INTERNATIONAL STANDARD

ISO 5796

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Rubber compounding ingredients — Natural calcium carbonate — Test methods

Ingrédients de mélange du caoutchouc — Carbonate de calcium naturel — Méthodes d'essai

Reference number
ISO 5796:1990(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 5796 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

It cancels and replaces ISO 5796-1:1984, to which an annex has been added concerning the classification and typical physical and chemical properties of natural calcium carbonate.

Annex A of this International Standard is for information only.

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Rubber compounding ingredients — Natural calcium carbonate — Test methods

1 Scope

This International Standard specifies the methods to be used for the evaluation of natural calcium carbonate (chalk or limestone) ground to a dry powder for use in the rubber industry.

NOTE 1 Classification of natural calcium carbonate according to fineness and chemical purity, and typical physical and chemical properties for natural calcium carbonate for use in the rubber industry, are given in informative annex A.

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 565:1990, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings.*

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

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

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

ISO 3262:1975, *Extenders for paints.*

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

3 Sampling

Sampling shall be carried out in accordance with ISO 842.

4 Methods of test

WARNING — All recognized health and safety precautions shall be observed when carrying out these tests.

During the analysis, all reagents used shall be of recognized analytical reagent quality. Distilled water or water of equal purity shall be used throughout the tests.

4.1 Residue on sieve

Determine the sieve residue in accordance with clause 8 of ISO 3262:1975, using 45 µm and 125 µm opening test sieves in accordance with ISO 565.

4.2 Calcium carbonate (on dry sample)

Determine the calcium carbonate content in accordance with clause 16 of ISO 3262:1975.

4.3 Loss on heating at 105 °C

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

4.4 Loss on ignition at 1 000 °C (on dry sample)

Determine the loss on ignition at 1 000 °C in accordance with clause 11 of ISO 3262:1975.

4.5 Matter insoluble in hydrochloric acid

4.5.1 Reagent

4.5.1.1 Hydrochloric acid, 73 g/dm³ solution.

Dilute 170 cm³ of concentrated hydrochloric acid (ρ = 1,18 g/cm³) to 1 dm³ with water and mix.

4.5.2 Apparatus

4.5.2.1 Beaker, of capacity 250 cm³, and **watch-glass**, suitable for covering the beaker, and **glass rod** suitable for stirring.

4.5.2.2 Analytical balance, accurate to 1 mg.

4.5.2.3 Sintered-glass crucible, porosity grade P 40 in conformity with the requirements of ISO 4793.

4.5.2.4 Oven, capable of being maintained at a temperature of 105 °C ± 2 °C.

4.5.2.5 Desiccator.

4.5.3 Procedure

4.5.3.1 Weigh, to the nearest 1 mg, approximately 2 g of sample into the beaker (4.5.2.1).

4.5.3.2 Pour 100 cm³ of the hydrochloric acid solution (4.5.1.1) into the beaker and cover with the watch-glass.

4.5.3.3 Swirl the mixture gently at room temperature, avoiding the formation of foam. Boil the mixture gently for 5 min to 10 min, then leave to cool for 30 min to 60 min, stirring from time to time.

4.5.3.4 Filter off the insoluble matter through the crucible (4.5.2.3) which has previously been washed, dried at 105 °C and weighed. Wash with water until the washings are free from chloride. Discard the filtrate and washings.

4.5.3.5 Dry the crucible containing the insoluble residue in the oven (4.5.2.4), maintained at 105 °C ± 2 °C, until constant mass is achieved, i.e. until further oven-drying, cooling and weighing yields a mass change of less than 1 mg.

4.5.3.6 Cool in the desiccator (4.5.2.5).

4.5.3.7 Weigh to nearest 1 mg.

4.5.4 Expression of results

The matter insoluble in hydrochloric acid is given, expressed as a percentage by mass, by the formula

$$\frac{m_2 - m_1}{m_0} \times 100$$

where

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

m_1 is the mass, in grams, of the empty dried crucible;

m_2 is the mass, in grams, of the crucible containing the insoluble matter.

Express the result to the nearest 0,1 % (m/m).

4.6 Alkalinity

4.6.1 Reagents

4.6.1.1 Distilled water, boiled to remove carbon dioxide.

4.6.1.2 Phenolphthalein, 0,5 % (m/m) solution in 95 % (V/V) ethanol.

4.6.1.3 Hydrochloric acid, standard volumetric solution, c(HCl) = 0,01 mol/dm³.

4.6.2 Apparatus

4.6.2.1 Analytical balance, accurate to 1 mg.

4.6.2.2 Conical flask, narrow-mouth, of capacity 250 cm³.

4.6.2.3 Filter paper, fine grade.

4.6.2.4 Burette, accurate to 0,1 cm³.

4.6.3 Procedure

4.6.3.1 Weigh, to the nearest 1 mg, about 10 g of sample and place this test portion in the flask (4.6.2.2). Add 150 cm³ of distilled water (4.6.1.1). Leave the mixture for 1 h, shaking it from time to time.

4.6.3.2 Filter the mixture through the filter paper (4.6.2.3) and keep all the residue on the filter. Wash three times with a minimum amount of the distilled water, adding the washings to the filtrate.

4.6.3.3 Add a few drops of the phenolphthalein solution (4.6.1.2) as indicator to the filtrate and titrate with the hydrochloric acid solution (4.6.1.3) until colourless. Read the volume used for the titration to the nearest 0,1 cm³.

4.6.4 Expression of results

The alkalinity, expressed in grams of sodium carbonate (Na_2CO_3) per 100 g of sample, is given by the formula

$$\frac{Vc \times 0{,}00053}{m} \times 100$$

where

V is the volume, in cubic centimetres, used for the titration;

c is the actual concentration, expressed in moles of HCl per cubic decimetre of the hydrochloric acid solution (4.6.1.3);

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

0,00053 is the mass, in grams, of sodium carbonate corresponding to 100 cm^3 of hydrochloric acid solution, c(HCl) = 0,010 mol/dm^3.

4.7 Determination of total copper, manganese and iron

4.7.1 Preparation of stock test solution

4.7.1.1 Reagents

4.7.1.1.1 Nitric acid, ρ = 1,42 g/cm^3.

4.7.1.1.2 Hydrofluoric acid, 40 % (*m*/*m*) solution.

4.7.1.1.3 Sulfuric acid, 50 % (*V*/*V*) solution.

4.7.1.1.4 Octyl alcohol (Octan-1-ol).

4.7.1.1.5 Hydrochloric acid, ρ = 1,18 g/cm^3.

4.7.1.2 Apparatus

4.7.1.2.1 Beaker, of capacity 250 cm^3.

4.7.1.2.2 Volumetric flask, of capacity 250 cm^3.

4.7.1.2.3 Platinum crucible, of capacity 20 cm^3.

4.7.1.2.4 Muffle furnace.

4.7.1.2.5 Fume cupboard.

4.7.1.2.6 Quartz triangle.

4.7.1.2.7 Analytical balance, accurate to 1 mg.

4.7.1.3 Procedure

4.7.1.3.1 Weigh, to the nearest 1 mg, about 5 g of sample into the beaker (4.7.1.2.1), dissolve this test portion carefully in 25 cm^3 water and 15 cm^3 of the nitric acid (4.7.1.1.1) and heat to boiling. If foam tends to rise during the dissolution of the test portion, break the foam by adding a drop of the octyl alcohol (4.7.1.1.4).

4.7.1.3.2 Filter through a medium filter paper, wash the paper with hot water and allow the combined filtrate plus washings to cool. Then transfer the solution into the volumetric flask (4.7.1.2.2) and retain for 4.7.1.3.7.

4.7.1.3.3 Lift out the filter paper, fold it carefully to enclose any residue and place in the platinum crucible (4.7.1.2.3). Heat gently until dry, then heat more to char the paper. Then place the crucible in the muffle furnace (4.7.1.2.4) at 1 000 °C ± 50 °C for 30 min to oxidize and to remove all char.

4.7.1.3.4 Cool the crucible and add 2 cm^3 of the hydrofluoric acid solution (4.7.1.1.2), drop by drop, to the crucible in such a way that the contents are all wetted. Then add 0,5 cm^3 of the sulfuric acid solution (4.7.1.1.3) drop by drop.

Place the crucible on a hotplate in the fume cupboard (4.7.1.2.5) and evaporate to dryness, taking care to avoid overheating and consequent bumping or spitting. Then continue heating until white fumes appear.

4.7.1.3.5 Transfer the crucible still in the fume cupboard to a quartz triangle on a stand and heat to a dull red heat until all white fumes have been driven off.

4.7.1.3.6 Allow the crucible to cool. Add 5 cm^3 of water and 1 cm^3 of the nitric acid (4.7.1.1.1) and warm on a hotplate. Stir with a glass rod to dissolve all salts.

4.7.1.3.7 Cool and transfer the solution quantitatively to the flask containing the original acid-soluble portion (see 4.7.1.3.2), rinsing the crucible thoroughly with water into the flask.

4.7.1.3.8 Finally dilute with water to the 250 cm^3 mark.

The flask now contains the stock test solution, aliquots of which will be required for determination of copper, manganese and iron.

4.7.2 Copper (total)

4.7.2.1 Reagents

4.7.2.1.1 Biquinolyl reagent, solution.

Dissolve 0,03 g of 2,2′-biquinolyl in 100 cm^3 of the *n*-hexanol (4.7.2.1.8) that has been freshly distilled from solid sodium hydroxide.

4.7.2.1.2 Hydroxylammonium chloride, solution.

Dissolve 25 g of hydroxylammonium chloride in about 80 cm^3 of water. Filter, if necessary, and dilute to 100 cm^3 with water.

If any appreciable amounts of copper are present in the solution, extract with successive 10 cm^3 portions of a 0,01 % (*m*/*m*) solution of dithizone in carbon tetrachloride until there is no more violet coloration due to copper, hence no change in the green colour of the dithizone solution. Then extract the solution with carbon tetrachloride until all colour has been removed from the aqueous solution.

4.7.2.1.3 Sodium acetate buffer solution.

Dissolve 136 g of sodium acetate trihydrate in water and dilute to 1 dm^3 with water. If the reagent contains more than a trace of copper, purify this solution by extraction with 0,01 % (*m*/*m*) dithizone solution in carbon tetrachloride as for the hydroxylammonium chloride solution (4.7.2.1.2).

4.7.2.1.4 Hydroquinone, solution.

Dissolve 1 g of hydroquinone in 100 cm^3 of redistilled ethanol.

4.7.2.1.5 Copper, standard stock solution.

Dissolve exactly 0,1 g of pure copper in 3 cm^3 of the nitric acid (4.7.1.1.1), add 1 cm^3 of the sulfuric acid solution (4.7.1.1.3) and evaporate in the fume cupboard until white fumes appear. Allow to cool, dissolve the residue in water and dilute to 500 cm^3.

1 cm^3 of this solution contains 200 µg of Cu.

4.7.2.1.6 Copper, 4 µg/cm^3 standard working solution.

Dilute exactly 5 cm^3 of the stock solution (4.7.2.1.5) to 250 cm^3 with water.

1 cm^3 of this solution contains 4 µg of Cu. This solution is used for the calibration of the 1 cm spectrometer cells.

4.7.2.1.7 Copper, 1 µg/cm^3 standard working solution.

For the calibration of 4 cm cells, dilute exactly 5 cm^3 of the stock solution (4.7.2.1.5) to 1 000 cm^3 with water, to give a solution containing 1 µg of copper per cubic centimetre.

4.7.2.1.8 *n*-hexyl alcohol (Hexan-1-ol).

4.7.2.2 Apparatus

Ordinary laboratory apparatus and:

4.7.2.2.1 Balance, accurate to 0,1 mg.

4.7.2.2.2 Spectrometer, capable of being operated at 540 nm, with 1 cm and 4 cm cells.

4.7.2.2.3 Separating funnels, of capacity 250 cm^3.

4.7.2.2.4 One-mark volumetric flask, of capacity 10 cm^3.

4.7.2.3 Procedure

4.7.2.3.1 Transfer a 100 cm^3 aliquot portion of the stock test solution (4.7.1) to a separating funnel (4.7.2.2.3) and add 2,5 cm^3 of the hydroxylammonium chloride solution (4.7.2.1.2) and 25 cm^3 of the sodium acetate buffer solution (4.7.2.1.3).

4.7.2.3.2 Shake with 6 cm^3 of the biquinolyl reagent solution (4.7.2.1.1) for 5 min and allow the phases to separate.

4.7.2.3.3 Run the lower, aqueous layer into another separating funnel, add 2 cm^3 of hydroxylammonium chloride solution and extract again with 2,5 cm^3 of the biquinolyl reagent solution (4.7.2.1.1).

4.7.2.3.4 Separate the phases and again extract the aqueous layer with 2 cm^3 of the biquinolyl reagent solution.

4.7.2.3.5 Combine the three organic extracts in the one-mark volumetric flask (4.7.2.2.4) containing 0,5 cm^3 of the hydroquinone solution (4.7.2.1.4) and dilute the solution to volume with the *n*-hexyl alcohol (4.7.2.1.8).

4.7.2.3.6 Measure the absorbance of the solution in 1 cm or 4 cm cells with the spectrometer (4.7.2.2.2), set at a wavelength of 540 nm.

4.7.2.3.7 Measure also the absorbance (at the same wavelength and in the same size cell) of a reagent blank solution prepared in the same way as the sample solution but omitting the stock solution. Subtract the absorbance of this blank solution from the absorbance found in 4.7.2.3.6.

4.7.2.3.8 Obtain the amount of copper in the aliquot portion (4.7.2.3.1) by use of the calibration curve plotted in 4.7.2.4.3.

4.7.2.4 Calibration

Use the standard copper working solution containing 4 µg of copper per cm^3 (4.7.2.1.6) to calibrate the 1 cm cell and the 1 µg copper per cm^3 (4.7.2.1.7) for the 4 cm cell.

4.7.2.4.1 Transfer aliquot portions from 0 to 25 cm^3 into separating funnels (4.7.2.2.3), add 1,5 cm^3 of concentrated hydrochloric acid and dilute each solution to 100 cm^3 with water.

4.7.2.4.2 Add the hydroxylammonium chloride solution and buffer solution, extract the copper with the biquinolyl reagent solution and measure the absorbances as described in 4.7.2.3.6.

4.7.2.4.3 Plot the relation of absorbance to the copper concentration for the range 0 to 25 µg of copper (4 cm cells) to obtain the calibration curve.

NOTE 2 A solution containing 25 µg of copper in 10 cm^3 of organic extract should have an absorbance of about 0,984 in 4 cm cells or 0,246 in 1 cm cells.

4.7.2.5 Expression of results

The total copper content in the sample, expressed in milligrams per kilogram, is given by the formula

$$\frac{2{,}5m_2}{m_1}$$

where

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

m_2 is the mass, in micrograms, of copper found in the aliquot portion.

4.7.3 Manganese (total)

4.7.3.1 Reagents

4.7.3.1.1 Phosphoric acid, solution.

To 700 cm^3 of water add 200 cm^3 of orthophosphoric acid (ρ = 1,75 g/cm^3). Cool and dilute to 1 dm^3.

4.7.3.1.2 Manganese, standard solution.

Dissolve 0,143 6 g of potassium permanganate in 250 cm^3 of water, reduce with a very slight excess of sulfur dioxide gas dissolved in water and dilute to 500 cm^3.

1 cm^3 of this solution contains 100 µg of Mn.

4.7.3.1.3 Potassium periodate.

4.7.3.2 Apparatus

Ordinary laboratory apparatus and:

4.7.3.2.1 Balance, accurate to 0,1 mg.

4.7.3.2.2 Spectrometer, capable of being operated at 520 nm to 525 nm, with 4 cm cells.

4.7.3.2.3 Volumetric flask, capacity 100 cm^3.

4.7.3.2.4 Beakers, of capacity 250 cm^3.

4.7.3.3 Procedure

4.7.3.3.1 Transfer a 50 cm^3 aliquot portion of the stock test solution (4.7.1) to a 250 cm^3 beaker (4.7.3.2.4), add 25 cm^3 of the phosphoric acid solution (4.7.3.1.1) and 0,5 g of the potassium periodate (4.7.3.1.3).

4.7.3.3.2 Heat to boiling and simmer gently until the pink permanganate colour begins to develop.

4.7.3.3.3 Boil the solution gently for 3 min to 4 min, cool and dilute to 100 cm^3 in the one-mark volumetric flask (4.7.3.2.3).

Fill a cell of the spectrometer (4.7.3.2.2) with this solution.

4.7.3.3.4 Measure the absorbance of the solution in the cell at a wavelength of 520 nm to 525 nm.

4.7.3.3.5 Measure the reagent blank in a similar manner and deduct this value from the absorbance of the test solution.

4.7.3.3.6 Read the mass of manganese, in micrograms, from the calibration curve (see 4.7.3.4).

4.7.3.4 Calibration

To a series of 250 cm^3 beakers (4.7.3.2.4), add a range of accurately measured volumes of the standard manganese solution (4.7.3.1.2) between 0 and 30 cm^3. Treat them as above and construct a calibration curve by plotting the amount of manganese, in micrograms, against absorbance.

4.7.3.5 Expression of results

The total manganese content in the sample, expressed in milligrams per kilogram, is given by the formula

$$\frac{5m_3}{m_1}$$

where

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

m_3 is the mass, in micrograms, of the manganese found in the aliquot portion.

4.7.4 Iron (total)

4.7.4.1 Reagents

4.7.4.1.1 Bipyridine, solution.

Dissolve 0,2 g of 2,2′-bipyridine in 100 cm^3 of 7,3 g/dm^3 hydrochloric acid solution.

4.7.4.1.2 Sodium acetate buffer solution.

Dissolve 136 g of sodium acetate trihydrate in water and dilute to 1 dm^3 with water.

4.7.4.1.3 Iron, standard stock solution.

Dissolve exactly 0,5 g of pure iron in 15 cm^3 of the 73 g/dm^3 hydrochloric acid solution (4.5.1.1)); transfer to a 1 000 cm^3 graduated flask and dilute to the mark with water.

4.7.4.1.4 Iron, standard working solution.

Dilute exactly 25 cm^3 of the stock solution (4.7.4.1.3) to 250 cm^3 with water.

1 cm^3 of this solution contains 50 µg of Fe.

4.7.4.1.5 Hydroxylammonium chloride, 5 g/100 cm^3 solution in water.

4.7.4.2 Apparatus

Ordinary laboratory apparatus and:

4.7.4.2.1 Balance, accurate to 0,1 mg.

4.7.4.2.2 Spectrometer, capable of being operated at 520 nm, with 1 cm cells.

4.7.4.2.3 Volumetric flasks, of capacity 50 cm^3 and 1 000 cm^3.

4.7.4.2.4 pH-meter or **pH-indicator paper**, sensitive to 0,1 pH units.

4.7.4.3 Procedure

4.7.4.3.1 Transfer a 10 cm^3 aliquot of the stock test solution (4.7.1) to a 100 cm^3 beaker and add sodium acetate buffer solution (4.7.4.1.2) until the pH is 4,8 to 5,0.

4.7.4.3.2 Add 1 cm^3 of the hydroxylammonium chloride solution (4.7.4.1.5) and 5 cm^3 of the dipyridyl solution (4.7.4.1.1). Transfer quantitatively to a 50 cm^3 volumetric flask (4.7.4.2.3) and dilute to 50 cm^3 with water.

4.7.4.3.3 Measure the absorbance of the solution in the spectrometer (4.7.4.2.2) at a wavelength of 520 nm in a 1 cm cell.

4.7.4.3.4 Measure also the absorbance (at the same wavelength and in the same size cell) of a reagent blank solution prepared in the same way as the sample solution but omitting the stock test solution. Subtract the absorbance of the reagent blank from that of the test solution obtained in 4.7.4.3.3.

Read the mass of iron, in micrograms, from the calibration curve (see 4.7.4.4).

4.7.4.4 Calibration

To a series of 50 cm^3 graduated flasks (4.7.4.2.3), add a range of accurately measured volumes from 0 to 10 cm^3 of the standard iron working solution (4.7.4.1.4). Treat them as described under "Procedure" (4.7.4.3) and construct a calibration curve by plotting the amount of iron, in micrograms, against absorbance.

4.7.4.5 Expression of results

The total iron content in the sample, expressed in milligrams per kilogram, is given by the formula

$$\frac{25m_4}{m_1}$$

where

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

m_4 is the mass, in micrograms, of iron found in the aliquot portion.

5 Test report

The test report shall include the following information:

a) a reference to this International Standard;

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

c) the test conditions;

d) the mass of test portion used;

e) the results obtained;

f) any deviation from this International Standard which might have affected the test results.