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Barium chromate pigments for paints

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FOREWORD

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Barium chromate pigments for paints

1 SCOPE AND FIELD OF APPLICATION

This International Standard lays down the requirements and test methods for barium chromate pigments of approximate composition $BaCrO_4$, suitable for use in paints and/or corrosion-inhibiting coatings.

2 REFERENCES

ISO/R 787, *General methods of test for pigments.*
ISO/R 842, *Sampling raw materials for paints and varnishes.*

3 REQUIRED CHARACTERISTICS AND THEIR TOLERANCES

Barium chromate pigments for paints shall have the characteristics shown in the Table below.

4 SAMPLING

A representative sample of the pigment shall be taken in accordance with ISO/R 842.

TABLE – **Required characteristics and their tolerances**

Characteristic [1]		**Requirement**	**Test method**
Barium content	% BaO	min. 56	clause 5.1
Total chromate content	% CrO_3	min. 36.5	clause 5.2
Water-soluble chloride content	% Cl	max. 0.1	clause 5.3.2
Water-soluble nitrate content	% NO_3	max. 0.1	clause 5.3.3 or 5.3.4
Chromate content in 100 ml of extract from 10 g of pigment	g CrO_3/100 ml	max. 0.01	clause 5.3.5
Volatile matter at 105 °C	%	max. 1.0	ISO/R 787, Part II
Oil absorption value, compared with value agreed between the interested parties		within ± 15 %	ISO/R 787, Part V
Residue on sieve (63 μm)	oil method %	max. 0.5	ISO/R 787, Part VI
	water method %	max. 0.3	ISO/R 787, Part VII

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[1] If a value for density is agreed between the interested parties, the method for determination shall be that given in ISO/R 787, Part X.

5 METHODS OF TEST

All reagents used shall be of recognized analytical reagent quality. Distilled water or water of at least equivalent purity shall be used.

5.1 Determination of barium content

5.1.1 *Reagents*

1) **Acetic acid,** 80 % (m/m) solution.

2) **Hydrochloric acid,** 4 N.

3) **Sulphuric acid,** 50 g/l solution.

4) **Ammonia solution,** approximately 4 N.
Mix 1 part of concentrated ammonia solution, $d = 0.91$, and 4 parts by volume of water.

5) **Ethanol,** 95 % (V/V).

5.1.2 *Apparatus*

Sintered silica crucible, porosity P 16 (maximum pore size 10 to 16 µm).

5.1.3 *Procedure*

5.1.3.1 Test portion

Weigh, to the nearest 0.1 mg, 0.5 g of the sample.

5.1.3.2 Determination

Transfer the test portion into a 600 ml beaker and add 50 ml of hydrochloric acid (2). Heat to dissolve, and filter. Add 40 ml of ethanol (5) and continue heating until the chromate is reduced to chromium(III), which is indicated by a green coloration of the solution. Dilute the solution with about 100 ml of water and add such a quantity of ammonia solution (4) that a slight permanent precipitate remains.

Add hydrochloric acid (2) until the precipitate is redissolved and then add 30 ml of acetic acid (1). Heat the solution to boiling and add, drop by drop, 20 ml of sulphuric acid (3). Add 100 ml of ethanol (5) and allow to stand for some hours, or overnight. Filter the precipitate through the tared silica filter crucible (5.1.2), and wash several times with a solution consisting of equal parts of ethanol (5), sulphuric acid (3) and water.

Ignite at 800 °C. Cool in a desiccator and weigh. Continue the ignition and weighing of the crucible until constant mass is obtained.

5.1.4 *Expression of results*

Calculate the barium content, expressed as BaO, as a percentage by mass, by the formula

$$\frac{65.72\, m_1}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of residue.

Report the result to one decimal place.

5.2 Determination of total chromate content

5.2.1 *Reagents*

1) **Sodium thiosulphate,** 0.1 N standard volumetric solution.

2) **Starch solution,** 1 % (m/m).

3) **Hydrochloric acid,** 2 N.

4) **Potassium iodide,** 1 M solution.

5) **Sodium hydrogen carbonate.**

5.2.2 *Procedure*

5.2.2.1 Test portion

Weigh, to the nearest 0.1 mg, about 0.25 g of the sample.

5.2.2.2 Determination

Dissolve the test portion in 30 ml of hydrochloric acid (3), in a conical stoppered flask. Make up to 100 ml with water, and add 2 g of sodium hydrogen carbonate (5). Add 10 ml of potassium iodide solution (4) and allow the flask to stand for 5 min in the dark. Afterwards, titrate with sodium thiosulphate solution (1). Towards the end of the titration add 5 ml of starch solution (2) as indicator and titrate until the colour changes to green or blue-green.

5.2.3 *Expression of results*

Calculate the total chromate content as a percentage by mass, expressed as CrO_3, by the formula

$$\frac{3.33 \times V \times T}{m}$$

where

V is the volume, in millilitres, of 0.1 N sodium thiosulphate solution required;

T is the normality of the sodium thiosulphate solution;

m is the mass, in grams, of the test portion.

Report the result to one decimal place.

5.3 Determination of water-soluble chloride and nitrate contents, and water-soluble chromate content

The aqueous extract prepared according to 5.3.1 is used for the determination of

a) water-soluble chloride and nitrate contents;

b) water-soluble chromate content.

For the water-soluble nitrate content, two methods are provided:
Method A (5.3.3) for use when it is only required to determine whether the content is above or below the specified limit of 0.1 %;
Method B (5.3.4) for use when a precise determination of the content is required.

5.3.1 *Preparation of aqueous extract*

5.3.1.1 Apparatus

Mechanical agitator or stirrer.

5.3.1.2 Procedure

5.3.1.2.1 Test portion

Weigh 30 ± 0.1 g of the sample in a chemically resistant glass flask.

5.3.1.2.2 Preparation

Agitate the test portion with 300 ml of water for 1 h at room temperature in such a manner that the pigment is kept in continuous suspension without increasing the temperature of the water. Filter the mixture and reserve the perfectly clear filtrate for the determinations according to 5.3.2 to 5.3.5.

5.3.2 *Determination of water-soluble chloride content*

5.3.2.1 Reagents

1) **Potassium chromate**, 50 g/l solution.

2) **Silver nitrate**, 0.1 N standard volumetric solution.

5.3.2.2 Procedure

Take 100 ml of the clear aqueous extract (5.3.1) and add 1 ml of potassium chromate solution (1). Titrate the solution with silver nitrate solution (2), slowly and with vigorous shaking, until a faint reddish brown colour persists.

Carry out a blank determination by adding 1 ml of potassium chromate solution (1) to 100 ml of water and titrating with silver nitrate solution (2) until the colour matches 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.

5.3.2.3 Expression of results

Calculate the water-soluble chloride content as a percentage by mass, expressed as Cl, by the formula

$$0.035\,4\,(V_1 - V_0)$$

where

V_0 is the volume, in millilitres, of 0.1 N silver nitrate solution required in the blank determination;

V_1 is the volume, in millilitres, of 0.1 N silver nitrate solution required by the test portion.

Report the result to two decimal places.

5.3.3 *Determination of water-soluble nitrate content — Method A*

5.3.3.1 Reagents

1) **Hydrochloric acid,** $d = 1.18$.

2) **Sodium hydroxide** solution, 200 g/l.

3) **Ammonium chloride** solution, 17.2 mg/l.

4) **Devarda's alloy**, powdered.

5) **Ammonia-free water.**

NOTE — Ammonia-free water may be prepared by redistilling approximately 500 ml of distilled water to which has been added 1 g of anhydrous sodium carbonate and 1 g of potassium permanganate. Reject the first 100 ml of distillate and then collect about 300 ml.

6) **Nessler's reagent** prepared by either of the following methods:

a) Dissolve 5 g of potassium iodide in 3.5 ml of water. Add cold saturated mercury(II) chloride ($HgCl_2$) solutions, while stirring, until a faint red precipitate is formed. With continued stirring add 40 ml of 50 % potassium hydroxide solution, dilute to 100 ml with water, mix well, allow to settle, decant the clear supernatant liquid and store it in the dark.

or

b) Dissolve 3.5 g of potassium iodide and 1.25 g of mercury(II) chloride in 80 ml of water. Add cold saturated mercury(II) chloride solution, while stirring until a slight red precipitate remains, then add 12 g of sodium hydroxide, stir until dissolved, and finally add a little more saturated mercury(II) chloride solution and dilute to 100 ml with water. Stir occasionally during several days, allow to stand, and use the clear supernatant liquid for the test.

5.3.3.2 Apparatus

1) **Distillation apparatus.**

2) **Nessler cylinders,** 50 ml.

5.3.3.3 Procedure

Place 50 ml of the clear aqueous extract (5.3.1) into the distillation flask and dilute to 150 ml with ammonia-free water (5). Add 3 g of Devarda's alloy (4) and 30 ml of sodium hydroxide solution (2) and close the apparatus at once. Place 2 ml of hydrochloric acid (1) and 30 ml of ammonia-free water (5) in the receiver. Warm the flask gently until the reaction starts and then allow the reaction to proceed gently for about half an hour. Then distil about 70 ml of liquid, the receiver being kept cool with running water. Make up the distillate to 250 ml with ammonia-free water (5) and transfer 5 ml to a Nessler cylinder. Dilute to 50 ml with ammonia-free water (5). Transfer 5 ml of ammonium chloride solution (3) (equivalent to 0.1 % NO_3) into a similar Nessler cylinder and dilute to 50 ml with ammonia-free water. Add 1 ml of Nessler's reagent (6) to each cylinder and mix each thoroughly. Allow both cylinders to stand for 5 min and compare the intensity of colour of the two solutions.

5.3.3.4 Expression of results

Report the result as either greater than or less than 0.1 % NO_3.

5.3.4 *Determination of water-soluble nitrate content — Method B*

5.3.4.1 Principle

The nitrate present in the test solution is used to nitrate salicylic acid in sulphuric acid medium. The nitro-compound formed is of an intense yellow colour in alkaline solution, and the colour is measured spectrophotometrically at a wavelength of 410 nm.

5.3.4.2 Reagents

1) **Sulphuric acid,** $d = 1.84$.

2) **Sulphuric acid,** 5 N.

3) **Ethanol,** 95 % (V/V).

4) **Sodium salicylate** solution, 5 g/l, freshly prepared.

5) **Sodium hydroxide** solution, 300 g/l.

6) **Sodium hydroxide** solution, 4 N.

7) **Potassium nitrate,** dried at 120 °C and cooled in a desiccator.

5.3.4.3 Apparatus

1) **Spectrophotometer** suitable for measurements at a wavelength of 410 nm.

2) 10 mm **cells** for use with the spectrophotometer.

3) **pH meter.**

4) **Volumetric flasks,** of capacity 50 ml, 100 ml, 250 ml and 500 ml.

5.3.4.4 Preparation of calibration graph

Standard solution I. Weigh 163 ± 0.1 mg of potassium nitrate (7), dissolve it in water in a 100 ml volumetric flask, make up to the mark and mix well.

Standard solution II. Dilute 10 ml of standard solution I to a volume of 500 ml.

Measure 2, 4, 6, 8 and 10 ml of standard solution II (corresponding to 0.04, 0.08, 0.12, 0.16 and 0.2 mg of NO_3 respectively) into separate 100 ml glass beakers.

Treat each beaker as follows : Add 1 ml of sodium salicylate solution (4), evaporate to dryness on a water bath and allow to cool in a desiccator. Moisten the whole of the dried residue with 1 ml of sulphuric acid (1) and allow to stand in the desiccator for 10 min. Afterwards, wash the contents into 50 ml volumetric flasks with water, add 10 ml of sodium hydroxide solution (5) and cool to room temperature. Make up to the mark with water and mix well. Determine and record the optical density at 410 nm in a 10 mm cell against a water blank.

Construct a graph of optical density against milligrams of NO_3.

5.3.4.5 Procedure

Place 50 ml of clear aqueous extract (5.3.1) into a 250 ml glass beaker and add 5 ml of sulphuric acid (2) and 2 ml of ethanol (3). Warm the solution until the chromate is reduced as indicated by a change of colour to green. Boil the solution vigorously to drive off organic matter, taking care to avoid losses by splashing, cool and add sodium hydroxide solution (6) until just alkaline. Cool again and adjust the pH to 8.0 ± 0.5 measured by the pH meter. Filter through filter paper and wash with hot water, collecting the filtrate and washings. Cool, make up the volume to 250 ml and mix.

Transfer 10 ml (see Note) of this solution to a 100 ml glass beaker. Add 1 ml of sodium salicylate solution (4) and proceed as described in 5.3.4.4 including the determination of the optical density at 410 nm.

From the known optical density of the test solution, determine from the calibration graph the corresponding mass of nitrate in milligrams.

NOTE — If the nitrate content is more than 0.1 %, carry out a second determination, using 5 ml of solution.

5.3.4.6 Expression of results

Calculate the water-soluble nitrate content as a percentage by mass, expressed as NO_3, by the formula

$\frac{a}{2}$, when 10 ml of solution have been used;

a , when 5 ml of solution have been used (see Note to 5.3.4.5);

where a is the mass, in milligrams, of NO_3 corresponding to the optical density of the test solution.

5.3.5 *Determination of water-soluble chromate content*

5.3.5.1 Reagents

1) **Hydrochloric acid,** 2 N.

2) **Potassium iodide** solution, 1 M.

3) **Sodium thiosulphate,** 0.01 N standard volumetric solution.

4) **Starch solution,** 1 % (m/m).

5) **Sodium hydrogen carbonate.**

5.3.5.2 Procedure

Transfer 50 ml of clear aqueous extract (5.3.1) to a conical stoppered flask. Add 50 ml of water and 2 g of sodium hydrogen carbonate (5), followed by 30 ml of hydrochloric acid (1).

Then add 10 ml of potassium iodide solution (2) and allow the flask to stand for 5 min in the dark. Afterwards, titrate with sodium thiosulphate solution (3). Towards the end of the titration add 5 ml of starch solution (4) as indicator and titrate until the colour changes to green.