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Draft Indian Standard

**GREEN OXIDE OF
CHROMIUM FOR PAINTS — SPECIFICATION**

(Third Revision of IS 54)

(ICS 87.060.10)

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

Last Date for Comments: 18th April 2024

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FOREWORD

(Formal Clause shall be added later)

This standard was originally published in 1950 and was revised in 1975, incorporating additional requirements for *pH* value, resistance to acid and alkali; and modified the oil absorption requirement.

Subsequently, the International Organization for Standardization (ISO) brought out ISO 4621: 1986 ‘Chrome oxide green pigments - Specifications and methods of test’. The Committee responsible for the preparation of this standard decided to align it with the ISO standard.”

In the second revision in 1988, the limits for volatile matter and matter soluble in hot water; test methods for determination of resistance to alkali and acid were modified. New requirement for loss on ignition was added and *pH* value was prescribed as ± 1 *pH* unit of the approved sample instead of giving the *pH* range. The limit of lead for lead free material was reduced from 0.05 to 0.03 percent.

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 test method for colour and strength measurement has been changed to Vibro Shaker method in place of existing test method based on Muller. Additionally, in colour tinting strength, staining power and tone and ease of dispersion have been prescribed;
- b) For residue of sieve, the sieve size has been changed from 63 microns to 45 microns;

- c) To address health and safety concerns, restrictions for lead has been tightened and restriction for toxic heavy metals has been introduced;
- d) A suitable precautionary note has been added in the marking clause in order to prevent unforeseen events, and;
- e) 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
**GREEN OXIDE OF
CHROMIUM FOR PAINTS — SPECIFICATION**
(Third Revision)

1 SCOPE

This standard prescribes the requirements and methods of sampling and test for green oxide of chromium pigment used in paints and allied industries.

2 REFERENCES

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

<i>IS No.</i>	<i>IS Title</i>
IS 33 : 1992	Inorganic pigments and extenders for paints — Methods of sampling and test (<i>third revision</i>)
IS 101 (Part 4/Sec 2) : 2021	Methods of sampling and test for paints varnishes and related products: Part 4 optical tests, Sec 2 Colour-visual comparison of colour of paints (<i>fourth revision</i>)
IS 265 : 2021	Hydrochloric acid — Specification (<i>fifth revision</i>)
IS 266 : 1993	Sulphuric acid — Specification (<i>third revision</i>)
IS 376 : 2023	Sodium hydroxide analytical reagent — Specification
IS 798 : 2020	Orthophosphoric acid — Specification (<i>third revision</i>)
IS 1070 : 2023	Reagent grade water — Specification (<i>fourth revision</i>)
IS 1303 : 1983	Glossary of terms relating to paints (<i>second revision</i>)

3 TERMINOLOGY

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

4 REQUIREMENTS

4.1 Form and Condition

The material shall be in form of dry powder free from grit, or in such condition that it can be readily reduced to the powder form by crushing under a palette-knife without any grinding action.

4.2 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.

4.3 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.

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

TABLE 1 REQUIREMENTS FOR GREEN OXIDE OF CHROMIUM FOR PAINTS

(Clause 4.4)

Sl No.	Characteristics	Requirement	Method of Test Ref to
(1)	(2)	(3)	(4)
i)	Chromium content, expressed as Cr_2O_3 , percent by mass, <i>Min</i>	97.0	Annex A
ii)	Volatile matter at $(105 \pm 2)^\circ\text{C}$, percent by mass, <i>Max</i>	0.3	8 of IS 33
iii)	Loss of ignition at $(1\ 000 \pm 20)^\circ\text{C}$, percent by mass, <i>Max</i>	1.0	Annex B
iv)	Residue on sieve (45 microns), percent by mass, <i>Max</i>	0.5	9 of IS 33
v)	Oil absorption	Within ± 10 percent of the approved sample	10 of IS 33
vi)	Colour a) Tinting strength b) Staining power and tone c) Ease of dispersion	Close match to the approved sample	Annex C
vii)	Matter soluble in hot water, percent by mass, <i>Max</i>	0.2	19 of IS 33
viii)	pH if the aqueous extract	± 1 pH unit of the approved sample	21 of IS 33
ix)	Resistance to alkali and acid	Not inferior to the approved sample	Annex D

5 PACKING AND MARKING

5.1 Packing

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

5.2 Marking

5.2.1 The containers shall be marked with the following information:

- 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 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.

6 SAMPLING

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

6.2 Criteria for Conformity

A lot shall be declared as conforming to this standard if all the test results on the composite test sample satisfy the requirements prescribed under 4.

7 TEST METHODS

7.1 Tests shall be conducted as prescribed in IS 33 and in Annexes A to D, according to the requirements of Table 1.

7.2 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

[Table 1, Item (i)]

DETERMINATION OF CHROMIUM CONTENT

A-1 OUTLINE OF THE METHOD

Chromium oxide is estimated by converting it to chromate and titrating with potassium permanganate solution after allowing the chromate to react with a known excess of ferrous ammonium sulphate solution.

A-2 REAGENTS

A-2.1 Ferrous Ammonium Sulphate Solution (0.1 N) — Dissolve about 40 g of ferrous ammonium sulphate crystals in 950 ml of water and add 50 ml of concentrated sulphuric acid (r.d. 1.84).

A-2.2 Standard Potassium Permanganate Solution (0.1 N) — Dissolve about 3.2 g of pure potassium permanganate (KMnO_4) in 1 000 ml of water, allow it to stand for 8 days to 14 days and siphon off the clear solution into a glass stoppered bottle, painted black. Standardize it as described in A-2.2.1.

A-2.2.1 Weigh accurately about 0.25 g of pure potassium dichromate crystals and dissolve in about 300 ml of water. Add 20 ml of sulphuric acid (1 : 1 by volume), 100 ml of ferrous ammonium sulphate solution and 5 ml of syrupy phosphoric acid and titrate with potassium permanganate solution, noting the volume when the last drop of potassium permanganate solution leaves a permanent pink tinge. Titrate with potassium permanganate solution, a fresh quantity of 100 ml of ferrous ammonium sulphate solution acidified with sulphuric acid and diluted with water as before for blank.

A-2.2.2 Potassium dichromate equivalent of 1 ml of potassium permanganate solution is $\frac{m}{y-x}$ g, where x and y are volumes in ml of potassium permanganate solution required in the first and second titrations respectively, and m is the mass in g of potassium dichromate crystals.

A-2.3 Sodium Peroxide

A-2.4 Sulphuric Acid — *see* IS 266

A-2.5 Phosphoric Acid — *see* IS 798

A-3 PROCEDURE

Make a intimate mixture of about 0.1 g of the sample, dried at $(105 \pm 2)^\circ\text{C}$ as described in IS 33 and accurately weigh, with 5 g of sodium peroxide in a silver or nickel crucible. Fuse the mixture over a gas flame, keeping the molten mass at low red heat for 5 minutes. Tap the partly cooled fusion cake on to a plate, dissolve it in 200 ml of warm water in a covered beaker. Rinse the crucible with warm water and transfer the rinsing to the beaker. Add 1 g of sodium peroxide and boil the solution vigorously until the peroxide is completely destroyed. Cool and acidify with about 30 ml of sulphuric acid. Add 5 ml of phosphoric acid (r.d. 1.7) and make up the solution to about 500 ml in an 800 ml beaker. Add exactly 100 ml of ferrous ammonium sulphate solution with vigorous stirring. A deep green colour develops when reduction is complete. Titrate the excess of ferrous ammonium sulphate solution with standard potassium permanganate solution, taking the first faint darkening of the clear green colour as the end point. Run a blank, starting from peroxide fusion in the same manner and at the same time. Note the volumes of potassium permanganate solution required in both cases.

A-4 CALCULATION

$$\text{Chromium oxide, percent by mass} = \frac{50.67 a (V_1 - V_2)}{M}$$

where

a = potassium dichromate equivalent of 1 ml potassium permanganate solution, as found in A-2.2.2;

V_1 = volume in ml of potassium permanganate solution required for blank titration;

V_2 = volume in ml of potassium permanganate solution required for the titration with the sample: and

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

ANNEX B

[Table 1, Item (iii)]

DETERMINATION OF LOSS ON IGNITION

B-1 OUTLINE OF THE METHOD

The determination of loss on ignition is generally carried out in order to determine physically or chemically bound water. Discoloration, as a result of ignition, generally indicates the presence of small amounts of organic substances in chrome pigments.

B-2 APPARATUS

B-2.1 Muffle Furnace — Capable of being maintained at temperature of $(1\,000 \pm 20)^\circ\text{C}$.

B-2.2 Platinum Crucible

B-3 PROCEDURE

Weigh about 5 g of the pigment, to the nearest 0.1 mg into the platinum crucible that has previously been heated at $(1\,000 \pm 20)^\circ\text{C}$ for 15 minutes cooled and weighed. Heat the crucible in the furnace at $(1\,000 \pm 20)^\circ\text{C}$ for 15 minutes. Repeat ignition and cooling to obtain constant mass.

B-4 CALCULATION

$$\text{Loss on ignition, percent by mass} = \frac{M_1}{M} \times 100$$

where

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

M_1 = loss in mass in g on ignition.

ANNEX C

[Table 1, Item (vii)]

DETERMINATION OF COLOUR, STRENGTH AND DEGREE OF DISPERSION/FINENESS OF GRINDING

C-1 OUTLINE OF THE METHOD

To evaluate the performance of pigment with respect to colour difference, strength, and degree of dispersion against approved pigment sample

C-2 APPARATUS

C-2.1 Vibroshaker — 25 to 30 degree angular oscillation @ 640 / 660 spm simultaneously

C-2.2 Closed SS metal container —125 ml

C-2.3 Glass Beads — diameter 2.5 mm to 3.0 mm

C-2.4 Electronic Balance — accuracy 1 mg

C-2.5 Spatula

C-2.6 Mechanical Stirrer

C-2.7 Black and White Paper

C-2.8 Bar Coater K-7

C-3 PROCEDURE

C-3.1 Method of Preparation of the Pigment Concentrate:

- a) Add the material in 0.4 factor and add 60 g of glass beads^e in a closed SS metal container 125 ml
- b) Dispersion time after addition of Stage 1: 40 min.
- c) After dispersion, add Stage 2 and run for another 10 min.
- d) Collect the pigment concentrate and proceed for following testing:

Table – 2 Guideline Formulation of Preparation of Pigment Concentrate

Sl. No	Component	Weight (%)	Mixing Time
i)	Pigment	20.0 ± 0.001	
Stage 1			
ii)	Epoxy Resin [*]	8.0	Add in sequence and disperse for 40 minutes
iii)	n-Butanol	4.0	
iv)	2-Ethoxy ethanol	1.0	
v)	Aromatic Hydrocarbon Solvent C9	6.0	
vi)	Rheological additive for moderate to high polarity organic Media [#]	0.8	
vii)	Wetting and dispersing additive ^{\$}	1.0	

Stage 2			
viii)	Epoxy Resin [*]	28.0	Add in sequence and disperse for 10 minutes
ix)	n-Butanol	6.0	
x)	2-Ethoxy ethanol	1.0	
xi)	Aromatic Hydrocarbon Solvent C9	24.2	
Total		100.0	
[*] High-viscosity unmodified epoxy resin of bisphenol-A type at 75% solids in xylene, Viscosity of solution at 25°C 8.0 – 13.0 Pa.s and Epoxy equivalent 450 g/eq to 525 g/eq. [#] Organic derivative of a bentonite clay ^{\$} Alkyl ammonium salt of a high molecular weight copolymer (Amine value: (44 ± 5) mg KOH/g, Acid value: (38 ± 5) mg KOH/g) [€] Use glass beads as grinding media 60 g			

C-4 DETERMINATION OF DEGREE OF DISPERSION/FINENESS OF GRINDING:

To assess the degree of dispersion/fineness of grinding by Hegman gauge:

Fineness of grinding is expressed as maximum crowding of particles on a Hegman scale of 0 – 8

- Ensure that the gauge, Scraper, and Spatula are clean.
- Place the Hegman gauge on a flat surface.
- Put the sample under test into the deep end of channel with spatula.
- Hold the scraper between the thumbs and fingers of both hands.
- Ensure that the scraper is perpendicular to the surface of the gauge and place it edgewise in contact with the surface.
- Draw the paint at a uniform rate down the gauge passing the mark 8, within 2 s to 3 s.
- View the gauge sideways by reflected light as quickly as possible (within 10 s) and read the reading.
- Hegman gauge reading is defined as the point where crowding particles may be seen in a line across the gauge.

C-5 DETERMINATION OF COLOUR AND STRENGTH %

C-5.1 Colour Difference (Mass Tone)

C-5.1.1 To check the colour difference of pigment concentrate it needs to be cured with catalyst. Catalyst part contains some reactive group that reacts with the resin (binder) to build high molecular weight and initiate curing reaction.

C-5.1.2 Catalyst — Medium viscosity polyamide hardener

C-5.1.3 Amine Value — (300 ± 20) mg KOH/g

C-5.2 Calculation of Mixing Ratio:

Epoxy equivalent of Epoxy resin = E

Solid content of Epoxy resin = X percent

Loading of Epoxy resin in formulation (*see* Table 2) = Y percent

$$\text{Active content} = \frac{Y \times X}{100}$$

Amine value of catalyst: C

$$\text{Amine equivalent weight} = \frac{56100}{C}$$

$$\text{E.g Epoxy cured with } \frac{56100}{C} \text{ g Amine}$$

$$1 \text{ g Epoxy cured with } \frac{56100}{C \times E} \text{ g Amine}$$

$$\frac{Y \times X}{100} \text{ Epoxy cured with } \frac{56100 \times Y \times X}{100 \times C \times E} \text{ g Amine}$$

$$\text{Therefore, 100 g Pigment concentrate cured with } \frac{561 \times Y \times X}{C \times E} \text{ g Amine}$$

Mixing Ratio of Pigment concentrate:

$$\text{Catalyst (w/w)} = 100 : \frac{561 \times Y \times X}{C \times E}$$

C-5.3 Procedure

- Mix the pigment concentrate and catalyst as per above mentioned ratio and mix uniformly with a spatula by hand mixing with minimum foam generation.
- Make drawdowns side by side (approved sample vs. sample under evaluation) with the help of K-7 bar coater.
- 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.
- Dry the drawdown paper at 80 °C oven for 30 min for curing. After drying, check the colour difference (mass tone) of the specimen against approved sample both visually as well as in Spectro (*see* IS 101 Part 4/ Sec 2).

C-6 COLOUR DIFFERENCE (REDUCED TONE) AND STRENGTH%

C-6.1 To check the reduced tone and strength percent we need an epoxy based white base. The white base can be prepared following the same guideline formulation of preparation of pigment concentrate (Table 3) where pigment should be Rutile.

Table 3

Reduced tone and Strength percent [White Base : Pigment concentrate = 60 : 40 (w/w)]	
White Base (g)	Pigment concentrate (g)

30 ± 0.001	20 ± 0.001
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Catalyst: Medium viscosity polyamide hardener

Amine Value: (300 ± 20) mg KOH/g

C-6.2 Calculation of Mixing Ratio:

Epoxy equivalent of Epoxy resin = E

Solid content of Epoxy resin = X percent

Loading of Epoxy resin in formulation (Table 3) = Y percent

$$\text{Active content} = \frac{Y \times X}{100}$$

Amine value of catalyst: C

$$\text{Amine equivalent weight} = \frac{56100}{C}$$

$$\text{E.g Epoxy cured with } \frac{56100}{C} \text{ g Amine}$$

$$1 \text{ g Epoxy cured with } \frac{56100}{C \times E} \text{ g Amine}$$

$$\frac{Y \times X}{100} \text{ Epoxy cured with } \frac{56100 \times Y \times X}{100 \times C \times E} \text{ g Amine}$$

Therefore, 100 g Pigmented base cured with $\frac{561 \times Y \times X}{C \times E}$ g Amine

$$\text{Mixing Ratio of Pigmented base : Catalyst (w/w)} = 100 : \frac{561 \times Y \times X}{C \times E}$$

C-6.3 Procedure

- Mix the pigmented base and catalyst as per above mentioned ratio and mix uniformly with a spatula by hand mixing with minimum foam generation.
- Make drawdowns side by side (approved sample vs. sample under evaluation) with the help of K-7 bar coater.
- 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.
- Dry the drawdown paper at 80 °C oven for 30 min for curing. After drying, check the colour difference (reduced tone) and strength% of the specimen against approved sample both visually as well as in Spectro (CIE Lab. ~~D65-10⁰ observer~~ See IS 101 Part 4/Sec 2).

ANNEX D

[Table 1, Item (ix)]

TEST FOR RESISTANCE TO ALKALI AND ACID

D-1 OUTLINE OF THE METHOD

The determination of resistance to alkali and acid is the measure of degree of bleeding or change of colour from the approved sample.

D-2 REAGENTS

D-2.1 Dilute Hydrochloric Acid Solution (1 : 4) — Dilute 20 ml of hydrochloric acid (*see* IS 265) to 100 ml with water.

D-2.2 Dilute Sodium Hydroxide Solution (20 percent) — Dissolve 200 g in 1 000 ml water (*see* IS 376).

D-3 PROCEDURE

Shake about 2 g of the sample in a test tube with a convenient volume of dilute hydrochloric acid solution. Allow to stand for 1 hour. Treat the approved sample at the same time in the same manner. Note any difference of colour change in the suspensions of the pigments. Repeat the test on a fresh test portion using the dilute sodium hydroxide solution in place of dilute hydrochloric acid solution and again note any difference of colour in the suspensions of the pigments and report the change of colour, if any.