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ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION R 1249

ZINC CHROMATE PIGMENTS

BASIC ZINC POTASSIUM CHROMATE PIGMENTS
AND ZINC TETRAHYDROXYCHROMATE PIGMENTS

1st EDITION

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BRIEF HISTORY

The ISO Recommendation R 1249, *Zinc chromate pigments – Basic zinc potassium chromate pigments and zinc tetrahydroxychromate pigments*, was drawn up by Technical Committee ISO/TC 35, *Paints and varnishes*, the Secretariat of which is held by the Nederlands Normalisatie-instituut (NNI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1249, which was circulated to all the ISO Member Bodies for enquiry in November 1968. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

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

The following Member Body opposed the approval of the Draft :

France

The Netherlands Member Body opposed the approval of clause 4.5.4 of the Draft.

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided to accept it as an ISO RECOMMENDATION.

ZINC CHROMATE PIGMENTS

BASIC ZINC POTASSIUM CHROMATE PIGMENTS AND ZINC TETRAHYDROXYCHROMATE PIGMENTS

1. SCOPE

This ISO Recommendation specifies the requirements and the corresponding methods of test for the following zinc chromate pigments :

(1) **Basic zinc potassium chromate pigments (Type 1 a) :**

Pigments of approximate composition $K_2CrO_4 \cdot 3ZnCrO_4 \cdot Zn(OH)_2 \cdot 2H_2O$, suitable for use in paints and corrosion inhibiting coatings.

(2) **Basic zinc potassium chromate pigments, lead-containing (Type 1 b) :**

Pigments of approximate composition $K_2CrO_4 \cdot 3ZnCrO_4 \cdot Zn(OH)_2 \cdot 2H_2O$, in which a lead content up to 2 % maximum is allowed, calculated as PbO , suitable for use in paints and corrosion inhibiting coatings.

(3) **Zinc tetrahydroxychromate pigments (Type 2) :**

Pigments of approximate composition $ZnCrO_4 \cdot 4Zn(OH)_2$, suitable for use in corrosion inhibiting coatings.

2. REQUIRED CHARACTERISTICS AND THEIR TOLERANCES

Basic zinc potassium chromate pigments (Types 1 a and 1 b) and zinc tetrahydroxychromate pigments (Type 2) should have the characteristics shown in the following Table.

TABLE - Required characteristics

Characteristic*		Requirements according to Type			Test method
		Basic zinc potassium chromate pigments Type 1 a	Basic zinc potassium chromate pigments, lead-containing Type 1 b	Zinc tetrahydroxy-chromate pigments Type 2	
Zinc content	% ZnO	35 to 40	35 to 40	68.5 to 72	clause 4.1
Chromate content	% CrO ₃	min. 42	min. 42	17 to 19	clause 4.2
Alkali metal content	% K ₂ O	max. 12	max. 12	—	clause 4.3
Lead content	% PbO	—	max. 2.0	—	clause 4.4
Water-soluble sulphate content	% SO ₄	max. 0.1	max. 0.1	max. 0.1**	clause 4.5.2
Water-soluble chloride content	% Cl	max. 0.1	max. 0.1	max. 0.1**	clause 4.5.3
Water-soluble nitrate content	% NO ₃	max. 0.1	max. 0.1	—	clauses 4.5.4 and 4.5.5
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	—	clause 4.5.6
Matter soluble in water	%	—	—	max. 0.3	clause 4.5.7
Matter insoluble in ammoniacal ammonium chloride solution	%	max. 0.5	max. 3.0	max. 0.5	clause 4.6
Volatile matter at 105 °C	%	max. 1.0	max. 1.0	max. 1.0	ISO/R 787, Part II
Oil absorption value, compared with value of sample agreed between purchaser and vendor		within ± 15 %	within ± 15 %	within ± 15 %	ISO/R 787, Part V
Residue on sieve (63 µm)	— oil method %	max. 0.5	max. 0.5	max. 0.5	ISO/R 787, Part VI
	— water method %	max. 0.3	max. 0.3	max. 0.3	ISO/R 787, Part VII

* If zinc chromate pigments are used as colouring pigments, and the colour and relative tinting strength are agreed between purchaser and vendor, the test methods for the determination of these properties should be those given in ISO Recommendation R 787, *General methods of test for pigments*.

** For zinc tetrahydroxychromate, the water-soluble sulphate and chloride content are to be determined separately only if the content of matter soluble in water exceeds 0.2 %.

3. SAMPLING

- 3.1 A representative sample of the pigment should be taken in accordance with ISO Recommendation R 842, *Sampling raw materials for paints and varnishes*.
- 3.2 The sample agreed between purchaser and vendor, to which reference is made in the Table, should comply with all the requirements specified for the pigment under test.

4. METHODS OF TEST

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

4.1 Determination of zinc content

4.1.1 Reagents

- (1) Sodium thiosulphate, 0.1 N standard volumetric solution.
- (2) Starch solution, 1 % (m/m).
- (3) Hydrochloric acid, 1 N.
- (4) Potassium cyanoferrate (III), 0.1 M solution.
- (5) Barium acetate, 0.5 M solution.
- (6) Potassium chloride, crystalline.
- (7) Potassium iodide, 1 M solution.

4.1.2 Procedure

4.1.2.1 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 tetrahydroxochromate.

4.1.2.2 DETERMINATION. Dissolve the test portion in 10 ml of hydrochloric acid (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) and 50 ml of the potassium cyanoferrate (III) solution (4). Allow the flask to stand for 3 minutes and afterwards add, while stirring, 50 ml of barium acetate solution (5) and 10 ml of potassium iodide solution (7). Immediately afterwards titrate the liberated iodine with sodium thiosulphate solution (1); towards the end of the titration add 5 ml of the starch solution (2) as indicator and titrate until the colour changes to yellow.

4.1.3 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 grammes, of the test portion;

T is the standardization factor 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 4.1 and the determination of chromate content according to clause 4.2 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.

4.2 Determination of chromate content

4.2.1 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*.

4.2.2 Procedure

4.2.2.1 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 tetrahydroxochromate.

4.2.2.2 DETERMINATION. Dissolve the test portion in 30 ml of the hydrochloric acid (3), in a stoppered conical 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 minutes in the dark. Afterwards, titrate with sodium thiosulphate solution (1). Towards the end of the titration add 5 ml of the starch solution (2) as indicator and titrate until the colour changes to green or blue-green.

4.2.3 *Expression of results*. Calculate the chromate content expressed as CrO_3 , as a percentage by mass, by the following formula :

$$\frac{3.33 VT}{m}$$

where

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

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

T is the standardization factor of the sodium thiosulphate solution.

Report the result to one decimal place.

4.3 Determination of alkali metal content

4.3.1 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*.

4.3.2 Procedure

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

4.3.2.2 DETERMINATION. Heat the test portion at approximately 600 °C for 1 hour. 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 (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 (5) and then 30 ml of hydrochloric acid (3). Add 10 ml of potassium iodide solution (4) and allow the flask to stand for 5 minutes in the dark. Afterwards, titrate with sodium thiosulphate solution (1). Towards the end of the titration add 5 ml of the starch solution (2) as indicator and titrate until the colour changes to green.

4.3.3 *Expression of results.* Calculate the alkali metal content expressed as K_2O , as a percentage by mass, by the following formula :

$$\frac{3.13 VT}{m}$$

where

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

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

T is the standardization factor of the sodium thiosulphate solution.

Report the result to one decimal place.

4.4 Determination of lead content

NOTE. – The determination of the lead content of lead-containing basic zinc potassium chromate pigments (Type 1 b) is necessary only if the value for matter insoluble in ammoniacal ammonium chloride solution, determined according to clause 4.6, is higher than 2.0 %.

4.4.1 Reagents

- (1) *Hydrochloric acid*, diluted 1 + 4.
Mix 1 part by volume of concentrated hydrochloric acid ($d = 1.18$) and 4 parts by volume of water.
- (2) *Ammonia solution*, diluted 1 + 4.
Mix 1 part by volume of concentrated ammonia solution ($d = 0.91$) and 4 parts by volume of water.
- (3) *Sodium sulphide*, 50 g/l solution.
- (4) *Nitric acid*, $d = 1.42$.
- (5) *Sulphuric acid*, diluted 1 + 1.
Mix 1 part by volume of concentrated sulphuric acid ($d = 1.84$) and 1 part by volume of water.
- (6) *Ethanol*, 95 % (V/V).
- (7) *Washing solution*.
Mix 4 ml of concentrated sulphuric acid ($d = 1.84$), 100 ml of water and 100 ml of ethanol 95 % (V/V).

4.4.2 Procedure

4.4.2.1 **TEST PORTION.** Weigh to the nearest 1 mg, about 20 g of the sample.

4.4.2.2 **DETERMINATION.** Dissolve the test portion in hydrochloric acid (1), heating meanwhile. Neutralize the solution by adding such a quantity of ammonia solution (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 (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 (4). Evaporate the solution after adding 20 ml of sulphuric acid (5) until copious white fumes are evolved. After cooling, add about 100 ml of water and 100 ml of ethanol (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 (7), then with ethanol (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 hour. Allow to cool to room temperature in a desiccator and weigh the residue to the nearest milligramme.

4.4.3 *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_1 is the mass, in grammes, of residue (PbSO₄);

m_0 is the mass, in grammes, of the test portion.

Report the result to one decimal place.

4.5 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 clause 4.5.1 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 are used; thus the 300 ml of aqueous extract are sufficient for all the determinations including a certain reserve.

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

Method A (clause 4.5.4) for use when it is only required to determine whether the content is above or below the specified limit of 0.1 %.

Method B (clause 4.5.5) for use when a precise determination of the content is required.

4.5.1 Preparation of aqueous extract

4.5.1.1 APPARATUS

Mechanical agitator or stirrer.

4.5.1.2 PROCEDURE

4.5.1.2.1 *Test portion.* Weigh 30 ± 0.1 g of the sample in a chemically resistant glass flask.

4.5.1.2.2 *Preparation.* Agitate the test portion with 300 ml of water for 1 hour 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 clause 4.5.2 to 4.5.7.

4.5.2 Determination of water-soluble sulphate content

4.5.2.1 REAGENTS

- (1) *Hydrochloric acid*, $d = 1.18$.
- (2) *Barium chloride*, 50 g/l solution.
- (3) *Ethanol*, 95 % (V/V).

4.5.2.2 *PROCEDURE.* Acidify 50 ml of the clear aqueous extract (see clause 4.5.1) with 3 ml of the hydrochloric acid (1) and add a few millilitres 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 compounds, taking care to avoid losses by splashing. Add the barium chloride solution (2) drop by drop to the hot solution until it is in slight excess and allow to stand overnight. Decant the supernatant liquid through a tared porcelain filter crucible, transfer the precipitate and wash it with hot water until free from chloride, ignite gently, then at approximately 800 °C, cool in a desiccator and weigh.

- 4.5.2.3 EXPRESSION OF RESULTS. 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 grammes, of precipitate (BaSO_4).

Report the result to two decimal places.

4.5.3 Determination of water-soluble chloride content

4.5.3.1 REAGENTS

- (1) Potassium chromate, 50 g/l solution.
- (2) Silver nitrate, 0.1 N standard volumetric solution.

- 4.5.3.2 PROCEDURE. Take 50 ml of the clear aqueous extract (see clause 4.5.1) and add 1 ml of the potassium chromate solution (1). Titrate the solution with the 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 to 50 ml of water and titrating with the silver nitrate solution until the colour matches that of the previous titration, making due allowance for any opalescence or turbidity.

NOTE. – Alternatively, the endpoint of the titration may be determined by potentiometric indication.

- 4.5.3.3 EXPRESSION OF RESULTS. 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_1 is the volume, in millilitres, of silver nitrate solution required by the test portion;

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

T is the standardization factor of the silver nitrate solution.

Report the result to two decimal places.

4.5.4 Determination of water-soluble nitrate content – Method A

(See Note 2 to clause 4.5).

4.5.4.1 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 distilled water.

NOTE. – Ammonia-free distilled 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 method (a) or method (b) as follows :
 - (a) Dissolve 5 g of potassium iodide in 3.5 ml of water. Add cold saturated mercury (II) chloride (HgCl_2) solution while stirring until a faint red precipitate is formed. Continuing to stir, add 40 ml of potassium hydroxide solution, 500 g/l, dilute to 100 ml, mix well, allow to settle, decant the clear supernatant liquid and store it in the dark.
 - (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 shaking until a slight red precipitate remains, then add 12 g of sodium hydroxide, shake until dissolved, and finally add a little more of the saturated mercury (II) chloride solution and dilute to 100 ml with water. Shake occasionally during several days, allow to stand, and use the clear supernatant liquid for the test.