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Lithopone pigments — General requirements and methods of testing

Lithopone pour peintures — Exigences générales et méthodes d'essai

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 256, *Pigments, dyestuffs and extenders*.

This third edition cancels and replaces the second edition (ISO 473:1982), which has been technically revised. The main changes compared to the previous edition are as follows:

- a new specification of lithopone with a 20 % zinc sulphide (ZnS) content (lithopone 20 %) has been included;
- a new method of test, Method B (Na_2EDTA titration method) has been introduced;
- the text of the document has been editorially revised.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Over the last decade, requirements such as the hiding power for exterior coatings have become less stringent with a view to reducing cost. In addition, there is a growing demand in the international exterior coatings market for lithopone with a 20 % total zinc sulphide (ZnS) content rather than the more expensive lithopone with a 30 % or 60 % total zinc sulphide content (hereinafter referred to as lithopone 20 %, lithopone 30 % and lithopone 60 %, respectively). The previous edition of this document provided for only two specifications of lithopone, namely lithopone 30 % and lithopone 60 %. To avoid confusion and disputes related to the transportation, release and clearance of lithopone 20 %, it has been included as a third specification in this document.

The determination of the total zinc content in lithopone using the potassium hexacyanoferrate titration method is rather complicated to operate and apt to fail. With such a test method, fluctuations in the temperature of the solution may be experienced and it is difficult to read the titration end point. Therefore, the Na_2EDTA direct titration method has been added to this document, which is time-saving and easier to operate, and with a proven accuracy. This testing method is based on Reference [2].

Lithopone pigments — General requirements and methods of testing

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

1 Scope

This document specifies the requirements and the corresponding test methods for three types of lithopone pigments.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 787-1, *General methods of test for pigments and extenders — Part 1: Comparison of colour of pigments*

ISO 787-2, *General methods of test for pigments and extenders — Part 2: Determination of matter volatile at 105 °C*

ISO 787-3, *General methods of test for pigments and extenders — Part 3: Determination of matter soluble in water — Hot extraction method*

ISO 787-4, *General methods of test for pigments and extenders — Part 4: Determination of acidity or alkalinity of the aqueous extract*

ISO 787-5, *General methods of test for pigments and extenders — Part 5: Determination of oil absorption value*

ISO 787-7, *General methods of test for pigments and extenders — Part 7: Determination of residue on sieve — Water method — Manual procedure*

ISO 787-17, *General methods of test for pigments and extenders — Comparison of lightening power of white pigments*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

ISO 18451-1, *Pigments, dyestuffs and extenders — Terminology — Part 1: General terms*

ISO 18451-2, *Pigments, dyestuffs and extenders — Terminology — Part 2: Classification of colouring materials according to colouristic and chemical aspects*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18451-1, ISO 18451-2 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IECElectropedia: available at http://www.electropedia.org/

3.1
lithopone 20 %
white pigment consisting of approximately 20 % zinc sulphide (ZnS), the balance being made up mainly of barium sulphate ($BaS0_4$)

Note 1 to entry: The material is a calcined co-precipitate.

3.2
lithopone 30 %
white pigment consisting of zinc sulphide (ZnS) and barium sulphate ($BaS0_4$) in approximately equimolecular proportions

Note 1 to entry: The material is a calcined co-precipitate.

3.3
lithopone 60 %
white pigment consisting of approximately 60 % zinc sulphide (ZnS), the balance being made up mainly of barium sulphate ($BaS0_4$)

Note 1 to entry: The material is a calcined co-precipitate.

4 Marking and labelling

Lithopone with a content of about 20 %, 30 % or 60 % of zinc sulphide should be marked or labelled as such.

5 Required characteristics and their tolerances

Lithopone pigments shall have the characteristics shown in Table 1.

The sample agreed between the interested parties, to which reference is made in Table 1, shall be one and the same and shall comply with all the requirements specified for the pigment under test.

Table 1 — Required characteristics and their tolerances

Characteristic	Unit	Requirement	Test method
Total zinc, calculated as zinc sulphide	% (mass fraction)		Clause 7
Lithopone 30 %		≥ 28	
Lithopone 60 %		≥ 58	
Lithopone 20 %		≥ 18	
Zinc oxide	% (mass fraction)	≤ 1	Clause 8
Sum of total zinc, calculated as zinc sulphide, and barium sulfate	% (mass fraction)	≥ 99	Clause 7
Matter volatile at 105 °C	% (mass fraction)	≤ 0,5	ISO 787-2

Table 1 *(continued)*

Characteristic	Unit	Requirement	Test method
Matter soluble in water	% (mass fraction)	≤ 0,5	ISO 787-3
Residue on sieve (63 µm)	% (mass fraction)	≤ 0,1	ISO 787-7
Colour	—	Closely matching that of the agreed sample	ISO 787-1
Alkalinity of the aqueous extract	ml of 0,1 mol/l	Closely matching that of the agreed sample	ISO 787-4
Oil absorption value	g/100 g	To be agreed between the interested parties	ISO 787-5
Lightening power	%	To be agreed between the interested parties	ISO 787-17
Hiding power	—	To be agreed between the interested parties	To be agreed between the interested parties

6 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528.

7 Determination of barium sulfate and total zinc content

7.1 General

Two methods of test, Method A and Method B, are provided for the determination of the total zinc content. Method A shall be referred to in cases of dispute.

7.2 Method A

7.2.1 Principle

Dissolve the zinc sulphide (ZnS) and zinc oxide (ZnO) in the sample with hydrochloric acid. Add sulphuric acid to maintain a certain acidity (pH 1,5 to pH 3,0). Separate the solid from the liquid. Use the weight method to determine the content of the barium sulfate. Use diphenylamine as indicator and potassium hexacyanoferrate(II) as titrant to determine the total zinc content.

7.2.2 Reagents

During the analysis, use only reagents of recognized analytical grade and water of at least grade 3 purity according to ISO 3696.

7.2.2.1 Hydrochloric acid, concentrated, approximately 37 % (mass fraction), ρ approximately 1,19 g/ml.

7.2.2.2 Hydrochloric acid solution, diluted 1 + 2.

Add 1 part by volume of concentrated hydrochloric acid (7.2.2.1) to 2 parts by volume of water.

7.2.2.3 Sulphuric acid, concentrated, approximately 96 % (mass fraction), ρ approximately 1,84 g/ml.

7.2.2.4 Sulphuric acid solution, diluted 1 + 8.

Add carefully 1 part by volume of concentrated sulphuric acid (7.2.2.3) to 8 parts by volume of water.

7.2.2.5 Ammonia, concentrated, ρ approximately 0,9 g/ml.

7.2.2.6 Ammonia solution, diluted 1 + 3.

Add 1 part by volume of concentrated ammonia (7.2.2.5) to 3 parts by volume of water.

7.2.2.7 Diphenylamine, 50 g/l ethanolic solution.

7.2.2.8 Congo red paper.

7.2.2.9 Lead acetate paper.

7.2.2.10 Zinc chloride, standard reference solution, containing approximately 5 g of zinc per litre (concentration c, in grams of zinc per millilitre).

Weigh about 5 g of high purity zinc to the nearest 0,1 mg, dissolve in 300 ml of the hydrochloric acid solution (7.2.2.2) and dilute the solution obtained with water to 1 000 ml in a one-mark volumetric flask.

7.2.2.11 Potassium hexacyanoferrate(II)[1], standard volumetric solution $c[K_4Fe(CN)_6]$ approximately 0,05 mol/l (titre T expressed in grams of zinc per millilitre).

7.2.2.11.1 Preparation

Dissolve 21,0 g of potassium hexacyanoferrate(II), 300 mg of potassium hexacyanoferrate(III)[1] and 2 g of anhydrous sodium carbonate (to stabilize the solution) in water and dilute to 1 000 ml in a one-mark volumetric flask.

7.2.2.11.2 Standardization

Pipette 25,0 ml of the zinc chloride solution (7.2.2.10) into a flask and add ammonia solution (7.2.2.6) until a piece of Congo red paper (7.2.2.8), when touched with the solution, just turns to a pure red colour. Then carefully neutralize the solution with the hydrochloric acid solution (7.2.2.2) from a dropping bottle. Add a few drops in excess until the Congo red paper turns to a lasting red-blue or blue-red colour (pH 1,5 to pH 3,0).

Make up to 150 ml with water, heat the solution to boiling, and add 10 drops of the diphenylamine solution (7.2.2.7).

Immediately titrate the solution with the potassium hexacyanoferrate(II) solution (7.2.2.11) until the colour turns to a lasting yellow or yellowish green.

Then back-titrate the solution with the zinc chloride solution (7.2.2.10) until the colour just turns to blue again.

7.2.2.11.3 Calculation of titre

Calculate the titre, T, of the potassium hexacyanoferrate(II) solution, expressed in grams of zinc per millilitre, by using Formula (1):

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[1] IUPAC name; formally called potassium ferrocyanide, $K_4Fe(CN)_6$.

$$T=\frac{c\times(25+V_2)}{V_1} \tag{1}$$

where

c is the concentration, in grams of zinc per millilitre, of the standard zinc chloride solution (7.2.2.10);

V_1 is the volume, in millilitres, of the potassium hexacyanoferrate(II) solution (7.2.2.11) required for the titration;

V_2 is the volume, in millilitres, of the standard zinc chloride solution (7.2.2.10) required for the back-titration.

7.2.3 Apparatus

Use ordinary laboratory apparatus and burettes, pipettes and one-mark volumetric flasks complying with the requirements of ISO 385, ISO 648 or ISO 1042, respectively.

7.2.4 Procedure

Weigh, to the nearest 0,1 mg, about 0,6 g of lithopone 30 %, or about 0,3 g of lithopone 60 %, or about 0,6 g of lithopone 20 %, all previously dried at (105 ± 2) °C, into a beaker and add 25 ml of the hydrochloric acid solution (7.2.2.2). Immediately cover with a watch-glass and boil until the evolution of hydrogen sulphide has ceased [test with the lead acetate paper (7.2.2.9)]. Dilute with 100 ml of water, add 5 ml of the sulphuric acid solution (7.2.2.4).

Boil the solution again and allow the precipitate to settle while hot and filter the supernatant solution through a fine filter paper. Transfer the precipitate to the filter paper and wash with hot water containing some sulphuric acid until a drop of the washings shows no reaction with the potassium hexacyanoferrate(II) solution (7.2.2.11). Fold the filter paper over the precipitate. Transfer it while still wet to a weighed porcelain crucible and ignite it in contact with air at low temperatures and then burn to constant mass at (800 ± 20) °C. The residue is assumed to be barium sulfate. Add a few drops of the sulphuric acid solution (7.2.2.4) to the contents of the crucible. No trace of hydrogen sulphide should be noticeable; otherwise, the sulphuric acid shall be driven off and the residue re-ignited.

Combine the washings with the filtrate. Add a slight excess of the ammonia solution (7.2.2.6) [verify on Congo red paper (7.2.2.8)], followed by the hydrochloric acid solution (7.2.2.4) from a dropping bottle until a small piece of Congo red paper (7.2.2.8), when touched with the solution, just turns to a lasting red-blue or blue-red colour (pH 1,5 to pH 3,0).

If necessary, make up to 150 ml with water, heat the solution to boiling, add 10 drops of the diphenylamine solution (7.2.2.7) and immediately titrate the solution as specified for the standardization of the potassium hexacyanoferrate(II) solution in 7.2.2.11.2.

7.2.5 Expression of results

Calculate the barium sulfate content of the lithopone, w_1, expressed as a percentage mass fraction, by using Formula (2):

$$w_1=\frac{m_2}{m_1}\times 100 \tag{2}$$

where

m_1 is the mass, in grams, of the test portion;

m_2 is the mass, in grams, of the residue.

Calculate the total zinc content of the lithopone, w_2, expressed as a percentage mass fraction, calculated as zinc sulphide, by using Formula (3):

$$w_2 = \frac{1{,}490\,5 \times (TV_3 - cV_4) \times 100}{m_1} \quad (3)$$

where

m_1 is the mass, in grams, of the test portion;

T is the titre, expressed in grams of zinc per millilitre, of the potassium hexacyanoferrate(II) solution (7.2.2.11), as calculated in 7.2.2.11.3;

c is the concentration, in grams of zinc per millilitre, of the standard zinc chloride solution (7.2.2.10);

V_3 is the volume, in millilitres, of the potassium hexacyanoferrate(II) solution (7.2.2.11) required for the titration;

V_4 is the volume, in millilitres, of the standard zinc chloride solution (7.2.2.10) required for the back-titration;

1,4905 is the conversion factor from zinc to zinc sulphide.

Calculate the sum of total zinc, w_3, calculated as zinc sulphide, and barium sulfate of the lithopone, expressed as a percentage mass fraction, by using Formula (4):

$$w_3 = w_1 + w_2 \quad (4)$$

7.3 Method B

7.3.1 Principle

Dissolve the zinc sulphide (ZnS) and zinc oxide (ZnO) in the sample with hydrochloric acid. Use potassium fluoride as masking agent. Use the xylenol orange as indicator in an acetic acid - sodium acetate buffer solution (pH 6,0). Use the Na_2EDTA solution as titrant to determine the total zinc content.

7.3.2 Reagents

During the analysis, use only reagents of recognized analytical grade and water of at least grade 3 purity according to ISO 3696.

7.3.2.1 Hydrochloric acid solution, diluted 1 + 1.

Add 1 part by volume of concentrated hydrochloric acid (7.2.2.1) to 1 part by volume of water.

7.3.2.2 Hydrochloric acid solution, diluted 1 + 5.

Add 1 part by volume of concentrated hydrochloric acid (7.2.2.1) to 5 parts by volume of water.

7.3.2.3 Lead acetate paper.

Permeate the filter paper into a 10 % lead acetate solution, air-dry the paper for use.

7.3.2.4 Bromothymol blue, 5 g/l solution in ethanol, at least 95 % (by volume).

7.3.2.5 Xylenol orange, 5 g/l solution, with a one week validity period.

7.3.2.6 Acetic acid, approximately 98 % (mass fraction), ρ approximately 1,05 g/ml.

7.3.2.7 Sodium acetate, chemically pure.

7.3.2.8 Acetic acid - sodium acetate buffer solution.

Adjust the 10 % sodium acetate solution (7.3.2.7) to pH 6,0 with acetic acid (7.3.2.6).

7.3.2.9 20 % potassium fluoride solution, 200 g/l solution.

7.3.2.10 High purity zinc with purity of at least 99,9 %.

7.3.2.11 Ammonia, concentrated, ρ approcimately 0,9 g/l.

7.3.2.12 Na_2EDTA standard volumetric solution, c[Na_2EDTA · $2H_2O$] approximately 0,05 mol/l (titre *T* expressed in grams of zinc per millilitre).

7.3.2.12.1 Preparation

Weigh about 18,6 g of Na_2EDTA · $2H_2O$, dissolve it in hot water and cool to room temperature. Transfer the solution into a 1 000 ml volumetric flask and add water to the required scale, shaking at intervals.

7.3.2.12.2 Procedure

Weigh, to the nearest 0,1 mg, about 1 g of the metal zinc (7.3.2.10) into a 200 ml beaker. Add 100 ml of hydrochloric acid (7.3.2.1). Cool the solution and then transfer it into a 500 ml volumetric flask and add water to the required scale, shake and pipette 50 ml of the prepared solution into a 300 ml conical flask, add 2 drops of the bromothymol blue solution (7.3.2.4). Then neutralize the solution with the ammonia (7.3.2.11) until it turns to blue-green, acidize the solution with the acetic acid (7.3.2.6) until it turns to a yellow colour. Add 5 ml of the acetic acid (7.3.2.6) in excess and 30 ml of the acetic acid - sodium acetate buffer solution (7.3.2.8). Add 2 to 3 drops of xylenol orange solution (7.3.2.5) and titrate the solution with the Na_2EDTA standard volumetric solution (7.3.2.12) until the solution turns from aubergine to luminous yellow.

7.3.2.12.3 Calculation of titre

Calculate the titre, *T*, of the Na_2EDTA standard volumetric solution, expressed in grams of metal zinc per mllilitre, by using Formula (5):

$$T = \frac{m_3}{10V_5} \quad (5)$$

where

m_3 is the mass of the weighed metal zinc, in grams;

V_5 is the volume, in millilitres, of the Na_2EDTA standard volumetric solution required for the titration.

7.3.3 Apparatus

Use ordinary laboratory apparatus and burettes, pipettes and one-mark volumetric flasks complying with the requirements of ISO 385, ISO 648 or ISO 1042, respectively.

7.3.4 Procedure

Weigh, to the nearest 0,1 mg, about 0,5 g of the lithopone sample into a 300 ml conical flask. Add 40 ml of the hydrochloric acid solution (7.3.2.1) and heat to dissolve until the evolution of hydrogen sulphide has ceased [test with lead acetate paper (7.3.2.3)]. Cool to room temperature. Then add 5 ml of 20 % potassium fluoride solution (7.3.2.9) and 2 drops of bromothymol blue solution (7.3.2.4). Neutralize the solution with ammonia (7.3.2.11) until the solution turns to blue-green, acidize the solution with acetic acid (7.3.2.6) until it turns to a yellow colour, add 5 ml of the acetic acid (7.3.2.6) in excess and 30 ml of the acetic acid - sodium acetate buffer solution (7.3.2.8). Add 3 to 4 drops of the xylenol orange solution (7.3.2.5) and titrate the solution with the Na_2EDTA standard solution (7.3.2.12) until the solution turns from aubergine to lemon-yellow.

7.3.5 Expression of results

7.3.5.1 Carry out two measurements and report the mean value.

7.3.5.2 Calculate the total zinc content of lithopone, w_4, expressed as a percentage mass fraction, calculated as zinc sulphide by using Formula (6):

$$w_4 = \frac{1{,}490\,5 T V_6}{m_4} \times 100 \tag{6}$$

where

V_6 is the volume, in millilitres, of the Na_2EDTA standard solution(7.3.2.12) used in the determination;

m_4 is the mass, in grams, of the test portion;

T is the titre, expressed in grams of zinc per millilitre, of the Na_2EDTA standard solution, as determined in 7.3.2.12.3;

1,490 5 is the conversion factor from zinc to zinc sulphide.

If the two parallel test results differ by more than 0,2 % (mass fraction), repeat the procedure.

Calculate the mean value of the two valid determinations and report to the nearest 0,1 % (mass fraction).

8 Determination of zinc oxide content

8.1 Reagents

During the analysis, use only reagents of recognized analytical grade and water of at least grade 3 purity according to ISO 3696.

8.1.1 Ammonium chloride.

8.1.2 Hydrochloric acid solution, diluted 1 + 2.

Add 1 part by volume of concentrated hydrochloric acid (7.2.2.1) to 2 parts by volume of water.