INTERNATIONAL STANDARD ISO 1249

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Zinc chromate pigments — Basic zinc potassium chromate pigments and zinc tetrahydroxychromate pigments

Pigments à base de chromate de zinc — Pigments à base de chromate basique de zinc et de potassium et pigments à base de tétrahydroxychromate de zinc

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up has the right to be represented on that Committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, International Standard ISO 1249 replaces ISO Recommendation R 1249-1970 drawn up by Technical Committee ISO/TC 35, *Paints and varnishes.*

The Member Bodies of the following countries approved the Recommendation :

Australia
Austria
Denmark
Egypt, Arab Rep. of
Germany
Greece
India
Iran
Ireland
Israel
Italy
Netherlands
Peru
Poland
Portugal
South Africa, Rep. of
Spain
Sweden
Switzerland
Turkey
United Kingdom
U.S.S.R.

The Member Body of the following country expressed disapproval of the Recommendation on technical grounds :

France

The Netherlands Member Body had opposed the approval of clause 4.5.4 of the Recommendation.*

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* Subsequently, this Member Body approved the Recommendation.

Printed in Switzerland

Zinc chromate pigments — Basic zinc potassium chromate pigments and zinc tetrahydroxychromate pigments

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies the requirements and corresponding test methods for zinc chromate pigments suitable for use in paints and/or corrosion-inhibiting coatings.

2 REFERENCES

ISO 787, *General methods of test for pigments.*

ISO 842, *Raw materials for paints and varnishes — Sampling.*

3 DESCRIPTION

Zinc chromate pigments are pigments based on basic zinc chromate or zinc tetrahydroxychromate. The following types are distinguished :

a) **Basic zinc potassium chromate pigments (type 1a) :** Pigments of approximate composition $K_2CrO_4.3ZnCrO_4.Zn(OH)_2.2H_2O$.

b) **Basic zinc potassium chromate pigments, lead-containing (type 1b) :** Pigments of approximate composition $K_2CrO_4.3ZnCrO_4.Zn(OH)_2.2H_2O$, in which a lead content up to 2 % maximum is allowed, calculated as PbO.

c) **Zinc tetrahydroxychromate pigments (type 2) :** Pigments of approximate composition $ZnCrO_4.4Zn(OH)_2$.

4 REQUIRED CHARACTERISTICS AND THEIR TOLERANCES

Basic zinc potassium chromate pigments (types 1a and 1b) and zinc tetrahydroxychromate pigments (type 2) shall have the characteristics shown in the table.

5 SAMPLING

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

5.2 The sample agreed between the interested parties, to which reference is made in the table, shall comply with all the requirements specified for the pigment under test.

TABLE — **Required characteristics and their tolerances**

Characteristic[1]		**Requirement according to type**			**Test method**
		Basic zinc potassium chromate pigments **Type 1a**	**Basic zinc potassium chromate pigments lead-containing** **Type 1b**	**Basic zinc potassium chromate pigments** **Type 2**	
Zinc content	% (*m/m*) ZnO	35 to 40	35 to 40	68,5 to 72	Clause 6
Chromate content	% (*m/m*) CrO_3	min. 42	min. 42	17 to 19	Clause 7
Alkali metal content	% (*m/m*) K_2O	max. 12	max. 12	—	Clause 8
Lead content	% (*m/m*) PbO	—	max. 2,0	—	Clause 9
Water-soluble sulphate content	% (*m/m*) SO_4	max. 0,1	max. 0,1	max. 0,1[2]	Sub-clause 10.2 and ISO 787, Part XIII
Water-soluble chloride content	% (*m/m*) Cl	max. 0,1	max. 0,1	max. 0,1[2]	Sub-clause 10.3 and ISO 787, Part XIII
Water-soluble nitrate content	% (*m/m*) NO_3	max. 0,1	max. 0,1	—	Sub-clauses 10.4 and 10.5 and ISO 787, Parts XIII and XIX
Chromate content in 100 ml of extract (from 10 g of pigment)	g CrO_3/100 ml	0,06 to 0,15	0,06 to 0,15	—	Sub-clause 10.6
Matter soluble in water	% (*m/m*)	—	—	max. 0,3	Sub-clause 10.7
Matter insoluble in ammoniacal ammonium chloride solution	% (*m/m*)	max. 0,5	max. 3,0	max. 0,5	Clause 11
Matter volatile at 105 °C	% (*m/m*)	max. 1,0	max. 1,0	max. 1,0	ISO 787, Part II
Oil absorption value, compared with value of sample agreed between the interested parties		within ± 15 %	within ± 15 %	within ± 15 %	ISO 787, Part V
Residue on sieve (63 μm) — oil method	% (*m/m*)	max. 0,5	max. 0,5	max. 0,5	ISO 787, Part VI
— water method	% (*m/m*)	max. 0,3	max. 0,3	max. 0,3	ISO 787, Part VII

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[1] If zinc chromate pigments are used as colouring pigments, and the colour and relative tinting strength are agreed between the interested parties, the test methods for the determination of these properties shall be those given in ISO 787.

[2] For zinc tetrahydroxychromate, the water-soluble sulphate and chloride content should be determined separately only if the content of matter soluble in water exceeds 0,2 % (*m/m*).

METHODS OF TEST

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

6 DETERMINATION OF ZINC CONTENT

6.1 Reagents

6.1.1 Sodium thiosulphate, 0,1 N standard volumetric solution.

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

6.1.3 Hydrochloric acid, 1 N.

6.1.4 Potassium cyanoferrate(III), 0,1 M solution.

6.1.5 Barium acetate, 0,5 M solution.

6.1.6 Potassium chloride, crystalline.

6.1.7 Potassium iodide, 1 M solution.

6.2 Procedure

6.2.1 *Test portion*

Weigh, to the nearest 0,1 mg, about 0,8 g of basic zinc potassium chromate or about 0,4 g of zinc tetrahydroxychromate.

6.2.2 *Determination*

Dissolve the test portion in 10 ml of hydrochloric acid (6.1.3), in a conical stoppered flask. If necessary, warm the solution slightly. Make up the total volume to 150 ml by adding water and add 2 g of potassium chloride (6.1.6) and 50 ml of the potassium cyanoferrate(III) solution (6.1.4). Allow the flask to stand for 3 min and afterwards add, while stirring, 50 ml of barium acetate solution (6.1.5) and 10 ml of potassium iodide solution (6.1.7). Immediately afterwards, titrate the liberated iodine with sodium thiosulphate solution (6.1.1); towards the end of the titration add 5 ml of the starch solution (6.1.2) as indicator and titrate until the colour changes to yellow.

6.3 Expression of results

Calculate the zinc content expressed as ZnO, as a percentage by mass, by the following formula :

$$\frac{12{,}21\,V\,T}{m}$$

where

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

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

T is the normality of the sodium thiosulphate solution.

Report the result to one decimal place.

NOTE — The use of a single solution of the test portion in hydrochloric acid both for the determination of zinc content according to clause 6 and the determination of chromate content according to clause 7 cannot be recommended because of possible sources of error. For the determination of zinc content, to use a stronger hydrochloric acid than 1 N would cause interference. On the other hand, for the determination of chromate content, the solution must not be warmed because of the possibility of chromate reduction.

7 DETERMINATION OF CHROMATE CONTENT

7.1 Reagents

7.1.1 Sodium thiosulphate, 0,1 N standard volumetric solution.

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

7.1.3 Hydrochloric acid, 2 N.

7.1.4 Potassium iodide, 1 M solution.

7.1.5 Sodium hydrogen carbonate.

7.2 Procedure

7.2.1 *Test portion*

Weigh, to the nearest 0,1 mg, about 0,25 g of basic zinc potassium chromate or about 0,5 g of zinc tetrahydroxychromate.

7.2.2 *Determination*

Dissolve the test portion in 30 ml of the hydrochloric acid (7.1.3), in a stoppered conical flask. Make up to 100 ml with water, and add 2 g of sodium hydrogen carbonate (7.1.5). Add 10 ml of potassium iodide solution (7.1.4) and allow the flask to stand for 5 min in the dark. Afterwards, titrate with sodium thiosulphate solution (7.1.1). Towards the end of the titration add 5 ml of the starch solution (7.1.2) as indicator and titrate until the colour changes to green or blue-green.

7.3 Expression of results

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

$$\frac{3{,}33\,V\,T}{m}$$

where

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

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

T is the normality of the sodium thiosulphate solution.

Report the result to one decimal place.

8 DETERMINATION OF ALKALI METAL CONTENT

8.1 Reagents

8.1.1 Sodium thiosulphate, 0,1 N standard volumetric solution.

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

8.1.3 Hydrochloric acid, 2 N.

8.1.4 Potassium iodide, 1 M solution.

8.1.5 Sodium hydrogen carbonate.

8.2 Procedure

8.2.1 *Test portion*

Weigh, to the nearest 1 mg, about 1 g of the sample.

8.2.2 *Determination*

Heat the test portion at approximately 600 °C for 1 h. Cool and extract the alkali metal chromate from the residue with hot water, filter and wash the residue free from soluble chromate.

Collect the filtrate and washings in a conical flask and acidify with hydrochloric acid (8.1.3) until a change in colour from yellow to orange occurs.

Make up the volume to about 100 ml with water, add 2 g of sodium hydrogen carbonate (8.1.5) and then 30 ml of hydrochloric acid (8.1.3). Add 10 ml of potassium iodide solution (8.1.4) and allow the flask to stand for 5 min in the dark. Afterwards, titrate with sodium thiosulphate solution (8.1.1). Towards the end of the titration, add 5 ml of the starch solution (8.1.2) as indicator and titrate until the colour changes to green.

8.3 Expression of results

Calculate the alkali metal content expressed as K_2O, as a percentage by mass, by the following formula :

$$\frac{3{,}13\,V\,T}{m}$$

where

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

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

T is the normality of the sodium thiosulphate solution.

Report the result to one decimal place.

9 DETERMINATION OF LEAD CONTENT

NOTE — The determination of the lead content of lead-containing basic zinc potassium chromate pigments (type 1b) is necessary only if the value for matter insoluble in ammoniacal ammonium chloride solution, determined according to clause 11, is higher than 2,0 %.

9.1 Reagents

9.1.1 Hydrochloric acid, diluted 1 + 4.

Mix 1 part by volume of concentrated hydrochloric acid, ρ 1,18 g/ml, and 4 parts by volume of water.

9.1.2 Ammonia solution, diluted 1 + 4.

Mix 1 part by volume of concentrated ammonia solution, ρ 0,91 g/ml, and 4 parts by volume of water.

9.1.3 Sodium sulphide, 50 g/l solution.

9.1.4 Nitric acid, ρ 1,42 g/ml.

9.1.5 Sulphuric acid, diluted 1 + 1.

Mix 1 part by volume of concentrated sulphuric acid, ρ 1,84 g/ml, and 1 part by volume of water.

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

9.1.7 Washing solution

Mix 4 ml of concentrated sulphuric acid, ρ 1,84 g/ml, 100 ml of water and 100 ml of ethanol 95 % (*V/V*).

9.2 Procedure

9.2.1 *Test portion*

Weigh, to the nearest 1 mg, about 20 g of the sample.

9.2.2 *Determination*

Dissolve the test portion in hydrochloric acid (9.1.1), heating meanwhile. Neutralize the solution by adding such a quantity of ammonia solution (9.1.2) that the precipitation of zinc hydroxide just does not take place, and heat to boiling. Precipitate the lead as lead sulphide by adding 50 ml of sodium sulphide solution (9.1.3).

Allow to stand overnight and filter off the precipitate using a sintered glass filter. Dissolve the precipitate from the filter with hot concentrated nitric acid (9.1.4). Evaporate the solution after adding 20 ml of sulphuric acid (9.1.5) until copious white fumes are evolved. After cooling, add about 100 ml of water and 100 ml of ethanol (9.1.6). Stir, allow to stand overnight and filter off the precipitate using a porcelain filter crucible tared to the nearest 1 mg. Wash the residue first with washing solution (9.1.7), then with ethanol (9.1.6) and dry it at 100 °C. Place the crucible containing the residue in an outer crucible and ignite in a muffle furnace at 600 to 700 °C for 1 h. Allow to cool to room temperature in a desiccator and weigh the residue to the nearest 1 mg.

9.3 Expression of results

Calculate the lead content expressed as PbO, as a percentage by mass, by the following formula :

$$\frac{73{,}6\, m_1}{m_0}$$

where

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

m_1 is the mass, in grams, of the residue ($PbSO_4$).

Report the result to one decimal place.

10 DETERMINATION OF WATER-SOLUBLE SULPHATE, CHLORIDE AND NITRATE CONTENT, TOTAL MATTER SOLUBLE IN WATER AND WATER-SOLUBLE CHROMATE CONTENT

NOTES

1 The aqueous extract prepared according to 10.1 is used for the determination of

a) water-soluble sulphate, chloride and nitrate content;

b) total matter soluble in water (for zinc tetrahydroxychromate pigments only);

c) water-soluble chromate content (for zinc potassium chromate pigments only).

For each of these determinations, 50 ml of the extract is used; thus, the 300 ml of aqueous extract is sufficient for all the determinations, including a certain reserve.

2 For the water-soluble nitrate content, two methods are provided :

Method A (see 10.4) for use when it is only required to determine whether the content is above or below the specified limit of 0,1 %.

Method B (see 10.5) for use when a precise determination of the content is required.

10.1 Preparation of aqueous extract

10.1.1 *Apparatus*

Mechanical agitator or **stirrer.**

10.1.2 *Procedure*

10.1.2.1 TEST PORTION

Weigh 30 ± 0,1 g of the sample in a chemically resistant glass flask.

10.1.2.2 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 10.2 to 10.7.

10.2 Determination of water-soluble sulphate content

Proceed according to ISO 787, part XIII, with the following modifications in the procedure and in the calculation :

Add to the 50 ml of extract, after acidification with 3 ml of hydrochloric acid, 2 ml of ethanol 95 % (*V/V*). 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 compounds, taking care to avoid losses by splashing. [Then proceed as indicated in the procedure.]

Calculate the water-soluble sulphate content expressed as SO_4, as a percentage by mass, by the following formula :

$$8{,}2\, m$$

where m is the mass, in grams, of the precipitate ($BaSO_4$).

Report the result to two decimal places.

10.3 Determination of water-soluble chloride content

Proceed according to ISO 787, part XIII, with the following modification in the calculation :

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

$$0{,}708\, (V_1 - V_0)\, T$$

where

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

V_1 is the volume, in millilitres, of silver nitrate solution required by the test portion;

T is the normality of the silver nitrate solution.

Report the result to two decimal places.

10.4 Determination of water-soluble nitrate content — Method A

(See note 2 at the beginning of clause 10.)

Proceed according to ISO 787, part XIII, but compare the colour with that of a standard solution containing 5 ml of the ammonium chloride solution (equivalent to 0,1 % NO_3) and 1 ml of Nessler's reagent per 50 ml.

Report the result as either greater than or less than 0,1 % NO_3.

10.5 Determination of water-soluble nitrate content — Method B

(See note 2 at the beginning of clause 10.)

Proceed according to ISO 787, part XIX, as indicated for extracts containing chromate, with the following modification in the calculation :

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

$$\frac{a}{2}$$

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

NOTE — If 5 ml has been taken because the nitrate content was greater than 0,1 %, the formula becomes a.

10.6 Determination of water-soluble chromate content

10.6.1 *Reagents*

10.6.1.1 Hydrochloric acid, 2 N.

10.6.1.2 Potassium iodide, 1 M solution.

10.6.1.3 Sodium thiosulphate, 0,1 N standard volumetric solution.

10.6.1.4 Starch, 1 % (m/m) solution.

10.6.1.5 Sodium hydrogen carbonate.

10.6.2 *Procedure*

Transfer 50 ml of the clear aqueous extract (see 10.1) to a stoppered conical flask. Add 50 ml of water and 2 g of sodium hydrogen carbonate (10.6.1.5), followed by 30 ml of the hydrochloric acid (10.6.1.1).

Then add 10 ml of potassium iodide solution (10.6.1.2) and allow the flask to stand for 5 min in the dark. Afterwards, titrate with sodium thiosulphate solution (10.6.1.3). Towards the end of the titration add 5 ml of the starch solution (10.6.1.4) as indicator and titrate until the colour changes to green.

10.6.3 *Expression of results*

Calculate the water-soluble chromate content expressed as CrO_3, in grams per 100 ml, by the following formula :

$$0,066\,7\ V\,T$$

where

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

T is the normality of the sodium thiosulphate solution.

Report the result to two decimal places.

10.7 Determination of total matter soluble in water

10.7.1 *Procedure*

Place 50 ml of the clear aqueous extract (see 10.1) into a tared flat-bottomed glass, glazed porcelain, platinum or silica dish and evaporate to dryness on a water bath. Dry the residue in an oven at 105 ± 2 °C, cool in a desiccator and weigh. Repeat the heating and cooling until the results of the last two weighings, at an interval including at least 30 min heating, do not differ by more than 10 % of the final figure obtained for the water-soluble matter.

10.7.2 *Expression of results*

Calculate the total matter soluble in water, as a percentage by mass, by the following formula :

$$20\ m$$

where m is the mass, in grams, of residue.

Report the result to two decimal places.

11 DETERMINATION OF MATTER INSOLUBLE IN AMMONIACAL AMMONIUM CHLORIDE SOLUTION

11.1 Reagent

Ammoniacal ammonium chloride solution

Dissolve 30 g of ammonium chloride in a mixture of 500 ml of ammonia solution, ρ 0,88 g/ml, and 600 ml of water.

11.2 Apparatus

11.2.1 Sintered glass crucible, porosity grade P 16 (pore size index 10 to 16 µm).

11.2.2 Mechanical shaker.

11.3 Procedure

11.3.1 *Test portion*

Weigh about 5 g of the sample to the nearest 1 mg and transfer to the shaker (11.2.2).

11.3.2 *Determination*

Shake the test portion with 100 ml of the reagent (11.1) for 1 h at room temperature. Allow to stand for 30 min and decant the supernatant liquid through the tared sintered glass crucible. To the residue add a further 100 ml of the reagent, shake for 5 min and filter the whole suspension through the same filter crucible, any adherent residue being transferred to the filter by means of a "policeman" and the minimum additional reagent. Wash the sides of the filter crucible and the residue with two successive 25 ml portions of water, and finally dry the crucible and residue to constant mass in an oven at 105 ± 2 °C.

11.4 Expression of results

Calculate the matter insoluble in ammoniacal ammonium chloride solution, as a percentage by mass, by the following formula :

$$\frac{100\,m_1}{m_0}$$

where

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

m_1 is the mass, in grams, of the residue.

Report the result to two decimal places.

NOTE — If the value for matter insoluble in ammoniacal ammonium chloride solution, determined according to clause 11, is higher than 2,0 % in the case of basic zinc potassium chromate pigments type 1b, the lead content shall be determined according to clause 9.