SLS 1139 : 1996
ISO 6745 : 1990

Sri Lanka Standard
SPECIFICATION FOR ZINC PHOSPHATE PIGMENTS FOR PAINTS

Gr. D

SRI LANKA STANDARDS INSTITUTION

Sri Lanka Standard
SPECIFICATION FOR ZINC PHOSPHATE PIGMENTS FOR PAINTS

NATIONAL FOREWORD

This Standard was approved by the Sectoral Committee on Polymers and Polymer Products and was athorized for adoption and publication as a Sri Lanka Standard by the Council of the Sri Lanka Standards Institution on 1996-10-17.

This standard is identical with ISO 6745 : 1990 Zinc phosphate pigments for paints - Specifications and methods of test, published by the International Organization for Standardization (ISO).

The text of the International Standard has been accepted as suitable for publication, without deviation, as a Sri Lanka Standard. However, certain terminology and conventions are not identical with those used in Sri Lanka Standards, attention is therefore drawn to the following:

a) Wherever the words "International Standard/publication" appear, referring to this standard, they should be interpreted as "Sri Lanka Standard".

b) The comma has been used throughout as a decimal marker. In Sri Lanka Standards it is the current practice to use a full point on the baseline as the decimal marker.

Wherever page numbers are quoted, they are ISO page numbers.

INTERNATIONAL
STANDARD

ISO
6745

First edition
1990-12-15

Zinc phosphate pigments for paints — Specifications and methods of test

Pigments de phosphate de zinc pour peintures — Spécifications et méthodes d'essai

Reference number
ISO 6745:1990(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 6745 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

Zinc phosphate pigments for paints — Specifications and methods of test

1 Scope

This International Standard specifies the requirements and the corresponding methods of test for zinc phosphate pigments suitable for use in corrosion-inhibiting paints.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 787-5:1980, *General methods of test for pigments and extenders — Part 5: Determination of oil absorption value.*

ISO 787-7:1981, *General methods of test for pigments and extenders — Part 7: Determination of residue on sieve — Water method — Manual procedure.*

ISO 787-9:1981, *General methods of test for pigments and extenders — Part 9: Determination of pH value of an aqueous suspension.*

ISO 787-10:1981, *General methods of test for pigments and extenders — Part 10: Determination of density — Pyknometer method.*

ISO 787-14:1973, *General methods of test for pigments — Part 14: Determination of resistivity of aqueous extract (Printed together with Part 13 and Part 17).*

ISO 842:1984, *Raw materials for paints and varnishes — Sampling.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

3 Definition

For the purposes of this International Standard, the following definition applies.

zinc phosphate pigment: A white corrosion-inhibiting pigment consisting either predominantly of zinc phosphate dihydrate [$Zn_3(PO_4)_2 . 2H_2O$] or of a mixture of zinc phosphate dihydrate and zinc phosphate tetrahydrate [$Zn_3(PO_4)_2 . 4H_2O$] or predominantly of zinc phosphate tetrahydrate, and free from extenders and other pigments.

4 Classification

In this International Standard, zinc phosphate pigments are classified as one of the following three types:

Type 1: consisting predominantly of zinc phosphate dihydrate and exhibiting a loss on ignition at 600 °C of greater than 8,5 % (*m*/*m*) but less than or equal to 10,0 % (*m*/*m*).

Type 2: consisting essentially of a mixture of zinc phosphate dihydrate and zinc phosphate tetrahydrate and exhibiting a loss on ignition at 600 °C of greater than 10,0 % (*m*/*m*) but less than or equal to 13,0 % (*m*/*m*).

Type 3: consisting predominantly of zinc phosphate tetrahydrate and exhibiting a loss on ignition at

600 °C of greater than 13,0 % (*m*/*m*) but less than or equal to 16,0 % (*m*/*m*).

NOTE 1 The corrosion-inhibiting properties of the various types of zinc phosphate pigment may differ.

5 Required characteristics and associated tolerances

5.1 For zinc phosphate pigments complying with this International Standard, the essential requirements are specified in table 1 and the conditional requirement is listed in table 2. The conditional requirement shall be specified by agreement between the interested parties.

5.2 The agreed reference pigment referred to in table 2 shall comply with the requirements of table 1.

6 Sampling

Take a representative sample of the product to be tested, as described in ISO 842.

7 Determination of loss on ignition

7.1 Apparatus

Use ordinary laboratory apparatus and glassware complying with the requirements of the relevant International Standards (see clause 2), together with the following.

7.1.1 Muffle furnace, capable of being maintained at 600 °C ± 20 °C.

7.1.2 Silica crucible.

7.1.3 Balance, capable of weighing to 0,1 mg.

7.2 Procedure

Carry out the determination in duplicate.

Heat the crucible (7.1.2) for 30 min in the muffle furnace (7.1.1), maintained at 600 °C ± 20 °C. Allow to cool to room temperature in a desiccator containing an active desiccant and weigh the crucible.

Table 1 — Essential requirements

Characteristic	Unit	Requirement Type 1	 Type 2	 Type 3	Method of test
Loss on ignition, LI	% (*m*/*m*)	$8,5 < LI \leqslant 10,0$	$10,0 < LI \leqslant 13,0$	$13,0 < LI \leqslant 16,0$	See clause 7
Zinc content (based on the ignited test portion), $w(Zn)$	% (*m*/*m*)	$50,5 \leqslant w(Zn) \leqslant 52,0$			See clause 8
Phosphate content (based on the ignited test portion), $w(PO_4)$	% (*m*/*m*)	$47,0 \leqslant w(PO_4) \leqslant 49,0$			See clause 9
Resistivity of the aqueous extract	Ω·m	min. 65			ISO 787-14
pH-value of the aqueous suspension	—	$6,0 \leqslant pH \leqslant 8,0$			ISO 787-9
Density, ρ	g/cm^3	$3,0 \leqslant \rho \leqslant 3,6$			ISO 787-10
Residue on sieve (45 µm)	% (*m*/*m*)	max. 0,5			ISO 787-7

Table 2 — Conditional requirement

Characteristic	Requirement	Method of test
Oil-absorption value	Shall not differ by more than 10 % from that of the agreed reference pigment (see 5.2)	ISO 787-5

Weigh, to the nearest 0,1 mg, approximately 2 g to 3 g of the sample (see clause 6) into the previously ignited and tared crucible. Heat the crucible and test portion for 30 min in the muffle furnace, maintained at 600 °C ± 20 °C. Allow to cool to room temperature in the desiccator and reweigh. Repeat the heating, cooling and weighing operations until the results of successive weighings do not differ by more than 1 mg.

NOTE 2 Zinc phosphate, especially the dihydrate, is hygroscopic.

Retain the ignited pigment for the determinations described in clause 8 and clause 9.

7.3 Expression of results

Calculate the loss on ignition LI of the pigment, expressed as a percentage by mass, using the equation

$$\mathrm{LI} = \frac{m_0 - m_1}{m_0} \times 100$$

where

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

m_1 is the mass, in grams, of the test portion after ignition.

If the two determinations differ by more than 0,2 % (m/m), repeat the procedure.

Calculate the mean of two valid determinations and report the result to the nearest 0,1 % (m/m).

8 Determination of zinc content

8.1 Principle

Dissolution of a test portion in hydrochloric acid. Complexometric titration of the zinc with EDTA solution at pH 5,0.

8.2 Reagents

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

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

8.2.1 Hydrochloric acid, diluted 1 + 4.

Add 1 part by volume of concentrated hydrochloric acid [approximately 37 % (m/m), $\rho \approx 1{,}19$ g/ml] to 4 parts by volume of water.

8.2.2 EDTA, standard volumetric solution, $c(\mathrm{EDTA}) = 0{,}025$ mol/l.

Dissolve 9,306 3 g of disodium ethylenediamine tetraacetate dihydrate (EDTA disodium salt) in water in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix well.

8.2.3 Xylenol orange mixture.

Add 1 g of xylenol orange to 100 g of sodium chloride (or potassium nitrate) and mix well.

8.2.4 Hexamethylene tetramine.

8.3 Apparatus

Use ordinary laboratory apparatus and glassware complying with the requirements of the relevant International Standards (see clause 2).

8.4 Procedure

Carry out the determination in duplicate.

8.4.1 Preparation of the test solution

Weigh out, to the nearest 0,1 mg, approximately 1 g of pigment which has been freshly ignited as described in 7.2. Boil this test portion with 50 ml of 1 + 4 hydrochloric acid (8.2.1) for 20 min. After cooling to room temperature, transfer the solution to a 500 ml one-mark volumetric flask, dilute to the mark and mix well.

NOTE 3 This test solution is also used for the determination of the phosphate content as described in 9.1.

8.4.2 Determination

Pipette 50 ml of the test solution prepared in 8.4.1 into a 150 ml beaker. Add 0,1 g of xylenol orange mixture (8.2.3), followed by small portions of hexamethylene tetramine (8.2.4) until the colour changes from yellow to pink. Then add an excess of 0,4 g to 0,5 g of hexamethylene tetramine. Afterwards, whilst stirring, titrate with EDTA solution (8.2.2) until the colour just changes to yellow.

8.5 Expression of results

8.5.1 Calculation

Calculate the zinc content $w(\mathrm{Zn})$ of the pigment, expressed as a percentage by mass, using the equation

$$w(\mathrm{Zn}) = \frac{V \times 10 \times 1{,}6343 \times 10^{-3}}{m_2} \times 100$$

$$= \frac{V \times 1{,}6343}{m_2}$$

where

V	is the volume, in millilitres, of the EDTA solution (8.2.2) used;
m_2	is the mass, in grams, of the test portion;
$1{,}6343 \times 10^{-3}$	is the factor for the conversion of millilitres of EDTA solution, c(EDTA) = 0,025 mol/l, to grams of Zn.

If the two determinations differ by more than 0,2 % (*m*/*m*), repeat the procedure.

Calculate the mean of two valid determinations and report the result to the nearest 0,1 % (*m*/*m*).

8.5.2 Precision

No precision data are currently available.

9 Determination of phosphate content

For the determination of the phosphate content, two methods (one gravimetric, the other titrimetric) are specified.

The method to be used shall be agreed on between the interested parties. The gravimetric method (9.1) shall be used as the referee method in cases of dispute.

9.1 Gravimetric method

9.1.1 Principle

Addition of citromolybdate reagent to a portion of the test solution prepared for the determination of zinc content (see 8.4.1) and weighing of the precipitated quinoline phosphomolybdate.

9.1.2 Citromolybdate reagent

Prepare the reagent as follows:

a) Dissolve 70 g of disodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) in 150 ml of water.

b) Dissolve 60 g of citric acid monohydrate ($C_6H_8O_7.H_2O$) in 150 ml of water and add 85 ml of concentrated nitric acid [approximately 65 % (*m*/*m*), $\rho \approx 1{,}40$ g/ml].

c) Add solution a) to solution b), mixing continuously during the addition.

d) Add 35 ml of concentrated nitric acid, followed by 5 ml of freshly distilled quinoline, to 100 ml of water.

e) Pour solution d) into solution c) and mix well. Allow to stand for at least 12 h (for example, overnight) and filter through a sintered-glass filter crucible (9.1.3.1).

f) Add 280 ml of acetone to solution e) and dilute to 1 000 ml with water. Keep this solution in a securely stoppered flask and store away from light, but no longer than 1 week.

9.1.3 Apparatus

Use ordinary laboratory apparatus and glassware complying with the requirements of the relevant International Standards (see clause 2), together with the following.

9.1.3.1 Filter crucibles, with sintered-glass disc, grade P 10, complying with the requirements of ISO 4793.

9.1.3.2 Electric oven, capable of being maintained at 250 °C ± 10 °C.

9.1.4 Procedure

Carry out the determination in duplicate.

9.1.4.1 Precipitation and filtration

Pipette 25 ml of the test solution (see 8.4.1) into a 400 ml beaker, dilute with 50 ml of water and add 100 ml of citromolybdate reagent (9.1.2).

Place the beaker, covered with a watch-glass, on a hotplate in a fume cupboard. Warm the beaker until its contents reach 75 °C ± 5 °C and maintain at this temperature for about 30 s.

WARNING — In order to avoid coagulation of the precipitate, do not use a flame and do not mix the contents of the beaker, either during the addition of the reagent or during heating.

Allow to cool to room temperature, stirring three or four times with a glass rod during cooling.

Heat a filter crucible (9.1.3.1) for 15 min in the oven (9.1.3.2), maintained at 250 °C ± 10 °C. Allow to cool to room temperature in a desiccator containing an active desiccant and weigh to the nearest 0,1 mg. Decant the liquid through the crucible, placed on a filter flask, and wash the precipitate six times, by decantation, using about 30 ml of water each time. Transfer all the precipitate to the filter crucible by means of a jet of water from a wash bottle.

Wash the precipitate four times, removing each portion of water with the aid of suction.

9.1.4.2 Drying and weighing

Place the filter crucible in the oven, maintained at 250 °C ± 10 °C.

Fifteen minutes after the temperature in the oven has stabilized, remove the crucible, allow to cool for not more than 30 min in the desiccator containing an active desiccant and weigh to the nearest 0,1 mg. Repeat the heating, cooling and weighing operations until the results of two consecutive weighings do not differ by more than 1 mg.

9.1.5 Expression of results

9.1.5.1 Calculation

Calculate the phosphate content $w(\mathrm{PO_4})$ of the pigment, expressed as a percentage by mass, using the equation

$$w(\mathrm{PO_4}) = \frac{m_3 \times 20 \times 42{,}915 \times 10^{-3}}{m_2} \times 100$$

$$= \frac{m_3 \times 85{,}83}{m_2}$$

where

m_2	is the mass, in grams, of the test portion taken in 8.4.1;
m_3	is the mass, in grams, of the precipitate;
$42{,}915 \times 10^{-3}$	is the factor for the conversion of grams of quinoline phosphomolybdate to grams of $\mathrm{PO_4}$.

If the two determinations differ by more than 0,2 % (*m*/*m*), repeat the procedure.

Calculate the mean of two valid determinations and report the result to the nearest 0,1 % (*m*/*m*).

9.1.5.2 Precision

No precision data are currently available.

9.2 Titrimetric method

9.2.1 Principle

Dissolution of the phosphate contained in the pigment by means of strong cation-exchange resins and subsequent titration of the phosphoric acid formed.

The trivalent phosphoric acid, formed by strong cation-exchange resins in the hydrogen form, can be considered as a mixture of three monovalent acids with dissociation constants $K_1 = 7{,}5 \times 10^{-3}$ (pH 4,6), $K_2 = 6{,}2 \times 10^{-8}$ (pH 9,7) and $K_3 = 5 \times 10^{-13}$ (no specific pH).

To minimize interference from other acidic products present, the phosphate content is calculated from the titration of the acid extract between the pH values corresponding to K_1 and K_2 respectively.

9.2.2 Reagents and materials

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

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

9.2.2.1 Hydrochloric acid, diluted 1 + 2.

Add 1 part of concentrated hydrochloric acid [approximately 37 % (*m*/*m*), $\rho \approx 1{,}19$ g/ml] to 2 parts by volume of water.

9.2.2.2 Strong cation-exchange resin, in the hydrogen form, of the sulfonated polystyrene resin type, cross-linked with divinyl benzene, in bead form, particle size in the range 300 µm to 1 200 µm.[1)]

Resins shall be pretreated before use by the following method:

Place the resin on a clean sieve of nominal mesh aperture 250 µm and wash well with water to remove extraneous matter (for example, insoluble pigments from previous determinations).

Regenerate the separated resin by soaking for 24 h with occasional stirring in 1 + 2 hydrochloric acid (9.2.2.1). After regeneration, wash the resin free from acid by shaking with water for several hours, decanting off the water at 30 min intervals and replacing it with fresh water.

9.2.2.3 Mixed indicator solution, consisting of:

methyl red	0,2 g/l
bromocresol green	0,6 g/l
o-cresolphthalein	2,4 g/l
metanil yellow	0,3 g/l
xylene cyanol FF	0,1 g/l

Prepare the solution as follows:

Warm 0,06 g of bromocresol green, 0,24 g of *o*-cresolphthalein and 0,03 g of metanil yellow with 50 ml of a mixture of 1 part by volume of 95 % (*V*/*V*) ethanol and 1 part by volume of water

---

1) Suitable resins are available commercially.

until dissolved. Add 0,01 g of xylene cyanol FF to the warm solution and swirl until dissolved. Cool and transfer the solution to a 100 ml graduated cylinder. Warm 0,02 g of methyl red in 30 ml of acetone until dissolved, and add the solution to the graduated cylinder. Make up to 100 ml with water and mix well.

9.2.2.4 Sodium hydroxide, standard volumetric solution, $c(\text{NaOH}) = 0{,}2$ mol/l.

9.2.3 Apparatus

Use ordinary laboratory apparatus and glassware complying with the requirements of the relevant International Standards (see clause 2), together with the following.

9.2.3.1 Mechanical shaker.

9.2.3.2 Flask, of capacity 250 ml, with stopper.

9.2.3.3 Glass filter funnel.

9.2.4 Procedure

Carry out the determination in duplicate.

9.2.4.1 Test portion

Take a test portion, containing approximately 0,35 g to 0,4 g of zinc phosphate, of pigment which has been freshly ignited as described in 7.2. Weigh, to the nearest 1 mg, the test portion and place it into the 250 ml flask (9.2.3.2).

9.2.4.2 Determination

Add 20 g of the wet cation-exchange resin (9.2.2.2) and 100 ml of water to the flask containing the test portion. Stopper the flask and shake for 1 h on the mechanical shaker (9.2.3.1).

Separate the resin and any insoluble pigment by quantitatively transferring the contents of the flask to the glass filter funnel (9.2.3.3) containing a glass-wool plug. Wash with successive 25 ml portions of water until the washings are no longer acid to litmus paper. Collect the filtrate and washings in a 250 ml conical flask.

Add 8 drops of mixed indicator solution (9.2.2.3) and titrate with sodium hydroxide solution (9.2.2.4) until the first hydrogen end-point is reached, as shown by a colour change from red through very pale red to colourless. Note the volume of sodium hydroxide solution used (V_1).

Continue the titration to the second hydrogen end-point, as shown by a change in colour from colourless through blue-green to violet-blue. Note the volume of sodium hydroxide solution used (V_2).

9.2.4.3 Blank test

Carry out a blank test in parallel with the determination, following the same procedure and using the same reagents as in the determination, but omitting the test portion.

9.2.5 Expression of results

9.2.5.1 Method of calculation

Calculate the phosphate content $w(\text{PO}_4)$ of the pigment, expressed as a percentage by mass, using the equation

$$w(\text{PO}_4) = \frac{[(V_2 - V_1) - (V_4 - V_3)] \times c \times 9{,}497}{m_4}$$

where

V_1 is the volume, in millilitres, of sodium hydroxide solution (9.2.2.4) required to reach the first hydrogen end-point with the test solution;

V_2 is the volume, in millilitres, of sodium hydroxide solution (9.2.2.4) required to reach the second hydrogen end-point with the test solution;

V_3 is the volume, in millilitres, of sodium hydroxide solution (9.2.2.4) required to reach the first hydrogen end-point in the blank test;

V_4 is the volume, in millilitres, of sodium hydroxide solution (9.2.2.4) required to reach the second hydrogen end-point in the blank test;

c is the actual concentration, in moles of NaOH per litre, of the sodium hydroxide solution (9.2.2.4);

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

9,497 is the factor for the conversion of millilitres of sodium hydroxide solution, $c(\text{NaOH}) = 1{,}000$ mol/l, to centigrams of PO_4.

If the two determinations differ by more than 0,2 % (*m*/*m*), repeat the procedure.

Calculate the mean of two valid determinations and report the result to the nearest 0,1 % (*m*/*m*).

9.2.5.2 Precision

No precision data are currently available.

10 Test report

The test report shall contain at least the following information:

a) all details necessary for the identification of the product tested;

b) a reference to this International Standard (ISO 6745);

c) whether the phosphate content was determined by the gravimetric (9.1) or the titrimetric (9.2) method;

d) the results of the tests and whether or not the product complies with the relevant specification limits;

e) any deviation from the methods of test specified;

f) the date(s) of the tests.

UDC 667.622.2

Descriptors: paints, pigments, white pigments, zinc phosphate, classification, specifications, tests.

Price based on 7 pages