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IS 56 : XXXX

BUREAU OF INDIAN STANDARDS

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Draft Indian Standard

PRUSSIAN BLUE (IRON BLUE) FOR PAINTS — SPECIFICATION

(*Third Revision* of IS 56)

(ICS 87.060.10)

Raw materials for Paints, Varnishes and Related Product Sectional Committee, CHD 21	**Last Date for Comments: 26 November 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 co-ordinated draft produced with the assistance of representatives of manufacturers and of various departments and authorities of the Government of India by the Co-ordinating Subcommittee of the No. 5 Standing Committee on Specifications for Paints and Allied Stores of the General Headquarters (now Army Headquarters), India.

In the first revision, the requirements for oil absorption and *p*H value were modified. In the second revision in 1993, requirement for volatile matter was modified and an additional requirement for residue on sieve was added.

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 color difference, tinting strength, and ease of dispersion has been changed to the Vibro Shaker method, replacing the existing method based on Muller. The requirements have been accordingly modified to reflect this change;

b) To address health and safety concerns, restrictions for lead and toxic heavy metals have been introduced;

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

d) Additionally, 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.

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PRUSSIAN BLUE (IRON BLUE) FOR PAINTS — SPECIFICATION

(*Third Revision*)

1 SCOPE

This standard prescribes requirements and methods of sampling and test for prussian blue (iron blue) pigment for paints.

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:

IS No.	*Title*
IS 33 : 1992	Inorganic pigments and extenders for paints — Methods of sampling and test (*third revision*)
IS 1070 : 2023	Reagent grade water — Specification (*fourth revision*)
IS 1303 : 1983	Glossary of terms relating to paints (*second revision*)
IS 15556 : 2005	Volumetric and spectrophotometric estimation of iron

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

4.2 Composition

The Pigment shall be essentially an iron blue Pigment formed by the reaction of solutions of iron salts with ferrocyanide or ferricyanide solution. The analysis shall show that;

a) The sum of the basic iron (as Fe) and iron cyanogen complex [expressed as $Fe(CN)_6$] is not less than 70 percent.
b) The total iron (expressed as Fe) is not less than 30 percent.

4.2.1 The composition of the material shall be determined as prescribed in Annex A.

4.3 Lead-Free Material

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.

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 Absorption/Emission Spectroscopic methods.

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

Table 1 Requirements for Prussian Blue (Iron Blue) for Paints

(*Clause* 4.5)

Sl No.	**Characteristic**	**Requirements**	**Method of Test, Ref to**
(1)	(2)	(3)	(4)
i)	Volatile matter, 60 °C for 16 hours*, percent by mass, *Max*	4.0	IS 33
ii)	Oil absorption	± 10 percent of approved sample	IS 33
iii)	Colour		Annex B
	a) Tinting strength, percent	95 – 105 of approved sample/ as agreed between the parties	
	b) Colour difference (Mass tone), ΔE, *Max*	1.5	
iv)	Ease of dispersion/ Fineness of grind, microns, *Max* (by Hegman gauge scale 0 to 8, *Min*)	15 (6.5)	Annex B
v)	Matter soluble in water, percent by mass, *Max*	2.0	IS 33
vi)	*p*H value of the aqueous extract	4.5 to 6	IS 33
vii)	Residue on 63 micron IS Sieve percent by mass, *Max*	0.5	IS 33

*The method given in IS 33 [heating at (105 ± 2) °C] is not suitable as the water of crystallization tends to be lost at such a high temperature and reproduceable results are not obtained. Moreover, it is a fire hazard.

5 PACKING AND MARKING

5.1 Packing

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

5.2 Marking

5.2.1 The containers shall be marked with the following information:

a) Name of the material,
b) Indication of the source of manufacture,
c) Mass of the material,
d) Batch No. or lot No. in code or otherwise, and
e) Month and year of manufacture.
f) Lead content (Maximum);
g) Toxic heavy metals content
h) A cautionary note as below:
    i) Keep out of reach of children; or
    ii) 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

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

7 TEST METHOD

7.1 Test shall be conducted as prescribed in IS 33 and in Annexes A and B mentioned in **4.2.1** and col 4 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.

8 CRITERIA FOR CONFORMITY

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

ANNEX A

(*Clauses* 4.2.1 *and* 7.1)

DETERMINATION OF BASIC IRON AND IRON CYANOGEN COMPLEX

A-1 GENERAL

A-1.1 Outline of the Method

Prussian blue is decomposed by cold aqueous caustic potash. The iron cyanogen complex $[Fe(CN)_6]$ forms a soluble potassium ferrocyanide while the basic iron is converted into insoluble iron hydroxide which may be separated from the solution of potassium ferrocyanide by filtration.

A-2 REAGENTS

A-2.l Standard Potassium Permanganate Solution (0.1 N)

Dissolve 3.2 g of pure potassium permanganate in 1 000 ml of water and allow it to stand for 8 days to 14 days. Siphon off the clear supernatant solution into a glass stoppered bottle painted black. Weigh accurately about 3.3 g of sodium oxalate, previously dried for a few hours at 100 °C and cooled over fused calcium chloride in a desiccator. Dissolve it in water and make up solution to exactly 500 ml. Transfer 25 ml of sodium oxalate to a conical flask, add 50 ml of water and 10 ml of dilute sulphuric acid (1 : 1 by volume). Heat the liquid to about 60°C and titrate with potassium permanganate solution.

$$\text{Strength of potassium permanganate solution} = \frac{M \times 25}{67 \times V}$$

where

M = mass, in g, of sodium oxalate in 1 000 ml of solution; and

V = volume in ml of potassium permanganate solution required for titration.

A-2.2 Standard Sodium Thiosulphate Solution (0.1 N)

Dissolve about 25 g of crystallized sodium thiosulphate in 1 000 ml of recently boiled water in a volumetric flask. Titrate the solution against approximately 0.1 N standard solution of iodine using starch solution as indicator.

A-2.3 Potassium Iodide

A-2.4 Saturated Solution of Sodium Bicarbonate

A-2.5 Standard Iodine Solution (0.l N)

Dissolve in a 1 000 ml flask about 12 g of resublimed iodine in a concentrated solution of 15 g to 18 g of potassium iodide. Make up the solution to 1 000 ml and standardize it against pure dry arsenious oxide. For this, dissolve about 0.25 g of arsenious oxide, accurately weighed, in the minimum quantity of hot sodium hydroxide solution. Cool and neutralize the solution with dilute hydrochloric acid, using methyl orange as indicator. Add 10 ml of sodium bicarbonate solution and dilute the solution to about 100 ml. Titrate the solution against iodine solution, using starch solution as indicator towards the end of the reaction.

A-2.6 Starch Solution

Stir up 3 g of potato starch with 10 ml of al percent solution of salicylic acid and boil till starch is completely dissolved. Dilute to 1 000 ml.

A-3 PROCEDURE

A-3.1 Decomposition of Prussian Blue

Place about 0.5 g of the pigment, dried as described in IS 33 and accurately weighed, in a 200 ml beaker. Swirling the beaker to ensure complete wetting of the material, add 10 ml of a 10 percent potassium hydroxide solution till the colour is destroyed. Filter the mixture through a large Gooch crucible, packed with prepared asbestos, and wash the residue with water. Use the residue so obtained for the determination of basic iron and the filtrate for the determination of the iron cyanogen complex.

A-3.2 Determination of Basic Iron

Extract the residue in the Gooch crucible with hot dilute hydrochloric acid and determine the iron in the solution so obtained by any suitable method (*see* IS 15556).

A-3.2.1 If the acid extract is coloured blue, it is an indication that the residue has not been properly washed. The test shall then be repeated.

A-3.3 Determination of Iron Cyanogen Complex

A-3.3.1 Transfer the filtrate as obtained in **A-3.1** to a stoppered flask or bottle of about 1 1itre capacity and dilute to 400 ml. Add 15 ml of concentrated hydrochloric acid (relative density l.16 g/ml) and 45 ml of sodium acetate solution (500 g of the pure crystallized salt to 1 litre of water) and add the permanganate solution in excess until a distinct red-brown colour is obtained and the turbidity, first formed, disappears. Add 10 ml of a 10 percent solution of potassium iodide and allow the mixture to stand for 4 minutes. Titrate the iodine liberated by the excess of potassium permanganate with standard 0.1 N sodium thiosulphate solution.

A-3.3.1.1 The quantity of potassium permanganate consumed as determined in **A-3.3.1** represents not only that necessary for the conversion of potassium ferrocyanide in potassium ferricyanide but also that necessary for the oxidation of any traces of organic matter which may be present resulting in too high a value for the iron cyanogen complex. A precise determination of the actual iron cyanogens complex can be obtained by following the procedure described in **A-3.3.2**.

A-3.3.2 Add 10 ml of hydrochloric acid (relative density 1.16 g/ml), 10 ml of a 10 percent potassium iodide solution and 10 ml of zinc sulphate solution (25 g of $ZnSO_4 \cdot 7H_2O$ in 100 ml of water) to the solution from the previous titration and allow the turbid mixture to stand for 3 minutes. Determine the liberated iodine by titration with 0.1 N sodium thiosulphate solution.

A-3.4 Calculation

Use the following factors for evaluating the results:

a) One millilitre of 0.1 N sodium thiosuphate solution is equivalent to 0.021 2 g of [Fe(CN)$_6$],
b) One millilitre of 0.1 N sodium thiosulphate solution is equivalent to 0.005 585 g of iron (as Fe).
c) The sum of the basic iron (as Fe) and iron cyanogen complex [Fe (CN)$_6$] is the sum of the values determined in **A-3.2** and **A-3.3**, and
d) The total iron (as Fe) is the sum of the values determined under **A-3.2** and the value calculated for the iron cyanogen complex.

ANNEX B

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

DETERMINATION OF TINTING STRENGTH, COLOUR DIFFERENCE (MASS TONE) AND EASE OF DISPERSION

B-1 OUTLINE OF THE METHOD

To evaluate the performance of pigment with respect to colour, tinting strength, colour difference (mass tone) and ease of dispersion against approved pigment sample.

B-2 APPARATUS

B-2.1 Vibroshaker — 25 degree to 30 degree angular oscillation at 640 / 660 spm (shakes per minute) simultaneously

B-2.2 Closed SS metal container — 125 ml

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

B-2.4 Electronic Balance — accuracy 1 mg

B-2.5 Spatula

B-2.6 Mechanical Stirrer

B-2.7 Black and White Paper — Charts, all of same size and measuring at least 100 x 200 mm, printed and varnished to give adjacent black and white areas readily wetted by, but impervious to solvent or water-thinned paints. The black and white areas shall each be of dimensions not less than 80 x 80 mm. The reflectance of white areas of the cards shall be 80 ± 2 percent when measured over a white tile using a spectrophotometer complying with **B-5.4.2** and that of the black areas shall be not greater than 1 percent, unless otherwise agreed.

To avoid errors due to-variation, from one batch of charts to another, the charts used for a given test should come from the same batch.

B-2.8 Film Applicator — A film applicator giving a uniform film of maximum wet thickness of 80 µm is required. The film laid down shall be at least 70 mm wide, with areas of dimensions not less than 60 x 60 mm and of uniform thickness over both black and white areas of the card. The application of uniform films is facilitated by the use of automatic applicators.

B-3 PROCEDURE

B-3.1 Method of Preparation of the Pigment Concentrate:

Table 2 gives a formulation for 100 percent completion. For this test, apply factor of 0.4 to all the materials given in Table 2 and weigh the ingredients accordingly. Add 60 g of glass beads[€] in a closed stainless steel (SS) metal container of volume 125 ml. The dispersion time after addition of materials mentioned in Stage 1 is 40 min. After dispersion in complete, add materials mentioned in Stage 2 and run for another 10 min. Collect the pigment concentrate and proceed for the testing.

Table – 2 Guideline Formulation of Preparation of Pigment Concentrate

(*Clause* 5.2)

Sl. No	Component	Weight (percent)	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

B-4 DETERMINATION OF EASE OF DISPERSION/FINENESS OF GRINDING:

To assess the ease of dispersion/fineness of grinding by gauge follow the procedure as given in IS 354 (Part 2).

B-5 DETERMINATION OF COLOUR DIFFERENCE (MASS TONE)

B-5.1 Colour Difference (Mass Tone)

B-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.

B-5.1.2 *Catalyst* — Medium viscosity polyamide hardener

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

B-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

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

Amine value of catalyst = C

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

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

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

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

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

Mixing Ratio of Pigment concentrate:

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

B-5.3 Procedure

Mix the pigment concentrate and catalyst as per ratio given in **B-5.2** and mix uniformly with a spatula by hand mixing with minimum foam generation. Make drawdowns side by side (approved sample/as agreed between parties vs. sample under evaluation) with the help of film applicator. 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/as agreed between parties in Spectrophotometer (*see* **B-5.4**).

B-5.4 Degree of colour change

B-5.4.1 The colour of the test panel shall be compared against the stipulated shade as given in IS 5 or any agreed standard sample between purchaser and supplier. The colour difference between a pair of painted panels shall be calculated in terms of ΔE (Delta E) by using CMC (2:1) colour difference equation. From spectral measurement, QC program calculate CIE colour specifications- L* a* b* C* h* based on daylight illumination, as described in **B-5.4.2**.

B-5.4.2 A reflectance spectrophotometer is used for reflectance measurement. Like Visual Assessment requirement, the sample should be sufficiently large enough to measure using Large Area of View (LAV). Small sized samples measured using Small Area of View (SAV) may not have high repeatability. Sample size should be minimum 2 x 2". The spectral measurement should be carried out using a reflectance spectrophotometer having following features:

Repeatability – Short-Term	: Better than 0.15 ΔE_{CIELAB}
Inter-Instrument Agreement	: Better than 0.25 ΔE_{CIELAB}
Wavelength Range	: 400-700 nm (360-780 nm preferable)
Wavelength Increment	: 10 nm

B-6 DETERMINATION OF TINTING STRENGTH:

B-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

Catalyst — Medium viscosity polyamide hardener

Amine Value — (300 ± 20) mg KOH/g

B-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 (*see* Table 3) = Y percent

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

Amine value of catalyst = C

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

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

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

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

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

Mixing Ratio of Pigment concentrate:

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

B-6.3 Procedure

Mix the pigmented base and catalyst as per ratio given in **B-6.2** and mix uniformly with a spatula by hand mixing with minimum foam generation. Make drawdowns side by side (approved sample/as agreed between parties vs. sample under evaluation) with the help of film applicator. 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 tinting strength percent of the specimen against approved sample/as agreed between parties by Spectroscopic method (*see* **B-6.3.2**).

B-6.3.2 Measure the tinting strength of sample with the spectrophotometer (*see* **B-5.4.2**). The relative tinting strength can be calculated by taking ratio of the absorbance index of the test sample to that of an agreed reference pigment, expressed as a percentage.