_1 = mass in g, of barium sulphate precipitate; and

 M_2 = mass in g, of pigment in the aliquot.

Report the result in two decimal places.

B-3 DETERMINATION OF CHLORIDE

B-3.1 General

B-3.1.1 Outline of the Method

The aqueous extract is titrated with silver nitrate solution using potassium chromate solution as indicator.

B-3.2 Reagents

B-3.2.1 Silver Nitrate Solution — 0.01 N (see IS 2316).

B-3.2.2 *Potassium Chromate Solution* — 5 percent.

B-3.3 Procedure

Take 50 ml of the clear aqueous extract obtained in **B-1**, in a beaker and add 1 ml of 5 percent potassium chromate solution. Titrate with 0.01 N silver nitrate solution, slowly and with vigorous shaking, until a faint reddish brown colour persists. Carry out a blank determination by adding 1 ml of 5 percent potassium chromate solution to 50 ml of water and titrate with silver nitrate solution until the colour matches to that of the previous titration making due allowance for any opalescence or turbidity.

NOTE — Alternatively the end point of the titration may be determined by potentiometric indication.

B-3.4 Calculation

Calculate the water soluble chloride content expressed as Cl, percentage by mass, as given below:

Water soluble chloride

content, percent by mass =
$$0.1775 \times \frac{(V_1 - V_2)}{M}$$

where

 V_1 = the volume, in millilitres of 0.01 N silver nitrate solution required by the test portion;

 V_2 = the volume, in millilitres of 0.01 N silver nitrate solution required for the blank determination; and

M = the mass in g, of pigment in the aliquot.

Report the result in two decimal places.

B-4 SUM OF WATER SOLUBLE CHLORIDE AND SULPHATE

Add the water soluble sulphate content and chloride content, percent by mass *Sum of water soluble chloride and sulphates, percent by mass*

= Water soluble sulpahte, percent by mass

+ Water soluble chloride, percent by mass

ANNEX C

[Table 4, Sl No. (viii)]

TEST METHOD FOR LOSS ON IGNITION

C-1 PROCEDURE

Dry about 5 g of the sample at (105 ± 2) °C for two hours. Transfer about 1 g of the dried pigment weighed accurately to the nearest mg (M_1) to a previously ignited and weighed, porcelain crucible, and ignite at 900 °C to 1 000°C for one hour. Cool and weigh to the nearest mg. Repeat till a constant mass is obtained. Calculate the loss of mass on ignition and let it be M_2 .

C-2 CALCULATION

Calculate the percent of loss ignition, *L*, as follows:

$$L = \frac{M_2}{M_1} \times 100$$

where

 M_1 = mass of the sample, in g; and

 $M_2 =$ loss of mass on ignition, in g.

ANNEX D

[*Table 4, Sl No.* (ix) & (x)] **DETERMINATION OF COLOUR AND STRENGTH**

D-1 OUTLINE OF THE METHOD

A paint is prepared in a small-scale using pigment under testing along with a reference standard. Mass tone, reducing tone and strength are measured on paint drawdowns using color computer.

D-2 APPARATUS

D-2.1 Vibro Shaker

- D-2.2 Closed SS Metal Container (125 ml) with lid
- **D-2.3 Glass Beads** (1.2 to 1.6 mm)
- D-2.4 Electronic Balance weighing accuracy of 1 mg
- **D-2.5 Stainless Steel Spatula**
- **D-2.6 Mechanical Stirrer**
- **D-2.7 Black and White Paper**
- D-2.8 Bar Coater K-7
- D-2.9 80 mesh nylon filter cloth

D-3 REAGENTS

D-3.1 Long oil alkyd — oil length $\ge 60\%$ (see IS 11811)

D-3.2 Mineral spirit — (see IS 14314)

D-3.3 Zinc Octoate — complying to Grade 1 of IS 8766

- **D-3.4 Dipentine** (*see* IS 644)
- D-3.5 Cobalt Octoate complying to Grade 1 of IS 8766
- **D-3.6 Strontium Octoate** 10 percent active
- **D-3.7 Reference pigment** Approved sample

D-4 PROCEDURE

D-4.1 Method of preparation of the pigment concentrate:

D-4.1.1 Add the material in quantities corresponding to a factor of 0.4 and add 60 g of glass beads in a closed SS metal container 125 ml

D-4.1.2 Dispersion time after addition of Stage 1: 40 min.

D-4.1.3 After dispersion, add Stage 2 and run for another 10 min.

Guideline formulation of preparation of pigment concentrate

| Sl. No | Component | Weight (%) | Mixing Time | | | | |
|--------|--|------------|---------------------|--|--|--|--|
| 1 | Pigment | 15 | | | | | |
| | Stage 1 | | | | | | |
| 2 | Long oil alkyd (oil length $\geq 60\%$) | 15 | Add in sequence and | | | | |

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| 3 | МТО | 7 | disperse for 40 minutes |
|----------------------------|---|-----|-------------------------|
| 4 | Anti skinning additiver | 1 | |
| 5 | Zinc Octoate | 0.5 | |
| | Dipentine | 1 | |
| | Stage 2 | | |
| 6 | Long oil alkyd (oil length $\ge 60\%$) | 49 | |
| 7 | Combination of mixed drier (cobalt & strontium octoate) | 0.8 | Add in sequence and |
| | Anti skinning additiver | + | disperse for 10 minutes |
| 9 | Dipentine | 2 | |
| 10 | МТО | 9.9 | |
| | TOTAL | 100 | |
| *Non-volati **Use glass | le of alkyd resin 60.0% beads as grinding media 60 g | | |

D-4.1.4 Strain the sample using nylon filter cloth and collect the sample in a container for colour and strength measurements

D-4.2 Mass Tone, Reducing Tone and Strength Measurement

D-4.2.1 To measure the reducing tone and strength, use white tintable enamel base paint (PO base) and a neutral enamel base paint. Both these paints shall be air drying enamels with a gloss value of \geq 75 units on 60 ° gloss head. White base shall have rutile titanium dioxide content of at least 15 percent by mass.

| Mass | stone | Reduced tone | | | | |
|---------------|-------------------------|---------------|-------------------------|--|--|--|
| N Base (g) | Pigment concentrate (g) | PO Base (g) | Pigment concentrate (g) | | | |
| 100 ± 0.2 | 10 ± 0.001 | 100 ± 0.2 | 5 ± 0.001 | | | |

D-4.2.2 Mix the pigment concentrate and the base paint (as per the above-mentioned table) uniformly with a spatula and then stir it thoroughly by mechanical stirrer under proper vortex for 5 min. with minimum foam generation (RPM of 800 to 1 200).

D-4.2.3 Keep the mixture for 15 min in undisturbed condition for the foam to subside. Make drawdowns side by side (approved sample vs. sample under evaluation) with the help of K-7 bar coater.

D-4.2.4 Conduct a rub out test by finger on wet film at both upper corners of the drawdown paper (approved and sample both) and observe for difference in colour depth/intensity between rub out and adjacent areas to check colour acceptability.

D-4.2.5 Dry the drawdown paper at 60 $^{\circ}$ C oven for 1 hr. After drying, check the colour difference (mass tone and reduced tone) and colour strength (reduced tone) of the specimen against approved sample both visually as well as in Spectro (*see* IS 101 Part 4/ Sec 2).

ANNEX E

[Table 4, Sl No. (xi)]

DETERMINATION OF CALCIUM COMPOUNDS

E-1 GENERAL

For the determination of total calcium, two methods are provided. The flame atomic absorption spectrometric (AAS) method (**E-3**) shall be used as the reference method in cases of dispute.

E-2 METHOD 1 TITRIMETRIC METHOD

E-2.1 Outline of the Method

The material is converted into calcium oxalate and dissolved in sulphuric acid. The oxalic acid liberated is titrated against standard potassium permanganate.

E-2.2 Reagents

E-2.2.1 *Dilute Hydrochloric Acid* — 1 : 1 (*v/v*).

E-2.2.2 Ammonium Hydroxide

E-2.2.3 *Hydrogen Peroxide* — 30 percent (w | v).

E-2.2.4 Ammonium Oxalate Solution — saturated.

E-2.2.5 *Dilute Sulphuric Acid* — 1 : 4 (v | v).

E-2.2.6 *Standard Potassium Permanganate Solution* – 0.1 N (*see* IS 2316).

E-2.3 Procedure

Weigh accurately about 2.5 g of the material, transfer to a 500 ml beaker and add about 100 ml of hydrochloric acid. Heat to boiling to bring into solution. Add ammonium hydroxide solution in slight excess and about 2 ml of hydrogen peroxide. Cool and transfer to a 500 ml volumetric flask and make up to mark. Mix thoroughly and filter. Pipette out 100 ml of the filtrate and transfer to a 400 ml beaker. Add a few drops of ammonium hydroxide solution, heat to boiling and add an excess of saturated ammonium oxalate solution. Continue boiling until the precipitate becomes granular. Keep aside for 30 minutes, filter and wash the precipitate with hot water till the washings are free from ammonium oxalate. Place a beaker under the filter, puncture the filter paper and wash the precipitate into the beaker with hot water. Pour warm sulphuric acid through the filter paper and wash for a few times. Ensure that all the precipitate is washed down into the beaker. Add about 25 ml of sulphuric acid, heat to about 60 °C to 70°C and titrate the hot solution with standard potassium permanganate.

E-2.4 Calculation

Calcium compounds (as CaO), percent by mass = $\frac{2.804 \times V \times N \times 5}{M}$

where;

V = volume, in ml, of standard potassium permanganate solution required for titration;

N = normality of standard potassium permanganate solution; and

M = mass, in g, of the material taken for test.

E-3 METHOD 2 - DETERMINATION OF TOTAL CALCIUM BY FLAME ATOMIC ABSORPTION SPECTROMETRIC (AAS) METHOD

E-3.1 Principle

A test portion of the dried sample is dissolved in hydrochloric acid. Any silica present is volatilized by hydrofluoric acid. The test solution is then aspirated into an acetylene/dinitrogen oxide flame, and the absorbency of the 422.7 nm spectral line emitted by a calcium hollow cathode lamp or calcium discharge lamp is measured.

E-3.2 Reagents and Materials

During the analysis, use only reagents of recognized analytical grade and only water of IS 1070.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

E-3.2.1 *Hydrochloric Acid* — concentrated, approximately 37 percent (by mass), $\rho \approx 1.19$ g/ml.

E-3.2.2 *Hydrofluoric Acid* — concentrated, approximately 40 percent (by mass), $\rho \approx 1.13$ g/ml.

E-3.2.3 Sulfuric Acid — concentrated, approximately 96 percent (by mass), $\rho \approx 1.84$ g/ml.

E-3.2.4 Caesium Chloride — 76 g/l solution.

The caesium chloride used shall be of the highest purity available.

E-3.2.5 Calcium Standard Stock Solution, containing 1 g/l of Ca.

Two preparations are acceptable:

- a) transfer the contents of an ampoule of standard calcium solution containing exactly 1 g of Ca into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well; or
- b) weigh, to the nearest 1 mg, 2.497 g of calcium carbonate, dissolve in approximately 5 ml of hydrochloric acid (**E-3.2.1**) in a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this standard stock solution contains 1 mg of Ca.

E-3.2.6 Calcium Standard Solution — containing 100 mg/l of Ca.

E-3.2.6.1 Prepare this solution on the day of use.

E-3.2.6.2 Pipette 100 ml of the standard stock solution (**E-3.2.5**) into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

E-3.2.6.3 1 ml of this standard solution contains 100 µg of Ca.

E-3.2.7 *Acetylene* — commercial grade, in a steel cylinder.

E-3.2.8 Dinitrogen oxide

E-3.3 Apparatus

Use ordinary laboratory apparatus, and burettes, pipettes and one-mark volumetric flasks.

E-3.3.1 *Flame Atomic Absorption Spectrometer*, suitable for measurement at a wavelength of 422.7 nm and fitted with a burner suitable for use with acetylene and dinitrogen oxide.

E-3.3.2 Calcium Hollow-Cathode Lamp or Calcium Discharge Lamp.

E-3.4 Procedure

E-3.4.1 Preparation of the Calibration Graph

E-3.4.1.1 Preparation of the calibration solutions

Prepare these solutions on the day of use.

Into a series of seven 100 ml one-mark volumetric flasks, introduce from a burette the respective volumes of the standard calcium solution (**E-3.2.6**) shown in Table 5. Add 10 ml of caesium chloride solution (**E-3.2.4**) and 5 ml of hydrochloric acid (**E-3.2.1**) to each, dilute each to the mark with water and mix well.

Table 5 Calibration Solutions

(*Clause* 3.4.1.1)

| Sl. No. | Calibration solution No. | Volume of standard calcium solution (E-3.2.6) ml | Concentration of Ca in calibration solution µg/ml |
|---------|--------------------------|---|---|
| (1) | (2) | (3) | (4) |
| i) | 0 | 0 | 0 |
| ii) | 1 | 0.2 | 0.2 |
| iii) | 2 | 1 | 1 |
| iv) | 3 | 2 | 2 |
| v) | 4 | 4 | 4 |
| vi) | 5 | 8 | 8 |
| vii) | 6 | 10 | 10 |

E-3.4.1.2 Spectrometric measurements

- a) Install the calcium spectral source (**E-3.3.2**) in the spectrometer (**E-3.3.1**) and optimize the conditions for the determination of calcium. Adjust the instrument in accordance with the manufacturer's instructions and adjust the monochromator to the region of 422.7 nm in order to obtain the maximum absorbency.
- b) Adjust the flow of acetylene (**E-3.2.7**) and dinitrogen oxide (**E-3.2.8**) to suit the characteristics of the burner and ignite the flame. Set the scale expansion, if fitted, so that calibration solution No. 6 (*see* Table 5) gives almost full-scale deflection.
- c) Aspirate into the flame each of the calibration solutions (**E-3.4.1.1**), starting with calibration solution No. 0, and repeating with calibration solution No. 5 after calibration solution No. 6 to verify that the instrument has remained stable. Aspirate water through the burner between each measurement, taking care to keep the rate of aspiration constant.

E-3.4.1.3 Calibration graph

Plot a graph having the masses, in micrograms, of Ca contained in 1 ml of the calibration solutions as abscise and the corresponding values of the absorbency, corrected for the value for calibration solution No. 0, as ordinates.

E-3.3.2 Preliminary Treatment of the Test Portion

Carry out the determination in duplicate.

- a) Take a suitable quantity of the sample and dry it at 105 °C for 1 h. Weigh, to the nearest 1 mg, approximately 1 g of the dried sample into a 100 ml beaker and add 25 ml of hydrochloric acid (**E-3.2.1**).
- b) Cover the beaker with a watch glass and heat at 80 °C to 90 °C to dissolve the pigment. Evaporate the hydrochloric acid until the residue is almost dry. Add 50 ml of water and 5 ml of hydrochloric acid (E-3.2.1).
- c) Heat to dissolve the residue and filter the solution into a 100 ml one-mark volumetric flask. Make sure that any insoluble residue is completely transferred from the beaker to the filter. Then wash the filter once with warm water.
- d) Ash the filter with the insoluble residue in a platinum crucible. Add 10 ml of hydrofluoric acid (E-3.2.2) and 0.5 ml of sulfuric acid (E-3.2.3) and carefully evaporate to dryness to volatilize any silica present. Dissolve the residue using the minimum amount of hydrochloric acid (E-3.2.1) and transfer the solution to the 100 ml one-mark volumetric flask. Add 10 ml of caesium chloride solution (E-3.2.4) and dilute to the mark with water.

E-3.3.3 Determination

a) Measure the absorbency of the test solution in the spectrometer (**E-3.3.1**) after having adjusted it as described in **E-3.4.1.2**. If the absorbency is higher than that of the

calibration solution with the highest calcium concentration, dilute the test solution appropriately (dilution factor F) with a known volume of water.

b) Measure three times the absorbency of the test solution within the range of the calibration graph. Redetermine the absorbency of calibration solution No. 5 in order to verify that the response of the apparatus has not changed. Subtract from the three measurements the reading for calibration solution No. 0 and calculate the mean of the three corrected measurements. Read from the calibration graph the calcium concentration corresponding to the mean of the corrected measurements.

E-3.4 Expression of Results

E-3.4.1 Calculation

Calculate the calcium oxide content of the pigment, $w_{(CaO)}$, expressed as a percentage by mass, using the equation

 $w_{(CaO)} = \rho$ (Ca) x 100 x 1.3992 x F x 100 / m₃ x 10⁶ %

 $w_{(CaO)} = \rho$ (Ca) x 1.3992 x F / m₃ x 100 %

where

 ρ (Ca) is the calcium concentration of the test solution, in micrograms per millilitre, obtained from the calibration graph;

F is the dilution factor referred to in **E-3.4.1.3**;

 m_3 is the mass, in grams, of the test portion;

1.399 2 is the factor for the conversion of grams of Ca to grams of CaO.

E-3.4.2 If the two determinations differ by more than the values given in Table 6, repeat the procedure.

E-3.4.3 Calculate the mean of two valid determinations and report the result to two significant figures.

Table 6 Maximum Acceptable Difference between two Determinations

(*Clause* E-3.4.2)

| Calcium content | Maximum difference |
|-------------------|--------------------|
| % (by mass) | % (by mass) |
| 0.001 to 0.01 | 0.000 5 |
| above 0.01 to 0.1 | 0.005 |
| above 0.1 to 5 | 0.05 |

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