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Draft Indian Standard

**CUPROUS OXIDE FOR PAINTS —
SPECIFICATION**
(*Second Revision* of IS 70)

(ICS 87.060.10)

Raw materials for Paints, Varnishes and Related Product Sectional Committee, CHD 21	Last Date for Comments: 12th February 2024

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

FOREWORD

(Formal Clause shall be added later)

This standard was first published in 1950 and was largely based on the interim coordinated draft prepared with the assistance of the Coordinating Subcommittee of the No. 5 Standing Committee on Specifications for Paints and Allied Stores of the General Headquarters, India (now Army Headquarters).

In the first revision in 1980, additional requirements for combined chlorides and sulphates, metals other than copper and stability of the material were prescribed. The limit for residue on sieve was reduced from 2.5 percent to 0.5 percent by mass.

This revision has been taken to bring out the standard in the latest style and format of the Indian Standard. In addition, the following changes have been made:

a) To address health and safety concerns, requirement of lead has been stringent and restriction for toxic heavy metals has been introduced;

b) A suitable precautionary note has been added in the marking clause in order to prevent unforeseen events, and;

c) Additionally, the various editorial corrections, and references have been updated to ensure accuracy and relevance in the revised standards.

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

CUPROUS OXIDE FOR PAINTS— SPECIFICATION

(*Second Revision*)

1 SCOPE

This standard prescribes requirements and methods of sampling and test for cuprous oxide 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 (*third revision*)
IS 101 (Part 8/Sec 5) : 2022	Methods of sampling and test for paints varnishes and related products Part 8 Tests for pigments and other solids, Sec 5 Lead restriction test (*fifth revision*)
IS 264 : 2005	Nitric acid — Specification (*third revision*)
IS 265 : 2021	Hydrochloric acid — Specification (*fifth revision*)
IS 296 : 2023	Sodium carbonate anhydrous — Specification (*fourth revision*)
IS 1070 : 2023	Reagent grade water — Specification (*fourth revision*)

3 TERMINOLOGY

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

4 REQUIREMENTS

4.1 Composition — The material, dried as prescribed in IS 33, shall contain not less than 96 percent of cuprous oxide (Cu_2O) by mass when tested as prescribed in Annex A.

4.1.1 The total copper shall not be less than 85 percent, by mass, when tested as prescribed in Annex E.

4.2 Form and Condition — The material shall be supplied in the form of dry powder; or in such a condition that it can be reduced to the powder form by crushing, without grinding action, under a palette knife.

4.3 Lead Restriction

The material shall be tested for restriction from lead in accordance with 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 (*see* Note).

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

4.4 Toxic 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.

4.5 The material shall also conform to the requirements prescribed in Table 1.

Table 1 Requirements For Cuprous Oxide For Paints

(*Clause* 4.5)

SL No.	CHARACTERISTIC	REQUIREMENT	METHOD OF TEST, REF TO
(1)	(2)	(3)	(4)
i)	Volatile matter, percent by mass, *Max*	0.5	IS 33
ii)	Residue on sieve, percent by mass, *Max*	0.5	IS 33
iii)	Oil absorption value	Within ±10 of the approved sample	IS 33
iv)	Colour	Not inferior to the approved sample	IS 33
v)	Combined chlorides (calculated as Cl) and sulphates (calculated as SO_4), percent by mass, *Max*	0.5	Annex B
vi)	Metals other than copper, percent by mass, *Max*	0.5	Annex C
vii)	Stability (decrease in total reducing power after stability test), percent by mass, *Max*	2.0	Annex D

5 PACKING AND MARKING

5.1 Packing

The material shall be packed in suitable containers as agreed to between the purchaser and the supplier.

5.2 Marking

5.2.1 The containers shall be marked with the following particulars:

    a) Name of the material;
    b) Net mass of the material;

   c) Batch No. or Lot No. in code or otherwise; and

   d) Month and year of manufacture

   e) Expiry date/shelf life/best before

   f) Lead content (Maximum);

   g) Toxic heavy metals content

   h) A cautionary note as below:

       a. Keep out of reach of children; or

       b. This product may be harmful if swallowed or inhaled

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

5.2.3 *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 thereunder, and the products may be marked with the Standard Mark.

6 SAMPLING

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

6.2 Criteria for Conformity — A lot shall be declared as conforming to the requirements of this standard if the test results of the composite sample satisfy the requirements prescribed in **4.**

7 TEST METHODS

7.1 The colour and oil absorption values of the material shall be determined by comparison with those of the approved sample.

7.2 Tests shall be carried out as prescribed in Annex A to E and IS 33. Reference to the relevant clauses of that standard and Annexes are given in col 4 of Table 1.

7.3 Quality of Reagents — Unless specified otherwise, pure chemicals and distilled water (*see* IS 1070) shall be employed in tests.

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

ANNEX A

(*Clause* 4.1)

DETERMINATION OF CUPROUS OXIDE

A-1 GENERAL

A-1.1 Cuprous oxide is estimated by determining the total reducing power by dissolving it in acidulated ferric chloride solution and titrating with standard potassium dichromate solution.

A-1.2 Occasionally, samples of cuprous oxide (especially those of high purity) show some metallic copper, which is generally evident in the residue on sieve test. Metallic copper, if present in a sample, gets involved in the determination of cuprous oxide. In such a case advantage is taken of the fact that cuprous oxide is soluble in cold aqueous ammonia, whereas cupric oxide is but slightly soluble and metallic copper insoluble. The addition of hydrazine sulphate to the reagent tents to reduce any divalent copper entering into solution and prevents interaction of cupric oxide and copper metal. If the extraction is carried out in carbon dioxide atmosphere, the metallic copper-cupric oxide mixture may be separated and the metal determined by solution in acidulated ferric chloride, followed by titration with potassium dichromate.

A-2 APPARATUS

A-2.1 Filter — Place in a tube of the type used for small Gooch crucibles (85 mm in length), a perforated porcelain button, seated at right angles to the stem; build an asbestos pad over it and securely set it by tamping with a glass rod.

A-2.1.1 The filter should be packed in such a manner that the tube may be held in an inverted position without dislodging either the disc or the pad.

A-3 REAGENTS

A-3.1 Extraction Solution — Dissolve 6 g of hydrazine sulphate in 1 litre of liquid ammonia (relative density 0.9).

A-3.2 Acidulated Ferric Chloride — Dissolve 150 g of ferric chloride ($FeCl_3.6H_2O$) and 300 ml of hydrochloric acid (relative density 1.16) in 800 ml of air-free water, saturated with carbon dioxide.

A-3.3 Indicator — Suspend 2 g of barium diphenylamine sulphonate and 5 g of sodium sulphate in 50 ml of water, saturated with carbon dioxide, and shake until a uniform suspension of barium sulphate is obtained. Dilute with 50 ml of water and allow to settle. When clear, decant the supernatant liquid through a filter and preserve in a dark bottle.

A-3.4 Orthophosphoric Add — 85 percent by volume.

A-3.5 Standard Potassium Dichromate Solution (0.1 N) — Finely powder about 6 g of potassium dichromate, in a glass or agate mortar, and heat from 30 minutes to 60 minutes, in an air oven at 140 °C to 150 °C. Cool in a desiccator. Dissolve about 4.9 g of the powder, accurately weighed, in water in a 1 litre measuring flask, shake thoroughly and make the solution to 1 000 ml. Allow it to stand overnight.

A-3.5.1 *Strength of potassium dichromate solution* $(N) = \dfrac{4.9}{M} N$

where

M = mass in g of potassium dichromate dissolved.

A-3.6 Air-Free Water, Saturated with Carbon Dioxide — Boil water vigorously for several minutes and allow to cool in an atmosphere of carbon dioxide by passing a slow current of the gas continuously through the storage bottle.

A-3.7 Ethyl Alcohol — 95 percent by volume.

A-4 PROCEDURE

A-4.1 In Absence of Free Copper

A-4.1.1 Weigh accurately about 0.25 g of the material, dried as described in IS 33 transfer to a 250 ml glass-stoppered conical flask, add 10 to 15 ml of acidulated ferric chloride solution and a few glass beads. Stopper the flask and rotate gently until the cuprous oxide is completely dissolved, which generally takes place within a few minutes for high grade, finally ground sample. If necessary, warm gently on the water bath to accelerate dissolution. Much heating is not advisable unless the solution is protected from oxidation. When the cuprous oxide is completely dissolved, add 10 ml of orthophosphoric acid and three drops of the indicator and titrate the cold solution at once with 0.1 N potassium dichromate solution until a change of colour from pea-green to intense purple is reached. Run a blank on the reagents used.

A-4.1.2 Calculate the percentage of cuprous oxide using the following relationship:

1 ml of 0 1 N potassium dichromate is equivalent to 0.007 157 g of cuprous oxide.

A-4.2 In Presence of Free Copper

A-4.2.1 Determine the total reducing power as described under **A-4.1,** and from the percentage of cuprous oxide so ascertained, deduct the cuprous oxide equivalent found under **A-4.2.6.**

A-4.2.2 Weigh accurately about 0 25 g of the material, dried as described in IS 33 on a small watch glass and place the watch glass and contents in a dry, wide-mouthed, 250 ml conical flask. Displace the air in the flask with carbon dioxide, the carbon dioxide inlet being kept about 5 cm above the surface of the liquid, and add 10 ml of ethyl alcohol to dissolve any oil present in the sample. Without interrupting the flow of gas, add 150 ml of extraction solution, and break up any lumps of oxide with a stirring rod avoiding violent agitation.

A-4.2.3 The time required for complete solution of all cuprous oxide varies from 1 min to 7 min, depending upon the amount and character of sample under investigation.

A-4.2.4 When the cuprous oxide has completely dissolved, as evidenced by the total disappearance of red particles, connect the filter to a suction pump and slowly lower into the flask. As soon as the bulk of the solution is removed, rinse the flask with water saturated with carbon dioxide and continue the filtration and washing. Five or six 100 ml portions of wash water will be sufficient to remove all the original extraction solution and dissolved cuprous oxide.

A-4.2.5 Disconnect the filter and push the pad and contents back into the flask with a glass rod. Add 15 ml of acidulated ferric chloride solution and warm the flask to just below boiling point of the solution to dissolve the cupric oxide-copper residue. When all the particles have disappeared, cool the solution to below 40°C and add 10 ml of orthophosphoric acid and 3 drops of the indicator. Titrate the solution with standard potassium dichromate solution until a change in colour from pea-green to intense purple is reached.

A-4.2.6 Calculate the cuprous oxide equivalent of the metallic copper using the following relationship:

1 ml of 0.1 N potassium dichromate is equivalent to 0.007 157 g of cuprous oxide.

ANNEX B

[*Table* 1, *Item* (v)]

DETERMINATION OF COMBINED CHLORIDES

AND SULPHATES

B-1 REAGENTS

B-1.1 Barium Chloride Solution — Dissolve 100 g of barium chloride ($BaCl_2$) in water and dilute to 1 litre.

B-1.2 Silver Nitrate Solution — Dissolve 5 g of silver nitrate ($AgNO_3$) in 100 ml of water.

B-1.3 Sodium Carbonate Solution— Prepare a saturated solution of sodium carbonate (Na_2CO_3) that is free from both chloride (Cl) and sulphate (SO_4).

B-2 PROCEDURE

B-2.1 Weigh accurately approximately 10 g of the sample, add an excess of nitric acid (relative density 1.42) and heat gently until the sample is decomposed. Dilute with water to approximately 150 ml. Add an excess of sodium carbonate solution and bring to boil. Transfer to a 500 ml volumetric flask and dilute to the mark with water. Allow the precipitate to settle.

B-2.2 Draw off two separate 50 ml aliquots of the clear solution. Make each slightly acidic with nitric acid.

B-2.3 Determination of Chlorides — To one of the 50 ml aliquot add a few drops of silver nitrate solution. If no precipitate forms, report no chlorides present. If a precipitate forms, add slowly an excess of silver nitrate solution. Heat to boiling, after the precipitate has settled, filter through a Gooch crucible and wash with cold water. Dry at 130°C, cool and weigh.

B-2.3.1 *Calculation* — Calculate the percentage of chlorides (as Cl) as follows:

$$\text{Chlorides, percent by mass} = \frac{M_1 \times 0.247}{(M_2 \times 0.1)} \times 100$$

where,

M_1 = mass in g of silver chlorides, and

M_2 = mass in g of sample used.

B-2.4 Determination of Sulphates — Dilute the second 50 ml aliquot to approximately 200 ml. Add approximately 1 ml of hydrochloric acid (1:1). Heat to boiling and add slowly an excess of barium chloride. Allow the precipitate to settle, filter through a Gooch crucible, and wash. Dry, ignite at full red heat, cool in a desiccator and weigh.

B-2.4.1 *Calculation* — Calculate the percentage of sulphates (as SO_4), as follows:

Sulphates, percent by mass $= \frac{M_1 \times 0.412}{(M_2 \times 0.1)} \times 100$

where

M_1 = mass in g of barium sulphate, and

M_2 = mass in g of sample used.

ANNEX C

[*Table* 1, *Item* (vi)]

DETERMINATION OF METALS OTHER THAN COPPER

C-1 REAGENTS

C-1.1 Ceric Ammonium Nitrate, Standard Solution (0.1 N) — Mix 54 826 g of ceric ammonium nitrate [Ce $(NH_4)_2(NO_3)_6$] with 56 ml of sulphuric acid (1: 1). Dissolve the salt and acid in water, cool to room temperature, and dilute to 1 litre. Standardize this solution against analyzed bright copper foil that has been freed from all oxide coating.

C-1.2 Diphenylamine Indicator — Dissolve 1 g of diphenylamine in 100 ml of sulphuric acid (relative density 1.84).

C-1.3 Potassium Ferricyanide Solution — Dissolve 5 g of potassium ferricyanide [$K_3Fe(CN_6)$] in 100 ml of water. Keep tightly stoppered in a dark bottle.

C-1.4 Potassium Ferrocyanide, Standard Solution — Dissolve 5.0 g of potassium ferrocyanide [$K_4Fe(CN)_6.3H_2O$] in water and dilute to 1 litre. Standardize with analyzed zinc prior to use.

C-2 PROCEDURE

C-2.1 Weigh accurately 1.0 g of the sample and transfer to a 300 mi electrolytic beaker. Add 10 ml of nitric acid and boil several minutes. Add 10 ml of perchloric acid ($HClO_4$) (70 percent) and fume for 5 minutes. Cool, dilute to a volume of approximately 150 ml and add 1 ml of nitric acid and 1 g of ammonium sulphate. Electroplate the copper on a rotating platinum electrode at a current of 2A for 2h. Dilute with water and continue the electrolysis for 15 minutes. When the deposition is complete, remove the electrode. Filter the electrolyte, wash with water and acetone. Add 5 ml of sulphuric acid and evaporate just to dryness to remove all perchloric acid and nitric acid. Add approximately 150 ml of water and neutralize with ammonium hydroxide, add 5 ml in excess. Add 10 g of ammonium chloride solution. Boil the solution gently for several minutes and allow the precipitate to settle. Filter through a close-texture paper, and wash the precipitate with 50 ml of hot ammonium chlorides solution (20 g/litre).

C-2.2 Determination of Iron — Dissolve the precipitate from the filter paper with hot hydrochloric acid (1 : 1). Determine iron by the usual procedure of reduction with stannous chloride ($SnCl_2$) solution, followed by addition of mercuric chloride ($HgCl_2$) and titration with 0 IN ceric ammonium nitrate solution.

C-2.2.1 *Calculation* — Calculate the percentage of iron as follows:

Iron, percent by mass $= \left[\frac{(V N \times 0056)}{M_1}\right] \times 100$

where

V = volume in ml of ceric ammonium nitrate solution required to titrate the sample,

N = normality of the ceric ammonium nitrate solution, and

M_1 = mass in g of sample used.

C-2.3 Determination of Cobalt and Nickel — Evaporate the filtrate (*see* **C-2.1**) to 15 ml to 20 ml. If the solution is coloured, the presence of nickel or cobalt, or both, may be indicated. If present, they shall be removed before determining zinc, and shall be determined by any standard procedure and reported as percentage of cobalt or nickel, or both.

C-2.4 Determination of Zinc — Neutralize the solution (*see* **C-2.3**) with sulphuric acid (1:2) and add 15 ml in excess. Dilute to 300 ml with water. Add 10 drops of potassium ferricyanide solution and 5 drops of diphenylamine indicator solution. Heat to 75 °C and titrate with potassium ferrocyanide solution (1 ml = 0.001 g of zinc). A colour change from blue to greenish yellow occurs at the end point.

C-2.4.1 *Calculation* — Calculate the percentage of zinc as follows:

Zinc, percent by mass $= \left(\frac{V \times N}{M}\right) \times 100$

where

V = volume in ml of potassium ferrocyanide solution required for titration of the sample,

N = zinc equivalent of the potassium ferrocyanide solution, and

M_1 = and mass in g of sample used.

C-3 REPORT

Report as percentage of metals other than copper, the total of the percentage of metals determined in accordance with **C-2.**

ANNEX D

[*Table* 4, *Item* (vii)]

DETERMINATION OF STABILITY

D-1 PROCEDURE

D-1.1 Spread approximately 100 g of the sample on a watch-glass and heat in an oven at a temperature of 40 °C and approximately 95 percent relative humidity for a period of 72 h. Remove from the oven. Note any change in colour of the sample. Determine its total reducing power as prescribed in Annex A.

D-1.2 Determine the percentage of moisture on 50 g of the sample remaining from the test described in **D-1.1** using a distillation method.

D-1.3 Calculation — Calculate the percentage of decrease in total reducing power as follows:

$$a = \frac{b}{(100 - c)}; d = [(e - a)e] \times 100$$

where

      a = total reducing power after, stability test, based on the dry sample,

      b = total reducing power as determined in **D-1.1,**

      c = percentage of moisture (**D-1.2**),

      d = percentage of decrease in total reducing power after stability test, and

      e = total reducing power of original sample *(see* Annex A).

ANNEX E

(Clause 4.1.1)

DETERMINATION OF TOTAL COPPER

E-1 PRINCIPLE OF THE METHOD

E-1.1 Copper is determined by titration of the iodine liberated on addition of potassium iodide to the weakly acidic solution. Difficulties with absorption of iodine on the cuprous iodide precipitate are avoided by the addition of potassium or ammonium thiocyanate.

E-2 REAGENTS

E-2.1 Concentrated Nitric Acid — sp gr 1.42 (*see* IS 264).

E-2.2 Urea

E-2.3 Sodium Carbonate — anhydrous (*see* IS 296).

E-2.4 Dilute Acetic Acid — 10 percent (*v/v*).

E-2.5 Potassium Iodide Solution — 30 percent (*m/v*).

E-2.4 Standard Sodium Thiosulphate Solution — 0.1 N, standardized against pure copper or against 0.1 N standard potassium dichromate solution (*see* **E-5**).

E-2.7 Starch Indicator Solution — One percent (*m/v),* freshly prepared.

E-2.8 Potassium or Ammonium Thiocyanate

E-3 Procedure

E-3.1 Weigh accurately about 0.4 g of the material into a 250 ml Erlenmeyer flask. Add 1ml to 2 ml of concentrated nitric acid and about 20 ml of water, and allow the material to dissolve by shaking. Boil the contents for 3 minutes to 5 minutes, remove the flask from the flame, add 1 g of urea and boil again for about 5 minutes. Cool and add sodium carbonate in small quantities until a faint permanent precipitate or blue colour appears. Add dilute acetic acid dropwise until the blue colour (or the precipitate) disappears. Add 2 ml to 3 ml of

potassium iodide solution and titrate the brown solution with the standard sodium thiosulphate solution to a pale-straw colour. Add about 2 ml of starch indicator solution and about 1.5 g to 2.5 g of potassium or ammonium thiocyanate, and continue titration until the blue colour is just discharged.

E-4 CALCULATION

E-4.1 Total copper content,

$$\text{percent by mass} = \frac{0.6357 \, vF}{M} \times 10$$

where

v = volume in ml of the standard sodium thiosulphate solution required for the test with the material *(see* **E-3.1**),

F = factor of the standard sodium thiosulphate solution (*see* **E-5.2.2.1** and **E-5.3.3.1**), and

M = mass in g of the material taken for the test (*see* **E-3.1**).

E-5 STANDARDIZATION OF SODIUM THIOSULPHATE SOLUTION

E-5.1 General — For standardization of sodium thiosulphate solution, two methods, namely titration against pure copper of not less than 99.9 percent purity and against standard potassium dichromate solution, have been specified. Experience has shown that the standardization against pure copper gives accurate results but due to difficulty of availability of pure copper, the alternate method has also been specified. Hence, either of these two methods may be used for the standardization of sodium thiosulphate solution, but the method employed should be stated while expressing the results of a test.

E-5.2 Standardization Against Pure Copper of not less than 99.9 Percent Purity

E-5.2.1 Weigh accurately 0.2 g of pure copper in a 500 ml Erlenmeyer flask. Dissolve the copper by adding 5 ml of concentrated nitric acid and, after 1 minute, add 5 ml of water. Follow the procedure as described in **A-4.1**.

E-5.2.2 Calculation

E-5.2.2.1 Factor F of 0.1 N sodium

$$\text{thiosulphate solution} = \frac{M}{0.6357 \times v}$$

where

M = mass in g of the pure copper taken for the test, and

v = volume in ml of the standard sodium thiosulphate solution required for the test with the material.

E-5.3 Standardization Against Standard Potassium Dichromate Solution

E-5.3.1 *Reagents*

E-5.3.1.1 *Standard potassium dichromate solution* — 0.1 N.

E-5.3.1.2 *Concentrated hydrochloric acid* — conforming to IS 265.

E-5.3.1.3 *Potassium iodide*

E-5.3.1.4 *Starch Indicator solution* — one percent (*m/v*), freshly prepared.

E-5.3.2 *Calculation*

E-5.3.2.1 Pipette out accurately 25 ml of standard potassium dichromate solution into a 600 ml Erlenmeyer flask. Add to this about 125 ml of water, 10 ml of concentrated hydrochloric acid and 4g to 5 g of potassium iodide. Stopper the Erlenmeyer flask and keep it in dark for about 15 minutes to complete the reaction. After 15 minutes, titrate this mixture against the standard sodium thiosulphate solution using about 2 ml of starch indicator solution towards the end.

E-5.3.3 *Calculation*

E-5.3.3.1 Factor F of 0.1 N sodium thiosulphate solution $= \dfrac{V \times N}{v}$

where

V = volume in ml of the standard potassium dichromate solution taken for the test (which in this case is equal to 25 ml),

N = normality of the standard potassium dichromate solution, and

v = volume in ml of the 0.1 N sodium thiosulphate solution required for titration of the volume of the standard potassium dichromate solution taken for the test.