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Rubber compounding ingredients — Determination of multipoint nitrogen surface area (NSA) and statistical thickness surface area (STSA)

Ingrédients de mélange du caoutchouc — Détermination de la surface par adsorption d'azote (NSA) et de la surface par épaisseur statistique (STSA) par méthode multipoints

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

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.

ISO 18852 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*.

This second edition cancels and replaces the first edition (ISO 18852:2005), in which a note has been added at the end of Clause 3, Subclauses 4.1, 4.3, 7.1, 7.5 and 8.5 have been modified, and the precision and bias clause (Clause 11 of ISO 18852:2005) has been moved to an informative annex.

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Rubber compounding ingredients — Determination of multipoint nitrogen surface area (NSA) and statistical thickness surface area (STSA)

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This 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.

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1 Scope

This International Standard specifies a method for the determination of the nitrogen surface area (NSA) of carbon blacks and other rubber compounding ingredients, like silicas and zinc oxides, based on the Brunauer, Emmett and Teller (BET) theory of gas adsorption using a multipoint determination. This test method specifies the sample preparation and treatment, instrument calibration, required accuracy and precision of the experimental data, and calculation of the surface area results from the data obtained. Also given is a procedure for calculating the statistical thickness surface area (STSA), otherwise known as the external surface area.

The test method specified uses an automatic static-volume vacuum apparatus, the surface area being calculated using the BET theory based on monolayer measurements.

The method can also be used for verifying “single-point” procedures described in ISO 4652-1 and other standards.

The automatic instruments described in these standards perform all the necessary computations, including that of the surface area based on statistical thickness. However, the automatic point-setting procedures used are not applicable to the STSA method.

NOTE Automatic instruments based on continuous flow using mixtures of nitrogen and helium gas in various ratios are also available. As good as they are, it is highly desirable to verify their accuracy of measurement against results obtained from vacuum-type instruments.

2 Normative references

The following referenced documents are indispensable for the application 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 4652-1:1994, *Rubber compounding ingredients — Carbon black — Determination of specific surface area by nitrogen adsorption methods — Part 1: Single-point procedures*

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

ISO 9298:1995, *Rubber compounding ingredients — Zinc oxide — Test methods*

3 Principle

A test portion of carbon black, silica, zinc oxide, etc, is placed in a cell of known volume and degassed. Using the ideal-gas equation, the volume of nitrogen required to give a predetermined relative pressure is calculated and dosed into the cell. Any additional nitrogen required to attain this relative pressure is due to adsorption by the test portion. The amounts of nitrogen adsorbed at different relative pressures are then used to calculate the specific surface area.

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When analysing the various materials cited above, the following degassing conditions shall be used:

Material	Temperature °C	Time, minimum h	Reference
Carbon black	300 ± 10	0,5	ISO 4652-1:1994 3.6.1.2; 4.4; 5.5.6; 6.7.4 and 6.7.5
Hydrated silica	155 ± 5	1,0	ISO 5794-1:2010 Annex D, D.4.6
Zinc oxide (type A or B) [a]	300 ± 10	0,5	
Zinc oxide (type C) [a]	155 ± 5	1,0	ISO 5794-1:2010 Annex D, D.4.6

[a] The various zinc oxide grades are listed in ISO 9298:1995 in Annex D, Table D.1.

In the method described below, the degassing conditions indicated are those for carbon black, and have to be replaced by those indicated in the table for silica or zinc oxide.

NOTE For better understanding of the method, refer to ISO 9277, *Determination of the specific surface area of solids by gas adsorption — BET method.*

4 Apparatus

4.1 Automatic static-volume vacuum apparatus for multipoint nitrogen surface area analysis, with vacuum system, Dewar flasks and all other accessories required for the analysis.

4.2 Adsorption cells, which, when attached to the adsorption apparatus, can be maintained at a pressure below 1,35 mPa (10 nmHg).

4.3 Vacuum gauge, capable of measuring the pressure of a medium vacuum.

4.4 Pressure gauge or transducer, with a reading accuracy of ±0,25 % or ±70 Pa (±0,5 mmHg), covering the range 0 kPa to 135 kPa (0 mmHg to 1 000 mmHg).

4.5 Small glass vials with caps (about 30 cm^3), for oven-drying samples.

4.6 Analytical balance, with 0,1 mg sensitivity.

4.7 Heating mantle or **degassing station**, capable of maintaining a temperature of 300 °C ± 10 °C.

4.8 Calibration volume, consisting of a cylindrical or spherical glass (or corrosion-resistant metal) reservoir, having an internal volume between 75 cm^3 and 500 cm^3, and with a valve or stopcock and a connector by which it can be connected to the sample port of the gas adsorption apparatus.

5 Reagents

5.1 Reagent-grade chemicals, conforming to the specified or recommended standards for laboratory chemicals, shall be used in all tests.

5.2 Water, distilled, or of equivalent purity.

5.3 Liquid nitrogen, 98 % or higher purity.

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5.4 **Ultra-high-purity nitrogen gas**, from a cylinder or other suitable source.

5.5 **Ultra-high-purity helium gas**, from a cylinder or other suitable source.

5.6 **High-vacuum stopcock grease**.

6 Preparation and calibration of static-volume vacuum apparatus

6.1 This procedure shall be performed for the initial calibration, periodically as a quality control measure, and following repairs or adjustments. If a commercial apparatus is used, consult the user's manual for specific instructions in carrying out the steps which follow.

6.2 Attach the vacuum and pressure gauges or transducers (4.3 and 4.4) to the apparatus and evacuate it, the manifold and all internal pressure/vacuum sensors to 2,7 Pa (20 μmHg) or below.

6.3 Verify that the internal vacuum sensor(s) are reading correctly and that the internal pressure sensor(s) are reading correctly in the vicinity of zero pressure, taking into account the expected resolution and stability limits. Make adjustments as needed.

6.4 Close the vacuum path and admit nitrogen gas to build 100 kPa ± 1 % (750 mmHg ± 7,5 mmHg) of pressure. Verify that the pressure sensors read the correct pressure to within ±0,25 %. Make adjustments as needed.

6.5 Thoroughly clean and dry an empty adsorption cell (4.2). Connect it to the apparatus and evacuate it to 2,7 Pa (20 μmHg). Apply a 300 °C heating mantle and continue evacuation for at least 1 h and until the rate of pressure rise upon temporarily closing the vacuum path is under 0,4 Pa (3 μmHg) per minute.

6.6 Perform a "blank analysis" on this clean empty cell at 0,05; 0,10; 0,15; 0,20 and 0,25p/p_0. Use a "p_0 value" of 101,325 kPa (760 mmHg) and a "test portion mass" of 1 g for the calculations.

6.7 Examine the mean value of the "adsorbed quantities" obtained. Ideally, this should be zero. A single reading exceeding 0,25 standard cm^3 makes the set-up unacceptable. As a rule, only readings below 0,125 standard cm^3 are acceptable, although one of them may go as high as 0,25 standard cm^3. A parabolic error versus pressure profile might indicate failure to correct properly for non-ideal gas behaviour or transducer linearity problems. A linear error profile indicates failure to properly measure or account for unadsorbed gas (free-space error). Erratic variation of data points indicates leaks or noisy measurements.

6.8 Determine the internal volume of the calibration-volume reservoir (4.8) below the valve or stopcock by the difference in mass when empty and then when filled completely with distilled water (5.2). Measure the water temperature and use the correct water density to obtain the exact volume of water contained. It might be necessary to immerse the device in boiling water to ensure complete filling and degassing. Repeat the procedure until the calibration volume is known to better than 0,1 %. Empty the calibration volume and thoroughly dry it overnight in a vacuum oven at 70 °C ± 5 °C.

6.9 Connect the calibration-volume reservoir to a sample port of the gas adsorption apparatus, open the valve or stopcock, and evacuate the reservoir to below 2,7 Pa (20 μmHg). Continue evacuation for one more hour. Close off the path to the vacuum source and note whether any rise in pressure occurs. The pressure shall remain below 2,7 Pa (20 μmHg), with a rate of increase of less than 0,04 Pa (0,3 μmHg) per minute. When this has been achieved, close the valve or stopcock to maintain the vacuum within the calibration-volume reservoir.

6.10 Leave the closed-off, evacuated calibration-volume reservoir in place. Raise a Dewar flask (or other insulating container) around it, and pack wet, crushed ice firmly in the Dewar flask. Place an insulating cover on

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the ice. Start an analysis with target relative pressures of 0,025; 0,05; 0,10; 0,15; 0,20 and 0,25p/p_0. Use a 1 g mass and a p_0 of 101,325 kPa (760 mmHg) for the calculations.

On completion of the 0,25p/p_0 point, open the valve or stopcock of the reservoir (4.8) and complete the analysis.

6.11 Examine the “volumes adsorbed”. Ideally, the first point at 0,025p/p_0 should show a zero amount. All other points should be within ±1 % of the gas volume V computed using the following equation:

$$V=\left(\frac{p}{101{,}325}\right)V_\mathrm{R}=\left(\frac{p}{p_0}\right)\left(\frac{p_0}{101{,}325}\right)V_\mathrm{R}$$

where

p and p_0 are expressed in kPa;

p/p_0 is the relative pressure at which the point was actually equilibrated;

V_R is the internal volume of the reservoir (4.8) (as determined in 6.8).

6.12 Successful completion of this series of tests indicates that the gas apparatus meets the basic adsorption requirements of adequate vacuum level, compensation for free-space errors, linearity and accuracy of nitrogen gas metering.

7 Preparation of apparatus

7.1 Connect a clean adsorption cell (4.2) to the degassing station of the apparatus (4.1), and heat at 300 °C with the heating mantle (4.7) for 0,5 h at a pressure below 2,7 Pa (20 µmHg), or keep under nitrogen flow. Insert a glass rod into the adsorption cell stem, if recommended by the manufacturer of the apparatus, to reduce the dead volume.

7.2 Remove the heating mantle, allow the adsorption cell to cool to room temperature and backfill, preferably with helium (5.5) or nitrogen (5.4), to atmospheric pressure. Disconnect the adsorption cell from the degassing station, stopper it, weigh it to the nearest 0,1 mg and record the mass, m_1.

7.3 Weigh into the cell a test portion of the material to be tested, so that the cell contains an amount of material equivalent to 20 m^2 to 50 m^2 of surface area. Clean the adsorption cell stem with a pipe cleaner. Continue to use a glass rod in the adsorption cell stem if recommended by the manufacturer of the apparatus.

7.4 Connect the adsorption cell to the degassing station, and open the vacuum valve.

7.5 Place the heating mantle (4.7) around the adsorption cell, and degas the test portion as required by the table in Clause 3. To be sure that a pressure less than 1,35 Pa (10 µmHg) has been obtained and is being held, check the vacuum periodically with the vacuum gauge (4.3). Degassing of fillers under nitrogen flow is also possible.

The degassing time might vary significantly from sample to sample, and a reasonable margin of excess time is recommended.

7.6 Remove the heating mantle, and allow the adsorption cell to cool to room temperature. Backfill the adsorption cell with helium or nitrogen (the same gas as used in 7.2) to atmospheric pressure, disconnect the cell from the degassing station, stopper it, weigh it to the nearest 0,1 mg and record the mass, m_2.

NOTE It is important to use the same gas for weighing the empty and material-filled adsorption cell. Inconsistent use of helium might introduce a weighing error of about 1 mg per cm^3 of cell.

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7.7 Calculate the mass of the test portion as follows:

$$m_0 = m_2 - m_1$$

where

m_0 is the test portion mass, in g;

m_2 is the mass of the adsorption cell, glass rod, stopper and test portion (see 7.6);

m_1 is the mass of the adsorption cell, glass rod and stopper (see 7.2).

8 Measurement procedure

8.1 Since most of the operations are conducted automatically, it is important to become thoroughly familiar with the procedures and to follow carefully the operating instructions.

8.2 Determine the saturation pressure of the liquid-nitrogen bath. This pressure (p_0) is affected by the purity of the liquid nitrogen and the ambient pressure. Simply assuming a p_0 of 2 kPa above the barometric pressure is not sufficient, as impurities dissolved in the liquid nitrogen usually cause the bath temperature to increase, with an associated increase in the saturation pressure of 1,4 kPa to 2,7 kPa (10 mmHg to 20 mmHg).

8.3 Connect the adsorption cell containing the degassed test portion to the surface area analyser.

8.4 Start the experiment. The instrument will complete the following steps:

— a leak test, to ensure that there is no leak in the connection between the adsorption cell and the instrument after application of the vacuum;

— calculation, and metering into the adsorption cell, of the successive volumes of pure nitrogen required to reach the selected relative pressures.

8.5 There are two ways of defining the relative pressures to be used by the instrument.

a) Procedure A: The relative pressures, or the number of data points within a given relative-pressure range, to be used are selected by the operator. The volume, V_{ads}, adsorbed at each of these data points is measured and the adsorption isotherm (which is the curve obtained by connecting the points that represent these relative pressures) is obtained. The relative pressures for the calculation are selected by the operator from this adsorption isotherm.

NOTE An adsorption isotherm with more data points is more accurate, but more time is required for the measurement.

b) Procedure B: The relative pressures (usually five or ten points) are selected, and the volume absorbed, V_{ads}, to be used for the calculation is measured. The equilibration procedure then aims to come as close as possible to these values. They may, for instance, be chosen to be equidistant from each other.

Regardless of the procedure, a minimum of five data points in the range from 0,05 p/p_0 to 0,30 p/p_0 shall be obtained. The data points should preferably be at as nearly equal spacing in terms of p/p_0 as possible.

The relative-pressure range from 0,05 to 0,30 is the usual range of applicability of the BET equation. However (see calculation in 9.4), for a given sample of material, the optimum range can be narrower. In the absence of prior knowledge, it is advisable to obtain more than five data points in the range from 0,05 to 0,30.

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9 Calculation of the nitrogen surface area

9.1 Most automatic instruments will perform the necessary computations on completion of the analysis, and the user shall verify that such computations conform to the following sequence.

NOTE The calculations used for determining the nitrogen surface area are the same for the two procedures given in 8.5.

9.2 For each relative pressure utilized, calculate the volume of nitrogen adsorbed by the test portion, V, in dm^3/kg of material, as follows:

$$V = \frac{V_{\text{ads}}}{m_0}$$

where

V_{ads} is as determined in 8.5;

m_0 is the mass of the test portion, as determined in 7.7.

9.3 Determine the surface area of the material, using the Brunauer, Emmett and Teller (BET) equation, as follows:

$$\frac{1}{V\left(\frac{p_0}{p}-1\right)} = \frac{C-1}{V_{\text{m}}C} \times \frac{p}{p_0} + \frac{1}{V_{\text{m}}C}$$

where

p is the equilibrium pressure, in kPa;

p_0 is the saturation vapour pressure of nitrogen, in kPa;

V is the volume of nitrogen adsorbed per gram of material at a given relative pressure, in dm^3/kg

V_{m} is the volume of nitrogen per gram of material which covers a monomolecular layer, in dm^3/kg;

C is the BET constant.

9.4 Within the relative-pressure range from 0,05 to 0,30, the relationship between $\frac{1}{V\left(\frac{p_0}{p}-1\right)}$ and $\frac{p}{p_0}$ is a linear function, which can be characterized by

— the slope $M = \frac{C-1}{V_{\text{m}}C}$;

— the intercept $B = \frac{1}{V_{\text{m}}C}$.

Using a standard linear regression, calculate the values of M and B to the nearest 0,000 01, as well as the corresponding correlation coefficient, which shall be at least 0,999 9. In order to achieve this requirement, it might be necessary to discard some of the data points measured at the limits of the 0,05 to 0,30 relative-pressure range, and to restart the calculation in order to select the relative-pressure range which leads to the best linearity (i.e. to the highest correlation coefficient). Such calculations can be part of the calculation programmes of automatic instruments.

NOTE It is possible to plot the values of $\frac{1}{V\left(\frac{p_0}{p}-1\right)}$ versus the corresponding values of $\frac{p}{p_0}$ in order to visualize the data points falling at the limits of the linear range. This procedure is not recommended, however, for the calculation of the values of M and B.

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9.5 From the M and B values, calculate the V_m value, in cm^3/g, as follows:

$$V_\mathrm{m} = \frac{1}{M + B}$$

9.6 Calculate the specific nitrogen surface area, in m^2/kg, to the nearest 0,1 × 10^3 m^2/kg (0,1 m^2/g), as follows:

$$\text{Specific surface area} = V_\mathrm{m} \times 4{,}35 \times 10^3$$

where 4,35 is the area, in m^2, occupied by 1 cm^3 of nitrogen, calculated from the area of a nitrogen molecule, taken to be 16,2 × 10^{-20} m^2, as follows:

$$\frac{\left(16{,}2 \times 10^{-20}\right)\left(6{,}02 \times 10^{23}\right)}{22\,400} = 4{,}35\ \mathrm{m}^2$$

NOTE The calculation of the BET constant C is advisable [from 9.4, $C = (M + B)/B$]. For carbon blacks, the value of C usually falls between +75 and +250. Values outside this range might reflect the use of an inadequate relative-pressure range, or some deviation from the BET equation.

10 Determination of statistical thickness surface area (STSA)

10.1 If the STSA is required, continue the adsorption of nitrogen till the ratio p/p_0 is 0,5.

10.2 Calculate, for each ratio p/p_0 in the range 0,2 to 0,5, the volume of nitrogen adsorbed:

$$V = \frac{V_\mathrm{ads}}{m_0} \qquad \text{as indicated in 9.2.}$$

10.3 Calculate, for each ratio p/p_0, the statistical thickness t from the equation

$$t = 0{,}88\left(\frac{p}{p_0}\right)^2 + 6{,}45\left(\frac{p}{p_0}\right) + 2{,}98$$

10.4 Using standard linear regression, calculate the slope M and the corresponding correlation coefficient r of t (X-axis) vs V (Y-axis).

Use the values in the range 0,2p/p_0 to 0,5p/p_0 that give the best correlation coefficient r, which shall in any case be at least 0,999 9.

10.5 Calculate the STSA to the nearest 0,1 m^2/g from the equation

$$\text{STSA} = 15{,}47 \times M$$

where

M is the slope of the regression line;

15,47 is a factor for the conversion of nitrogen in the gas phase to nitrogen in the liquid phase and conversion of the units to m^2/g.

11 Precision and bias

See Annex A.

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12 Test report

The test report shall include the following information:

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

b) a reference to this International Standard;

c) an indication of the procedure used in 8.5 (procedure A or B);

d) the specific nitrogen surface area, reported to the nearest $0{,}1 \times 10^3\ \mathrm{m^2/kg}$ ($0{,}1\ \mathrm{m^2/g}$);

e) the number of data points used to obtain the result, and the corresponding relative-pressure range;

f) the date of the determination.

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