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Extenders — Specifications and methods of test —

Part 19: Precipitated silica

Matières de charge — Spécifications et méthodes d'essai —

Partie 19: Silice précipitée

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Contents

Page

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.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of 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 www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 256, *Pigments, dyestuff and extenders*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 298, *Pigments and extenders*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 3262-19:2000), which has been technically revised.

The main changes compared to the previous edition are as follows:

— the main title has been changed from "Extenders for paints" to "Extenders";

— in Table 1, carbon content has been revised and organic surface has been refined;

— in 6.3.8, magnesium perchlorate has been changed to an example for a desiccant;

— in 7.2.3, suitable examples for carbon steel have been added;

— the text has been editorially revised and the normative references have been updated.

A list of all parts in the ISO 3262 series can be found on the ISO website.

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.

Extenders — Specifications and methods of test —

Part 19:
Precipitated silica

1 Scope

This document specifies requirements and corresponding methods of test for precipitated silica.

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

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

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

ISO 787-11, *General methods of test for pigments and extenders — Part 11: Determination of tamped volume and apparent density after tamping*

ISO 3262-1, *Extenders — Specifications and methods of test — Part 1: Introduction and general test methods*

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

ISO 5794-1:2010, *Rubber compounding ingredients — Silica, precipitated, hydrated — Part 1: Non-rubber tests*

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

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

3 Terms and definitions

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

— IEC Electropedia: available at http://www.electropedia.org/

3.1
precipitated silica
amorphous silica precipitated by reaction of sodium silicate solution with a mineral acid and/or carbon dioxide

4 Requirements and test methods

For precipitated silica complying with this document, the essential requirements are specified in Table 1 and the conditional requirements are listed in Table 2.

In order to determine the pH value of hydrophobic silica in an aqueous suspension, a 1 + 1 mass fraction mixture of water and methanol is used.

Table 1 — Essential requirements and test methods

Characteristic	Unit	Requirement		Test method according to
		Grade A	Grade B	
Silica content, min.	% mass fraction	95	95	See Clause 6
Carbon content[a]		<0,3	≥0,3[b]	See Clause 7
Organic surface treatment and surface coating	—	No	Yes	See Clause 7
Matter volatile at 105 °C	% mass fraction	max. 8		ISO 787-2
Loss on ignition	% mass fraction	3 to 8	3 to 15	ISO 3262-1
Oil absorption value[c]	g/100g	120		ISO 787-5
pH value of aqueous suspension	—	3,5 to 9		ISO 787-9

[a] The carbon content is also part of the loss on ignition.

[b] Usually does not exceed 15 %.

[c] A test method with higher reproducibility and repeatability is described in ASTM D2414. However, the results cannot be compared directly with oil absorption values determined in accordance with ISO 787-5.

Table 2 — Conditional requirements and test methods

Characteristic	Unit	Requirement		Test method according to
		Grade A	Grade B	
Residue on 45 μm sieve, max.	% mass fraction	To be agreed between the interested parties	Not applicable	Spray method (Clause 8)[a]
Particle size distribution (instrumental method)	% mass fraction	To be agreed between the interested parties		
Apparent density after tamping	g/ml	To be agreed between the interested parties		ISO 787-11
Specific surface area	m^2/g			ISO 5794-1:2010, Annex D

[a] Only for hydrophilic materials.

5 Sampling

Take a representative sample of the product to be tested according to ISO 15528.

6 Determination of silica content

6.1 Principle

A test portion is repeatedly treated with hydrochloric acid and evaporated to dryness. To render the dehydrated silicic acid thus formed as insoluble as possible, it is then heated for 2 h at (140 ± 5) °C. Any chlorides present are removed by extracting the precipitate with hot dilute hydrochloric acid.

The precipitate is ignited at 1 000 °C, giving impure silicon dioxide, which is treated with sulfuric and hydrofluoric acid. The silicon tetrafluoride formed is evaporated off and the silica content is calculated from the resulting loss in mass.

6.2 Reagents

WARNING — Hydrofluoric acid is corrosive and toxic. The related operations shall be performed in fume hood. This document does not point out all possible safety problems. It is the responsibility of the user to take proper safety and health measures, and to determine the applicability of regulatory limitations prior to use.

Use only reagents of recognized analytical grade and only water of at least grade 3 purity according to ISO 3696.

6.2.1 Hydrochloric acid (HCl), CAS-No 7647-01-0[1)], concentrated, approximately 32 % mass fraction, $\rho \approx 1{,}16$ g/ml.

6.2.2 Hydrochloric acid (HCl), CAS-No 7647-01-0, diluted 1 + 1.

Add 1 part by volume of concentrated hydrochloric acid (6.2.1) to 1 part by volume of water.

6.2.3 Sulfuric acid (H_2SO_4), CAS-No 7664-93-9, diluted 1 + 1.

Add 1 part by volume of concentrated sulfuric acid, approximately 96 % mass fraction, $\rho \approx 1{,}84$ g/ml, slowly to 1 part by volume of water.

6.2.4 Hydrofluoric acid (HF), CAS-No 7664-39-3, concentrated, approximately 40 % mass fraction, $\rho \approx 1{,}13$ g/ml.

6.3 Apparatus

Use ordinary laboratory apparatus and glassware, together with the following.

6.3.1 Dish.

6.3.2 Platinum crucible.

6.3.3 Water bath, capable of being maintained at 100 °C.

6.3.4 Infrared evaporator.

6.3.5 Muffle furnace, capable of being maintained at (1 000 ± 20) °C.

6.3.6 Drying oven, capable of being maintained at (140 ± 5) °C.

6.3.7 Filter paper.

The filter paper used for filtration of the silica shall be of such texture as to retain the smallest particles of precipitate and nevertheless permit rapid filtration[2)].

1) CAS-No – Chemical Abstracts Service Registry Number.

2) Whatman No. 40 or 41 or Schleicher und Schüll No. 589/2 "Weißband" are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

6.3.8 Desiccator, containing for example magnesium perchlorate as desiccant.

6.4 Procedure

6.4.1 Number of determinations

Carry out the determination in duplicate.

6.4.2 Test portion

Weigh, to the nearest 0,2 mg, approximately 1 g (m_0) of the sample (see Clause 5) into a dish (6.3.1).

6.4.3 Determination

Slowly add 20 ml of concentrated hydrochloric acid (6.2.1) and evaporate to dryness under the infrared evaporator (6.3.4). Add again 20 ml of concentrated hydrochloric acid and evaporate to dryness. Repeat this step once more. After the third evaporation, place the dish in the drying oven (6.3.6), maintained at (140 ± 5) °C, and leave for 2 h.

Remove the dish from the oven and allow to cool. Add 50 ml of 1 + 1 hydrochloric acid (6.2.2) to the residue in the dish and warm it for approximately 20 min on the water bath (6.3.3) at 100 °C. Filter through a suitable filter paper (6.3.7) and wash the residue on the filter with hot water until the washings are neutral.

Pour the filtrate and washings into the original dish and evaporate to dryness. Repeat this evaporation step another two times, adding each time 10 ml of concentrated hydrochloric acid to the residue. After the third evaporation, heat at (140 ± 5) °C for 2 h in the drying oven.

Add 20 ml of 1 + 1 hydrochloric acid to the residue in the dish and warm it for approximately 10 min on the water bath at 100 °C. Filter through a fresh filter paper and wash the residue on the filter with hot water until the washings are neutral.

If necessary, check the filtrate for any silicon which may have passed through the filter.

Place the two filter papers with the washed precipitates in the platinum crucible (6.3.2). Dry, char at low temperature, ignite in the muffle furnace (6.3.5) at (1 000 ± 20) °C to constant mass (this should take approximately 1 h) and allow to cool in the desiccator (6.3.8). Weigh the ignited precipitate to the nearest 0,2 mg (m_1).

Wet the ignited precipitate in the platinum crucible with 2 ml to 3 ml of water, add 1 ml of 1 + 1 sulfuric acid (6.2.3) and 15 ml of hydrofluoric acid (6.2.4) and evaporate to a syrup, taking care to avoid loss by spitting. Allow to cool and wash the sides down with small quantities of water. Then add a further 10 ml of hydrofluoric acid and evaporate to dryness. If the evaporation of the silicon tetrafluoride is not complete, add a further 10 ml of hydrofluoric acid and evaporate to dryness again.

Heat the residue until white fumes are no longer evolved, then ignite for 30 min in the muffle furnace at (1 000 ± 20) °C. Remove from the furnace, allow to cool in the desiccator and weigh to the nearest 0,2 mg (m_2).

6.4.4 Determination of the total loss on ignition

Weigh, to the nearest 0,2 mg, approximately 1 g (m_3) of the sample (see Clause 5) into a platinum crucible.

NOTE Weighing out the test portions for the determination of the silica content (see 6.4.2) and the total loss on ignition can be carried out at the same time.

Ignite the test portion to constant mass in the muffle furnace at (1 000 ± 20) °C (this takes approximately 2 h) and allow to cool in the desiccator. Weigh the ignited test portion to the nearest 0,2 mg (m_4).

Calculate the total loss on ignition w_{TLI}, expressed as a mass fraction in percent, using Formula (1):

$$w_{TLI} = \frac{m_3 - m_4}{m_3} \times 100 \quad (1)$$

where

m_3 is the mass, in grams, of the test portion before ignition;

m_4 is the mass, in grams, of the ignited test portion.

Calculate the mean of the two determinations and report the result to the nearest 0,1 %.

6.5 Expression of results

Calculate the silica content w (SiO_2), expressed as a mass fraction in percent, using Formula (2):

$$w(SiO_2) = \frac{(m_1 - m_2)}{m_0 \times \left[1 - \frac{w_{TLI}}{100}\right]} \times 100 \quad (2)$$

where

m_0 is the mass, in grams, of the test portion (see 6.4.2);

m_1 is the mass, in grams, of the dehydrated impure silica after ignition at (1 000 ± 20) °C to constant mass (see 6.4.3);

m_2 is the mass, in grams, of the silica after treatment with hydrofluoric acid and ignition to constant mass (see 6.4.3);

w_{TLI} is the total loss on ignition determined in 6.4.4.

Calculate the mean of the two determinations and report the result to the nearest 0,1 %.

6.6 Precision

6.6.1 Repeatability, *r*

The repeatability, *r*, is the value below which the absolute difference between two single test results, each the mean of duplicates, can be expected to lie when this method is used under repeatability conditions. In this case, the test results are obtained on identical material by one operator in one laboratory within a short interval of time. For this document, *r* is 0,6 %, with a 95 % probability.

6.6.2 Reproducibility, *R*

No reproducibility data are available at the time of publication.

7 Determination of carbon content

7.1 Principle

A test portion in a crucible is covered, if necessary, with a suitable catalyst, and combusted in a stream of oxygen in an induction furnace.

Sulfur compounds, halogens and water vapour are removed from the combustion products, which are then passed over a platinum catalyst to convert carbon monoxide to carbon dioxide, and the carbon dioxide concentration is measured using an infrared-cell detector.

Alternatively, the carbon can be determined by conductivity measurement. In this case, the specified combustion products are passed over a platinum catalyst and the carbon dioxide present is absorbed in a sodium hydroxide (NaOH) solution. The change in conductivity of the solution caused by the conversion of some of the NaOH to disodium carbonate (Na_2CO_3) is measured.

7.2 Reagents and materials

Use only reagents of recognized analytical grade and only water of at least grade 3 purity according to ISO 3696.

7.2.1 Oxygen, CAS-No 7782-44-7, purity min. 99,99 %.

7.2.2 Catalyst, comprising iron chips plus a mixture consisting of 9 parts by mass of tungsten and 1 part by mass of tin powder[3)].

NOTE The catalyst is used as required to obtain satisfactory results.

7.2.3 Carbon reference materials (carbon steels)[4)].

7.2.4 Platinum catalyst pellets, suitable for use at 400 °C to 450 °C, to convert carbon monoxide to carbon dioxide.

7.3 Apparatus

Use ordinary laboratory apparatus and glassware, together with the following.

7.3.1 Low-carbon analyser, consisting of an induction-heated furnace suitable for operation at about 1 800 °C, a scavenging unit, a platinum catalyst system operating at about 450 °C, and an infrared-cell detection system. Alternatively, a carbon dioxide absorption unit including an NaOH solution and equipment for measuring the change in conductivity can be used.

The system shall include a carbon dioxide absorbent based on NaOH, a moisture absorbent (magnesium perchlorate) for purification purposes and a flowmeter for control of the oxygen stream.

7.3.2 Crucibles, expendable, made of aluminia or similar refractory material. Both crucible and lid shall be ignited before use at a temperature of 1 000 °C or higher for a time (usually 20 min) sufficient to give a constant mass.

7.4 Procedure

7.4.1 Preparation of apparatus

Follow the operating instructions for the specific equipment used. After setting the controls, carry out several blank runs with a crucible (7.3.2) containing the required amount of catalyst but not the test portion. Successive blank values shall approach a low, constant value.

3) Lecocel II® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute and endorsement by ISO of this product.

4) NIST SRM 131h (containing 0,000 78 % C); BAM CRM-No D 231-2 (containing 0,014 % C); NIST SRM 139b (containing 0,403 % C); BAM CRM 476-3 (containing 3,39 % C) are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

7.4.2 Calibration

Weigh, to the nearest 0,1 mg, approximately 0,5 g of reference material (7.2.3) into a crucible, combust and record the result if using equipment which gives the result automatically as described in 7.4.3, or use Formula (3) if using equipment which does not. Repeat at least twice. Adjust the calibration controls to produce the correct readings on the direct-reading meter. Combust additional samples of the reference material as required to produce the correct direct reading.

7.4.3 Determination

Carry out the determination in duplicate.

Weigh, to the nearest 0,1 mg, approximately 0,5 g of the sample (see Clause 5) (m_0) into a crucible, cover with 0,7 g of iron chips and 1,0 g of tungsten/tin powder (7.2.2) and place the crucible in the induction furnace of the low-carbon analyser (7.3.1). It is especially important to cover the test portion completely with the catalyst when the test portion is a powder as this prevents possible blow-out of test portion during ignition.

If the analyser has an integral balance, the test portion mass is automatically stored in the memory. In this case, press the "analyse" key and the analysis proceeds automatically. The result is displayed on the screen and is printed as percent by mass of carbon in the test portion.

7.5 Expression of results

If the equipment used does not print the result automatically, calculate the carbon content w (C), expressed as a mass fraction in percent, using Formula (3):

$$w(\mathrm{C}) = \frac{m_t - m_b}{m_0 \times \left[1 - \frac{w_{\mathrm{TLI}}}{100}\right]} \times 100 \qquad (3)$$

where

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

m_b is the mass, in grams, of carbon recorded in the final blank determination;

m_t is the mass, in grams, of carbon in the test portion;

w_{TLI} is the total loss on ignition as determined in 6.4.4.

Calculate the mean of the two determinations and report the result to the nearest 0,1 %.

7.6 Precision

No precision data are available at the time of publication.

8 Determination of residue on sieve

8.1 Principle

The extender under test is suspended in water and the suspension is poured onto a sieve. Water is sprayed onto the sieve by means of a spray head, gently dispersing any agglomerates and flushing the fine particles through the sieve. The residue on the sieve is dried and weighed.

NOTE The spray method described in this document involves medium-level agglomerate-dispersing forces; these are necessary because of the particular physical characteristics of precipitated silica.

8.2 Materials

8.2.1 Tap water, filtered, at a pressure of approximately 200 kPa above atmospheric pressure. The pressure shall be adjusted to give a flow rate of (13,5 ± 0,3) l/min from the spray head.

8.3 Apparatus

Use ordinary laboratory apparatus and glassware, together with the following.

8.3.1 Sieve, consisting of a metal frame and wire gauze made from phosphor bronze or stainless steel, mesh size 45 µm, diameter 200 mm.

NOTE Loss of suspension by splashing during the sieving procedure can be prevented by using a splash guard made of a cylindrical metal sheet made from phosphor bronze or stainless steel having a height of approximately 200 mm and a diameter slightly less than 200 mm which fits into the top of the sieve.

8.3.2 Sieve holder.

8.3.3 Spray head, with a diameter of 60 mm, having 76 holes drilled with a diameter of (1,0 ± 0,1) mm.

8.3.4 Weighing bottle.

8.3.5 Drying oven, capable of being maintained at (105 ± 2) °C.

8.4 Procedure

8.4.1 Number of determinations

Carry out the determination in duplicate.

8.4.2 Test portion

Weigh, to the nearest 0,1 mg, a quantity (m_0) of the sample (see Clause 5) such that a sufficient residue is obtained on the sieve (8.3.1). Place this test portion in a suitable beaker. Generally, a test portion of 10 g to 100 g is necessary.

8.4.3 Determination

Disperse the test portion in a suitable quantity of water in the beaker by stirring with a glass rod to produce a free-flowing suspension.

Adjust the flow of water from the spray head (8.3.3) so that the flow rate is (13,5 ± 0,3) l/min. Transfer the suspension quantitatively, if necessary in portions, onto the sieve and rinse the beaker with water. Hold the spray head approximately 15 cm above the sieve. Move the spray head in a circular path to rinse down the wall of the sieve. Continue spraying for 5 min. Then dry the residue on the sieve in the drying oven (8.3.5) for 2 h at (105 ± 2) °C. Transfer the residue to a previously weighed bottle (8.3.4) and weigh to the nearest 0,1 mg (m_1).

Note the type of residue on the sieve (for example foreign matter).