INTERNATIONAL
STANDARD

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Rubber compounding ingredients — Zinc oxide — Test methods

Ingrédients de mélange du caoutchouc — Oxyde de zinc — Méthodes d'essai

Reference number
ISO 9298:1995(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 9298 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

Annexes A, B and C form an integral part of this International Standard. Annex D is for information only.

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Rubber compounding ingredients — Zinc oxide — Test methods

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. The standard 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 and to ensure compliance with any national regulatory conditions.

1 Scope

1.1 This International Standard specifies the methods to be used for the evaluation of zinc oxide for use in the rubber industry.

1.2 The analytical methods are applicable to all commercial zinc oxides, for example:

- direct type (American process);
- indirect type (French process);
- other types produced by different chemical methods, i.e. precipitation and calcination.

Zinc oxide can also be coated with organic materials, such as fatty acids, oil, wetting agents, etc., in order to improve the dispersion in rubber.

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 787-2:1981, *General methods of test for pigments and extenders — Part 2: Determination of matter volatile at 105 °C.*

ISO 787-4:1981, *General methods of test for pigments and extenders — Part 4: Determination of acidity or alkalinity of the aqueous extract.*

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

ISO 787-8:1979, *General methods of test for pigments and extenders — Part 8: Determination of matter soluble in water — Cold extraction method.*

ISO 1124:1988, *Rubber compounding ingredients — Carbon black shipment sampling procedures.*

ISO 5794-1:1994, *Rubber compounding ingredients — Silica, precipitated, hydrated — Part 1: Non-rubber tests.*

3 Sampling

Sampling shall be carried out in accordance with ISO 1124 for dry powders.

4 Methods of test for the determination of physical and chemical properties

4.1 General

Surface-coated zinc oxides shall be evaluated by the methods specified in table 1, without prior calcination or extraction since there would be little purpose in determining volatile-matter content, content of water-soluble matter or acidity if the coating were removed.

4.2 Matter volatile at 105 °C

Determine the loss on heating at 105 °C in accordance with ISO 787-2.

4.3 Water-soluble matter

Determine the percentage of water-soluble matter in accordance with ISO 787-8.

4.4 Acidity/alkalinity

Determine the acidity/alkalinity in cubic centimetres of 0,1 mol/dm^3 standard volumetric solution per 100 g of sample in accordance with ISO 787-4, except that the result shall be expressed in grams of sulfuric acid per 100 g (g H_2SO_4/100 g) by multiplying the result by $4,9 \times 10^{-3}$.

4.5 Residue on sieve

Determine the sieve residue in accordance with ISO 787-7.

4.6 Nitrogen-adsorption surface area

Determine the surface area in accordance with ISO 5794-1. The test portion shall be 0,7 g to 1,0 g, or more if indicated by the initial test or past experience.

5 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

b) all details necessary for the identification of the sample;

c) the zinc oxide content of the sample;

d) the lead, cadmium, copper and manganese contents of the sample;

e) the water-soluble matter content of the sample;

f) the acidity/alkalinity of the sample;

g) the residue on sieve;

h) the surface area by nitrogen adsorption;

i) the acid-insoluble matter;

j) the dates of the tests;

k) details of any deviation from the procedures specified in this International Standard.

Table 1

Property	Units	Test method
Matter volatile at 105 °C	% (*m/m*)	ISO 787-2
Water-soluble matter	% (*m/m*)	ISO 787-8
Acidity/alkalinity (H_2SO_4 equiv.)	g H_2SO_4/100 g	ISO 787-4
Residue on sieve	% (*m/m*)	ISO 787-7
Nitrogen-adsorption surface area	m^2/g	ISO 5794-1
Zinc oxide	% (*m/m*)	Annex A of this International Standard
Lead	% (*m/m*)	Annex B of this International Standard
Cadmium	% (*m/m*)	Annex B of this International Standard
Copper	% (*m/m*)	Annex B of this International Standard
Manganese	% (*m/m*)	Annex B of this International Standard
Acid-insoluble matter	% (*m/m*)	Annex C of this International Standard

Annex A

(normative)

Determination of zinc oxide content

A.1 Reagents

All reagents shall be of recognized analytical grade, and distilled, deionized or distilled/deionized water shall be used for sample preparation and required dilutions.

A.1.1 Nitric acid, 65 % (*m/m*), $\varrho \approx 1{,}4$ Mg/m^3.

A.1.2 Hydrochloric acid, 20 % (*m/m*), $\varrho \approx 1{,}1$ Mg/m^3.

A.1.3 Ammonia solution, 25 % (*m/m*), $\varrho \approx 0{,}91$ Mg/m^3.

A.1.4 Hydrogen peroxide solution, 3 % (*m/m*).

A.1.5 Iron(III) solution.

Dissolve 86 g of iron(III) ammonium sulfate in water and dilute to 1 000 cm^3.

A.1.6 Ammonium chloride solution.

Dissolve 250 g of ammonium chloride in water and dilute to 1 000 cm^3.

A.1.7 Masking solution.

Dissolve 30 g of ammonium fluoride, 100 g of ammonium thiosulfate and 250 g of ammonium acetate in water and dilute to 1 000 cm^3.

A.1.8 Bromothymol blue solution.

Dissolve 0,1 g of bromothymol blue in 100 cm^3 of ethanol.

A.1.9 Xylenol orange solution.

Dissolve 0,2 g of xylenol orange, tetrasodium salt, in 100 cm^3 of water.

A.1.10 EDTA, standard volumetric solution, $c(\text{EDTA}) = 0{,}1$ mol/dm^3.

Dissolve 37,225 g of ethylenedinitrilotetraacetic acid, disodium salt (Na_2EDTA), in water in a 1 000 cm^3 one-mark volumetric flask, dilute to the mark and mix well. Alternatively, commercially available standard solutions may be used.

A.1.11 Zinc metal, of minimum purity 99,995 % (*m/m*).

A.2 Apparatus

A.2.1 Volumetric flasks, class A, of capacity 250 cm^3, 500 cm^3 and 1 000 cm^3.

A.2.2 Pipettes, class A, of capacity 50 cm^3 and 100 cm^3.

A.2.3 Burette, class A, of capacity 50 cm^3.

A.2.4 Balance, of capacity 250 g, weighing to an accuracy of at least ± 1 mg.

A.2.5 Heating device, e.g. a hotplate.

A.2.6 Acid-washed, fluted filter paper.

A.2.7 Beakers, of capacity 600 cm^3 and 1 000 cm^3.

A.2.8 Conical flasks, of capacity 500 cm^3 and 1 000 cm^3.

A.3 Sampling

Take a representative sample in accordance with ISO 1124.

A.4 Procedure

Suspend 20 g of the zinc oxide sample, weighed to ± 0,01 g, in 100 cm^3 of water in a 1 000 cm^3 beaker (A.2.7) and dissolve carefully with approximately 90 cm^3 of nitric acid (A.1.1). When the zinc oxide has dissolved, boil for a short time, cool down the solution and transfer it to a 500 cm^3 volumetric flask (A.2.1). Carefully dilute the solution to the mark with water and shake.

Pipette 50 cm^3 of this solution into a 250 cm^3 *volumetric flask* (A.2.1). Add 10 cm^3 of iron(III) solution (A.1.5). Shake, and then add successively 5 cm^3 of hydrogen peroxide solution (A.1.4), 60 cm^3 of ammonium chloride solution (A.1.6) and 30 cm^3 of ammonia solution (A.1.3).

Shake briefly and cool down. Make up to the mark and filter through a dry folded filter paper (A.2.6) into a dry 500 cm^3 conical flask (A.2.8). Pipette 50 cm^3 of this solution into a 600 cm^3 beaker (A.2.7) and dilute with water to about 300 cm^3.

Add four drops of bromothymol blue solution (A.1.8) and neutralize with hydrochloric acid (A.1.2). The colour changes from blue to light yellow. Add 2 drops of hydrochloric acid in excess. After addition of 20 ml of masking solution (A.1.7) and 7 drops of xylenol orange solution (A.1.9), titrate with EDTA solution (A.1.10) until the colour changes from purple-red to orange-yellow.

After further dropwise addition of 0,5 cm^3 to 1 cm^3 of EDTA solution, the colour changes sharply to pale yellowish-green. Let the total volume of EDTA solution added be V_1.

A.5 Standardization procedure

Dilute concentrated nitric acid (A.1.1) to a concentration of approximately 30 % (m/m), $\varrho \approx 1{,}2$ Mg/m^3.

WARNING — Acid should be added carefully to water.

Then dissolve 20 g of refined zinc (A.1.11), weighed to ± 0,01 g, by heating in a beaker with 40 cm^3 of the diluted nitric acid. Allow the solution to cool, transfer to a 1 000 cm^3 volumetric flask (A.2.1) and dilute to the mark. Proceed as in A.4, starting at paragraph 2, to obtain the titration volume V_2.

1 cm^3 of 0,1 mol/dm^3 EDTA solution corresponds to 0,006 537 g of zinc or 0,008 138 g of zinc oxide.

A.6 Expression of results

Calculate the total zinc oxide content w_{ZnO}, expressed as a percentage by mass, using the equation

$$w_{ZnO} = \frac{V_1 \times 100 \times 1{,}245}{V_2}$$

where

V_1 is the volume, in cubic centimetres, of EDTA solution (A.1.10) required for titration of the zinc in the test portion in A.4;

V_2 is the volume, in cubic centimetres, of EDTA solution (A.1.10) required for titration of the zinc in the standardization procedure (A.5);

1,245 is the ratio of the relative molecular mass of zinc oxide to the relative atomic mass of zinc.

A.7 Interference

Lead and iron are precipitated as hydroxides when the ammonia solution is added. Copper will be masked by ammonium thiosulfate. Aluminium will be masked by ammonium fluoride. Cadmium is also titrated with the EDTA solution, but since the cadmium concentration is usually lower than 0,1 % (m/m) in rubber-grade zinc oxides, this error is negligible.

Annex B
(normative)

Determination of lead, cadmium, copper and manganese contents

B.1 Principle and range of application

B.1.1 A test portion of zinc oxide is dissolved in hydrochloric acid. Nitric acid is added, and each metal ion determined by atomic absorption spectroscopy at the following standard wavelengths:

cadmium	228,8 nm
copper	324,7 nm
lead	283,3 nm
manganese	279,5 nm

B.1.2 Any zinc oxide suitable for rubber compounding and having a lead content less than about 1,0 % may be analysed by this procedure.

B.1.3 The method is not suitable for zinc oxides with lead contents above about 1,0 % owing to dissolution problems.

B.2 Reagents

All reagents shall be of recognized analytical grade, and distilled, deionized or distilled/deionized water shall be used for sample preparation and required dilutions.

B.2.1 Lead, cadmium, copper and manganese, standard solutions.

Standard solutions for the metals to be determined in each zinc oxide sample may be prepared from pure metals or metallic compounds, or purchased from a chemical supply house as standard solutions. The usual concentration of such solutions is 1 µg of the metal per cubic centimetre of solution. Suitable dilutions with water will bring these solutions into the linear working range of the spectrometer (B.3.7). It is recommended that standards below 1 µg/cm^3 be prepared fresh, while those at 1 µg/cm^3 or above may be stored in plastic bottles (B.3.6).

Care shall be taken to ensure that all samples, and the standards used with them, contain the same concentration of acid(s).

B.2.2 Hydrochloric acid,
36 % (*m/m*), $\varrho \approx$ 1,18 Mg/m^3.

B.2.3 Nitric acid, 65 % (*m/m*), $\varrho \approx$ 1,4 Mg/m^3.

B.3 Apparatus

B.3.1 Balance, capable of weighing accurately to ± 0,1 mg.

B.3.2 Hotplate.

B.3.3 Common borosilicate glassware, especially 10 cm^3, 100 cm^3, 200 cm^3 and 500 cm^3 volumetric flasks.

B.3.4 Pipettes, of 1 cm^3, 2 cm^3, 5 cm^3 and 10 cm^3 capacity.

B.3.5 Microlitre syringes, of capacity 1 mm^3 and 10 mm^3.

B.3.6 Plastic bottles, suitable for storage of standard solutions.

B.3.7 Atomic absorption spectrometer, operating in the flame mode.

The instrument shall be operated in accordance with the manufacturer's instructions for optimum performance.

Instrument calibration methods (possible with more modern equipment) shall be carried out as suggested by the manufacturer.

B.4 Sampling

Take a representative sample in accordance with ISO 1124.

B.5 Procedure

B.5.1 Weigh 0,2 g to 10,0 g of the zinc oxide (see B.5.2, second paragraph) in a 150 cm^3 beaker. Weigh to ± 0,1 mg accuracy for small test portions (0,2 g to 2,0 g) and to ± 0,01 g for larger test portions (2,0 g to 10,0 g). Add enough water to make a thick "slurry". Add enough HCl to effect complete dissolution of the test portion. For small test portions, 10 cm^3 will suffice, for larger test portions, up to 30 cm^3 may be needed.

NOTE 1 Failure to observe this sequence will result in a hard cake of zinc oxide, which will be difficult to dissolve in the water/acid mixture.

B.5.2 Heat the solution on the hotplate (B.3.2) to the boiling point, then carefully add 1 cm^3 to 2 cm^3 of concentrated HNO_3 (B.2.3). Continue heating for no more than 5 min. Remove the beaker from the hotplate, allow it to cool and quantitatively transfer the solution to a 250 cm^3 volumetric flask (B.3.3), making it up to the mark with water.

Variations in the mass of the test portion and the final volume of the solution are left to the discretion of the analyst, and must be determined by prior knowledge of the approximate amounts of lead, cadmium, copper and manganese in the type of zinc oxide being analysed.

B.5.3 Carry a blank through the entire procedure, using the same quantities of reagents but without a test portion. Subtract any positive blank value, in an appropriate manner, before calculating the lead, cadmium, copper or manganese content of the zinc oxide.

B.5.4 Complete the analysis, using standard flame atomic absorption techniques appropriate to the instrument used and following the manufacturer's instructions for optimum instrument performance.

Zinc oxide solutions used for measurement must fall within the linear range of the calibration curve. Any solution that does not meet this criterion must be diluted suitably to fall within this range.

B.6 Expression of results

Calculation may be by graph, by equation or by calibration techniques appropriate to the atomic absorption spectrometer used.

Report the metal content as a percentage by mass if greater than or equal to 0,1 % (*m/m*), or as milligrams per kilogram if less than 0,1 % (*m/m*).

NOTE 2 Micrograms per gram, parts per million and milligrams per kilogram are equivalent. Milligrams per kilogram is the preferred SI unit.

Annex C

(normative)

Determination of acid-insoluble matter

C.1 Reagent

C.1.1 Hydrochloric acid, 36 % (*m/m*), $\varrho \approx 1{,}18$ Mg/m^3.

C.2 Apparatus

C.2.1 Balance, accurate to ± 0,1 mg.

C.2.2 Oven, operating at 105 °C ± 5 °C.

C.2.3 Filter-funnel suction flask.

C.2.4 Common borosilicate glassware.

C.2.5 Sintered-glass filter, P10 series (pore size: 5,0 µm.

C.3 Sampling

Take a representative sample in accordance with ISO 1124.

C.4 Procedure

Weigh out 10 g of the zinc oxide sample to the nearest 0,01 g. Suspend the zinc oxide in 100 cm^3 of distilled water in a 250 cm^3 beaker and carefully add 25 cm^3 of HCl (C.1.1). Dissolve the zinc oxide by stirring and gentle heating. Boil the solution for about 15 min. Dry the sintered-glass filter (C.2.5) for 15 min in the oven at 105 °C ± 5 °C. Allow to cool for 30 min in a desiccator and then weigh to the nearest 0,1 mg. Filter the zinc oxide solution through the weighed sintered-glass filter and wash the residue on the filter using three 25 cm^3 portions of dilute HCl (C1.1 diluted 1 + 9).

Dry the sintered-glass filter plus insoluble matter in the oven for 15 min at 105 °C ± 5 °C, allow to cool for 30 min in a desiccator and weigh to the nearest 0,1 mg.

The difference between the mass of the sintered-glass filter and the mass of the sintered-glass filter including the residue represents the amount of matter insoluble in hydrochloric acid.

NOTE 3 This method also gives a qualitative indication of the presence of basic zinc carbonate and/or zinc carbonate — if carbonates are present in the zinc oxide, gassing or foaming occurs.

C.5 Expression of results

Calculate the mass of acid-insoluble matter w_{ins}, expressed as a percentage by mass, using the equation

$$w_{\text{ins}} = \frac{m_2}{m_1} \times 100$$

where

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

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

Annex D

(informative)

Zinc oxides used as rubber compounding material — Classification and typical values

D.1 Classification

Three types of zinc oxide are used in the rubber industry, produced by different processes:

Type A: Direct zinc oxide (American process)

This zinc oxide is manufactured by the reduction of a zinc-bearing material such as a zinc ore and reoxidation of the zinc vapour in the same reactor. Direct zinc oxide particles are mostly acicular (needle-shaped), sometimes nodular. The nodular-type particle shape is generally preferred for rubber compounding.

Type B: Indirect zinc oxide (French process)

This zinc oxide is manufactured by burning zinc vapour (produced by boiling zinc metal). Commonly, indirect zinc oxide is characterized by a high degree of purity. Indirect zinc oxide particles are mostly nodular in shape.

Type C: Wet-process zinc oxide

This zinc oxide is manufactured by a wet process. Zinc is precipitated from zinc solutions (for example as the carbonate or hydroxide) and then calcined to zinc oxide. Wet-process zinc oxide can be manufactured to a very fine particle size and high purity. Surface areas from 5 m^2/g to 40 m^2/g may be obtained with the same level of purity.

Zinc oxide can be coated with organic materials such as fatty acids (most commonly propionic acid) in order to improve dispersion in rubber.

Zinc oxide can be supplied in the form of pellets manufactured with or without organic binders.

D.2 Typical values

Table D.1 shows typical values for some of the various types of zinc oxide, viz. one direct type, eight indirect types and two wet-process zinc oxides.

Classes B1a, B2a, B2b and B2c are of extremely high purity and have a low cadmium content, which is required in some countries where special regulations apply.

Table D.1

Property	Units	Typical values for										
		direct type (American)	indirect type (French)								wet-process type	
		Class A1a	Class B1a	Class B2a	Class B2b	Class B2c	Class B3b	Class B4a	Class B4b	Class B4c	Class C1b	Class C1d
Lead	% (*m/m*)	0,25	0,004	0,005	0,005	0,005	0,1	0,25	0,25	0,25	0,03	0,001
Cadmium	% (*m/m*)	0,02	0,001	0,005	0,005	0,005	0,05	0,05	0,05	0,05	0,005	0,001
Surface area	m^2/g	3,5	4,0	3,5	6,0	9,0	5,0	3,5	6,0	9,0	6,0	40,0
Zinc oxide	% (*m/m*)	98,5	99,5	99,5	99,5	99,5	99,0	99,0	99,0	99,0	98,0	93,0
Volatile matter	% (*m/m*)	0,3	0,25	0,25	0,25	0,25	0,25	0,3	0,3	0,3	0,5	0,5
Sieve residue 45 µm	% (*m/m*)	0,05	0,01	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,10	0,2
Acidity/alkalinity	g H_2SO_4/100 g	0,07	0,05	0,05	0,05	0,05	0,05	0,12	0,12	0,12	0,12	0,2
Copper	% (*m/m*)	0,005	0,000 5	0,000 5	0,000 5	0,000 5	0,000 5	0,001	0,001	0,001	0,001	0,001
Manganese	% (*m/m*)	0,005	0,000 5	0,000 5	0,000 5	0,000 5	0,000 5	0,001	0,001	0,001	0,001	0,001
Acid-insoluble matter	% (*m/m*)	1,0	0,01	0,01	0,01	0,01	0,01	0,1	0,1	0,1	1,0	1,0
Water-soluble matter	% (*m/m*)	1,0	0,01	0,2	0,2	0,2	0,2	0,2	0,2	0,2	1,0	1,0

NOTE — The classes of zinc oxide presented in this table are representative of most classes used commercially in the rubber industry worldwide; however, there are other acceptable grades of zinc oxide which vary greatly in surface area and other properties.

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