TECHNICAL SPECIFICATION

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Rubber compounding ingredients — Carbon black — Determination of the aggregate-size distribution at ultimate dispersion

Ingrédients de mélange du caoutchouc — Noir de carbone — Détermination de la distribution de la taille des agrégats à la dispersion ultime

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

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/TS 16176 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 Technical Specification specifies a new test method to determine the aggregate-size distribution at ultimate dispersion. An interlaboratory test programme (ITP) was carried out but, because not enough of the laboratories had the necessary equipment, the results could not be used to validate the method. It is for this reason that ISO/TC 45/SC 3 decided to publish the document as a Technical Specification. When enough laboratories have the equipment, an ITP will be organized and, assuming the result is satisfactory, the Technical Specification will be converted into an International Standard.

Rubber compounding ingredients — Carbon black — Determination of the aggregate-size distribution at ultimate dispersion

1 Scope

This Technical Specification specifies a method for determining the size distribution of carbon black aggregates dispersed in a liquid by means of a high-power ultrasonic device. The measurement is done with a disc centrifuge photosedimentometer. This technique is based on the hydrodynamic behaviour of carbon black in a centrifugal field. The determination of the aggregate-size distribution is important in the evaluation of carbon black used in the rubber industry.

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 1124, *Rubber compounding ingredients — Carbon black shipment sampling procedures*

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

3 Significance and use

Disc centrifuge photosedimentometry produces a rapid mass-differential aggregate-size distribution by continuously measuring the solution turbidity as a function of centrifugation time. In order to obtain a true mass distribution, a light-scattering correction has to be applied.

4 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

4.1
carbon black aggregate
discrete, rigid colloidal entity that is the smallest dispersible unit in a suspension

NOTE It is composed of extensively coalesced particles.

4.2
spin fluid
inert liquid injected into the disc of a disc centrifuge photosedimentometer prior to the sample and through which aggregates sediment

NOTE Alkaline conditions minimize agglomeration of dispersed aggregates in most cases.

4.3
dispersion fluid
liquid in which aggregates are dispersed

4.4
Stokes equation
mathematical description of the sedimentation of a spherical particle:

$$D_{st} = \sqrt{\frac{1{,}8 \times 10^{16} \eta \ln\left(\frac{R}{S}\right)}{(\rho_1 - \rho_2)\omega^2 t}}$$

where

D_{st} is the Stokes diameter (nm);

η is the viscosity of the spin fluid (Pa·s);

R is the distance of the photodetector from the centre of rotation (cm);

S is the distance of the air-liquid interface from the centre of rotation (cm);

t is the time of centrifugation (s);

ρ_1 is the density of the carbon black (mg/m^3);

ρ_2 is the density of the spin fluid (mg/m^3);

ω is the rotational velocity (rad/s).

NOTE $1{,}86 \times 10^9$ mg/m^3 is often used as a typical value for the carbon black density, ρ_1.

4.5
Stokes diameter
D_{st}
diameter of a sphere which sediments in a viscous medium in a centrifugal or gravitational field in accordance with the Stokes equation

NOTE 1 A non-spherical object, such as a carbon black aggregate, can also be represented in terms of an equivalent Stokes diameter if it is considered as behaving as a smooth, rigid sphere of the same density and with the same sedimentation rate as the object.

NOTE 2 For carbon black, the Stokes diameter is expressed in nanometres (nm).

4.6
mode Stokes diameter
d_{mode}
value at which the most frequent diameter occurrence is observed, which is portrayed as a peak in the distribution curve

NOTE In some cases, more than one peak can be observed.

4.7
average Stokes diameter
d_w
x-value of the point on the mass distribution curve that corresponds to the average in mass of the distribution

5 Apparatus

5.1 Disc centrifuge photosedimentometer (DCP)[1], capable of rotational speeds of 1 000 rpm to 10 000 rpm or greater, with integral spin feed-back control (accuracy and stability of rotational speed better than ±0,05 %), spin fluid volume from 10 cm^3 to 20 cm^3, stable temperature of spin fluid, stroboscope to monitor the rotating disc both for stability and streaming anomalies, and an appropriate optical turbidity measuring device.

5.2 Probe-type sonicator[2], rating 750 W.

5.2.1 This has been found to be an effective means of dispersing material into discrete aggregates. A probe with a tip diameter of 13 mm is recommended.

5.2.2 To determine the optimum sonication time, sonicate industry tint reference black (ITRB)[3]. Sufficient deagglomeration of the reference black will give a peak at 72 nm ± 5 nm in the aggregate-size distribution. Vary the sonication time and the amplitude scale setting of the probe until this value is obtained. Use the same conditions when analysing carbon black samples. Repeat this procedure each time the probe tip is changed.

NOTE With a 750 W probe-type sonicator, ultrasonic disintegration for 10 min at 60 % on the amplitude scale is normally sufficient.

5.2.3 Sonicator tips are consumed with time, therefore it is recommended

a) to test a reference material (for example ITRB) before testing actual samples;

b) to change the tip if the mode Stokes diameter is more than 5 nm higher than previously obtained values.

5.3 Analytical balance, capable of weighing to the nearest 0,1 mg.

5.4 Beaker, 50 cm^3, tall-form.

5.5 Two 1 000 cm^3 volumetric flasks, one fitted with a 100 cm^3 dispenser.

5.6 Syringes, 1 cm^3, 2 cm^3 and 20 cm^3.

5.7 pH-meter.

5.8 Ice bath.

1) An example of a DCP instrument which has been found to be acceptable is the BI-DCP Particle Sizer, available from Brookhaven Instruments Corporation, 750 Blue Point Rd., Holtsville, NY 11742, USA. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by ISO of the instrument named. Other instruments may be used provided they comply with the requirements specified.

2) A suitable example is the Model Vibra Cell 75043 Probe Sonicator, available from Sonics. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by ISO of the apparatus named. Other apparatus may be used provided it complies with the requirements specified.

3) ITRB is available from Balentine Enterprises, Inc., 227 Somerset St., Borger, TX 79007, USA. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to give the same results.

6 Reagents

Unless otherwise stated, use only reagents of recognized reagent grade[4)].

6.1 **Water**, distilled or deionized, grade 3 as defined in ISO 3696.

6.2 **Ethanol**, absolute.

6.3 **Surfactant**, non-ionic type[5)], 0,02 % to 0,05 % (by mass) solution.

6.4 **Dodecane**, purity 98 % (by mass) (GC grade).

6.5 **0,1 M sodium hydroxide solution**.

6.6 **Spin fluid**, prepared as follows.

Place approximately 0,5 g of surfactant, weighed to the nearest 0,1 mg, in a 1 l volumetric flask.

Make up to the mark with distilled or deionized water and homogenize.

Use a pH-meter to check that the pH is between 9 and 10.

If this is not the case, adjust the pH with 0,1 M sodium hydroxide solution.

6.7 **Dispersion fluid**, prepared as follows.

Place approximately 0,5 g of surfactant, weighed to the nearest 0,1 mg, in a 1 l volumetric flask.

Make up to the mark with a distilled or deionized water/ethanol mixture (80/20 by volume) and homogenize.

Use a pH-meter to check that the pH is between 9 and 10.

If this is not the case, adjust the pH with 0,1 M sodium hydroxide solution.

7 Sampling

Select carbon black samples from larger-sized lots at random, in either pelletized or non-pelletized form, in accordance with ISO 1124. Label the samples for analysis or for storage and subsequent analysis.

4) See *Reagent Chemicals: American Chemical Society Specifications*, American Chemical Society, Washington DC, USA. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Reagent Chemicals and Standards*, by Joseph Rosin, D. Van Nostrand Co., Inc., New York, USA, and the *United States Pharmacopeia*.

5) Nonidet P-40, from Shell Chemicals, has been found suitable for this test method. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by ISO of the product named. Any other equivalent non-ionic type of surfactant may be used.

8 Preparation of carbon black dispersion

Weigh out approximately 10 mg of carbon black in a 50 cm^3 tall-form beaker. Some software cannot handle high turbidity values. In such cases, use smaller test samples.

Place the beaker in an ice bath to prevent any heating.

Using a 100 cm^3 dispenser, add 50 cm^3 of dispersion fluid (6.7).

Introduce the sonicator probe into the beaker.

Disperse the carbon black with ultrasonic energy for the length of time determined in 5.2.2.

9 Computer and software set-up

Input the appropriate parameters, including a file name, the identification of the test sample, the temperature, density and viscosity of the carbon black dispersion, the spin fluid volume and the disc speed. The actual parameters which will need to be input, and the sequence in which they are input, will depend on the particular software used.

Light-scattering corrections appropriate to carbon black shall be applied. Software for doing this is available from Brookhaven Instruments[6)].

10 Procedure

10.1 The rotational speed of the disc is chosen so that it is suited to the specific surface area of the carbon black being analysed. Adjust it so that the amplitude of the variation in the output signal is greater than 50 min to ensure satisfactory resolution.

Start preparing the carbon black dispersion as specified in Clause 8. While the carbon black dispersion is being prepared, after approximately 6 min of ultrasonic dispersion, proceed as follows:

Using a 2 cm^3 syringe, inject 1,5 cm^3 of absolute ethanol into the disc while it is stationary. Start the rotation of the disc.

Using a 20 cm^3 syringe, inject 15 cm^3 of spin solution.

Using a 1 cm^3 syringe, inject approximately 0,1 cm^3 of dodecane.

NOTE Dodecane is added to prevent a break in the aggregrate-size gradient.

Using a 1 cm^3 syringe, inject approximately 0,25 cm^3 of the carbon black dispersion into the disc and immediately start data acquisition. At the same time, note the instrument temperature.

At the end of the analysis, again note the instrument temperature. Enter into the data-acquisition unit the average of the temperatures at the beginning and at the end of the measurement.

10.2 The data acquired are automatically stored. To calculate the results, first define the baseline manually. Take as the first baseline marker the level indicated by the software. Choose the second marker on a plate of approximately 5 min. Refer to the user's manual for further details.

6) This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by ISO of this software.

10.3 Remove the fluid from the disc, thoroughly wash the disc with water, and dry with a clean paper towel or soft cloth.

11 Precision

See Annex A.

12 Test report

The test report shall include the following information:

a) all information necessary for identification of the sample tested;

b) a reference to this Technical Specification (ISO/TS 16176);

c) the reference black used;

d) the test parameters (the sonication time and energy, the volume of spin fluid used, the density of the carbon black, the rotational speed of the disc);

e) the type of instrument and the software used;

f) the results of the test (i.e. the aggregate-size distribution);

g) any deviations from the procedure specified;

h) any unusual features (anomalies) observed during the test;

i) the date of the test.

Annex A
(informative)

Precision statement

A.1 Precision results

A.1.1 General

The precision of this test method was determined in accordance with ISO/TR 9272:2005. Refer to ISO/TR 9272:2005 for terminology and other statistical details.

The precision results give an estimate of the precision to be expected. The precision parameters shall not be used for acceptance/rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols that include this test method.

A type 1 precision interlaboratory-trial programme (ITP) was conducted. Both the repeatability and the reproducibility determined represent short-term testing conditions. Eight laboratories tested one industrial reference carbon black (ITRB). Each laboratory carried out measurements on two days, with a 7-day time span between the two measurement days. On each day, two replicate determinations were carried out.

The results of the precision calculations are given in Table A.1 and Table A.2.

Table A.1 — Mode Stokes diameter, d_{mode}

Material	Average	Within laboratory			Between laboratories		
	nm	s_r	r	(r)	s_R	R	(R)
ITRB	72	1,83	5,2	7,2	2,46	7,0	9,6
Number of laboratories after elimination of outliers: 3. Number of replicates: 2.							
s_r is the within-laboratory standard deviation; r is the repeatability, in measurement units; (r) is the repeatability, in percent (these values represent percent relative); s_R is the between-laboratory standard deviation; R is the reproducibility, in measurement units; (R) is the reproducibility, in percent (these values represent percent relative).							