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British Standard

# Sampling and testing carbon black for use in the rubber industry

## Part 12. Methods for determination of surface area by surfactant adsorption

[ISO title: Rubber compounding ingredients — Carbon black — Determination of surface area — Surfactant adsorption methods]

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Echantillonnage et essai du noir de carbone utilisé dans l'industrie du caoutchouc  
Partie 12. Méthodes de détermination de la surface spécifique par adsorption de CTAB

Probenahme und Prüfung von Ruß für die Kautschukindustrie  
Teil 12. Verfahren zur Bestimmung der spezifischen Oberfläche mittels Oberflächenadsorptionsverfahren

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## National foreword

This Part of BS 5293 has been prepared under the direction of the Rubber Standards Committee and is identical with ISO 6810-1985 'Rubber compounding ingredients — Carbon black — Determination of surface area — Surfactant adsorption methods', published by the International Organization for Standardization (ISO). The first edition of BS 5293 published in 1976 did not include a method for the determination of surface area.

With regard to sampling, and the degree of confidence that can be placed upon test results, attention is drawn to BS 2846 'Guide to statistical interpretation of data' and BS 6002 'Specification for sampling procedures and charts for inspection by variables for percent defective'. It should also be noted that ISO 1124 'Rubber compounding ingredients — Carbon black — Sampling shipments in bulk or in bins' which is technically equivalent to 3.1 of BS 5293 : 1976, and ISO 1310 'Carbon black for use in the rubber industry — Sampling packaged shipments' which is technically equivalent to 3.2 of BS 5293 : 1976 are being revised and combined by the responsible ISO Technical Committee. The BSI committee responsible for this British Standard intends to implement the revised combined version of ISO 1124 and ISO 1310, when published, as Part 1 of BS 5293.

**Terminology and conventions.** The text of the international standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

The comma has been used as a decimal marker. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

Wherever the words 'International Standard' appear, referring to this standard, they should be read as 'Part of BS 5293'.

## Cross-references

| International standard | Corresponding British Standard                                                                                                                               |
|------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|
| ISO 1126-1985          | BS 5293 Sampling and testing carbon black for use in the rubber industry<br>Part 5 : 1988 Method for determination of loss of mass on heating<br>(Identical) |
| ISO 1304-1985          | Part 10 : 1988 Method for determination of iodine adsorption number<br>(Identical)                                                                           |
| ISO 6809-1984          | *Part 9 Standard reference blacks<br>(Identical)                                                                                                             |

The Technical Committee has reviewed the provisions of ISO 385/1, ISO 648 and ISO 4652, to which reference is made in the text, and has decided that they are acceptable for use in conjunction with this standard.

British Standards related to ISO 385/1 and ISO 648 are BS 846 : 1985 'Specification for burettes' and BS 1583 : 1986 'Specification for one-mark pipettes' respectively. ISO 4652 is currently being revised. It is intended to implement the revised version of ISO 4652, when published, as an identical British Standard, i.e. BS 5293 : Part 11. The first edition of ISO 4652 was not implemented as a British Standard.

**Compliance with a British Standard does not of itself confer immunity from legal obligations.**

\*In preparation.

British Standard

# Sampling and testing carbon black for use in the rubber industry

## Part 12. Methods for determination of surface area by surfactant adsorption

### 1 Scope and field of application

This International Standard specifies methods for the determination of the surface area of carbon blacks, excluding the area of micropores that are too small to admit molecules of hexadecyltrimethylammonium bromide (cetyltrimethylammonium bromide, commonly referred to as CTAB).

The methods are suitable for characterizing rubber grade carbon blacks of all types.

### 2 References

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648, *Laboratory glassware — One-mark pipettes.*

ISO 1126, *Carbon black for use in the rubber industry — Determination of loss on heating.*

ISO 1304, *Carbon black for use in the rubber industry — Determination of iodine adsorption number.*

ISO 4652, *Rubber compounding ingredients — Carbon black — Determination of specific surface area — Nitrogen adsorption methods.*

ISO 6809, *Rubber compounding ingredients — Carbon black — Standard reference blacks.*

### 3 Principle

**3.1** The isotherm for adsorption on carbon black of CTAB from an aqueous solution has a long horizontal plateau corresponding to monomolecular coverage of the substrate surface from which the adsorbate is not sterically excluded. The CTAB adsorption by carbon black is not affected by tarry materials and functional groups containing hydrogen, oxygen, etc. Rapid equilibrium is achieved by using mechanical stirring and ultrasonic vibration. Titration with sodium di(2-ethylhexyl) sulfosuccinate solution to a maximum turbidity or colour end-

point, is used to determine the unadsorbed CTAB after removal of the colloiddally dispersed carbon black by filtration. All results are determined relative to a reference black, the CTAB surface area of which is assumed to be exactly as specified in ISO 6809.

**3.2** Titration of the unadsorbed CTAB is carried out using one of the following methods:

- a) method 1, using sodium di(2-ethylhexyl) sulfosuccinate solution by automatic titrimeter to a maximum turbidity end-point;
- b) method 2, using sodium di(2-ethylhexyl) sulfosuccinate solution by manual titration to a maximum turbidity end-point;
- c) method 3, using sodium di(2-ethylhexyl) sulfosuccinate solution by manual titration to a specified colour end-point;
- d) method 4, using sodium dodecyl sulfate (SDS) solution by manual titration to a specified colour end-point.

### 4 Reagents

All reagents shall be of recognized analytical grade. Distilled water, or water of equivalent purity prepared by passing it through a fixed bed of ion-exchange materials, shall be used. The purified water shall be stored in suitable vessels, and transfer tubing shall be made of polytetrafluoroethylene, polyethylene, quartz, or other materials resistant to chemical attacks.

**4.1 Buffer solution**, of pH 7, 0,05 mol/dm<sup>3</sup> solution.

Dissolve 2,722 g of potassium dihydrogenorthophosphate (KH<sub>2</sub>PO<sub>4</sub>), 4,260 g of disodium hydrogenorthophosphate (Na<sub>2</sub>HPO<sub>4</sub>) and 1,169 g of sodium chloride (NaCl) in water and dilute to 1 dm<sup>3</sup>.

NOTE — Further details concerning the preparation have been published (see clause 12). An equivalent buffer solution is available commercially.

#### 4.2 Hexadecyltrimethyl ammonium bromide (CTAB), 0,01 mol/dm<sup>3</sup> solution.

Dissolve 3,64 g of hexadecyltrimethyl ammonium bromide (CTAB) in 900 cm<sup>3</sup> of purified water in a suitable container. Add 100 cm<sup>3</sup> of the buffer solution (4.1) and warm the solution to a temperature of 27 to 37 °C to facilitate dissolution. Cool to a temperature between 22 and 25 °C before use.

NOTE — The temperature of this solution should not be allowed to fall below 22 °C at any time or slow crystallization will result.

#### 4.3 Formaldehyde, 37 % (m/m) solution.

#### 4.4 Sodium di(2-ethylhexyl) sulfosuccinate, approximately 0,002 2 mol/dm<sup>3</sup> solution (for methods 1, 2 and 3).

Dissolve 1,00 g of 100 % solid sodium di(2-ethylhexyl) sulfosuccinate in purified water containing 2,5 cm<sup>3</sup> of the formaldehyde solution (4.3) using the magnetic stirrer (5.5). Dilute to 1 dm<sup>3</sup> in a suitable polyethylene container, stirring vigorously by means of the magnetic stirrer for 48 h. Allow to stand for 12 days before standardization and use.

Stopper the container tightly and store in a cool place.

#### NOTES

1 Once its container has been opened, the 100 % solid reagent should be stored in a desiccator.

2 The reagent solution may be subject to slow bio-degradation in the absence of formaldehyde. It should be used within 6 months.

#### 4.5 Octylphenoxy polyethoxyethanol, 0,15 % (m/m) solution (for method 1).

Dissolve 1,5 g of 100 % liquid octylphenoxy polyethoxyethanol in purified water and dilute to 1 dm<sup>3</sup> in a suitable container, stirring vigorously by means of a magnetic stirrer (5.5) until the solution is homogeneous.

#### 4.6 Sodium dodecylsulfate (SDS), 0,002 1 mol/dm<sup>3</sup> solution (for method 4).

Dissolve 0,606 g of sodium dodecylsulfate (SDS) in water containing 2,5 cm<sup>3</sup> of the formaldehyde solution (4.3) and dilute to 1 dm<sup>3</sup> in a suitable container. Allow to stand for at least 24 h.

NOTE — The purity of the solid reagent is a critical factor. If the solution is not clear (i.e. if it is cloudy or contains precipitate), the reagent is not sufficiently pure and is unsuitable for this test.

#### 4.7 Dichlorofluorescein, 0,36 % (m/m) ethanolic solution (indicator for method 4).

Dissolve 0,20 g of solid 2,7-dichlorofluorescein in 70 cm<sup>3</sup> of ethanol and store in a dropping bottle (5.17).

#### 4.8 Bromophenol blue, 0,20 % (m/m) aqueous ethanolic solution (indicator for method 3).

Dissolve 0,10 g of solid bromophenol blue in 10 g of ethanol in an amber dropping bottle (5.17) of capacity 60 cm<sup>3</sup> and add 40 cm<sup>3</sup> of water.

#### 4.9 Standard reference black (see ISO 6809). Use ITRB.

### 5 Apparatus<sup>1)</sup>

#### 5.1 Analytical balance, accurate to 0,1 mg.

#### 5.2 Oven, capable of being controlled at 105 ± 2 °C or 125 ± 2 °C.

#### 5.3 Ultrasonic bath, modified to include a magnetic stirrer and vial holder. A separate shaker/stirrer apparatus may be used.

#### 5.4 Magnetic stirring bars, polytetrafluoroethylene coated.

diameter: 6 mm; length: 22 mm (all methods);

diameter: 10 mm; length: 32 mm (for methods 3 and 4);

diameter: 10 mm; length: 41 mm (for method 1).

#### 5.5 Magnetic stirrer.

#### 5.6 Dry compressed air or dry nitrogen (from either line or a cylinder with regulator).

#### 5.7 Pressure manifold, connected to the dry compressed air or dry nitrogen supply, regulated at 0,4 to 0,7 MPa.

A typical assembly of a pressure filtration manifold is shown schematically in figure 1.

#### 5.8 Pressure cell, capacity 30 cm<sup>3</sup>, of stainless steel, suitable for 0,7 MPa pressure.

NOTE — It is essential that this is thoroughly cleaned after use.

#### 5.9 Plastic membrane filters (of diameter 47 mm and openings of aperture size 0,1 µm).

#### 5.10 Filter holder.

NOTE — It is essential that this is thoroughly cleaned after used.

<sup>1)</sup> Details of suitable commercially available products may be obtained from the Secretariat of ISO/TC 45 (BSI).

**5.11 Glass funnel**, small.

**5.12 Glass vial**, of capacity 30 cm<sup>3</sup>, with a screw cap.

**5.13 Burette** (for methods 2, 3 and 4), of capacity 50 cm<sup>3</sup>, graduated in 0,1 cm<sup>3</sup> divisions, preferably of the automatic refilling and zeroing type with reagent reservoir, complying with the requirements of ISO 385/1, class A, or calibrated such that the proper corrections can be applied to achieve the required accuracy.

**5.14 Dispenser-type pipette**, capable of delivering 30 cm<sup>3</sup>, complying with the requirements of ISO 648, class A, attached to a suitable reservoir of the CTAB solution (4.2).

**5.15 Pipettes**, of capacity 5,00 and 10,00 cm<sup>3</sup>, complying with the requirements of ISO 648, class A.

**5.16 Flat bottom conical flasks**, of capacity 100 cm<sup>3</sup>, with ground glass stoppers.

**5.17 Dropping bottles** (for methods 3 and 4).

**5.18 Jar**, of capacity 100 to 200 cm<sup>3</sup>, wide mouthed, with a screw cap.

**5.19 Containers**, suitable for the preparation and storage of reagent solutions.

**5.20 Desiccators**.

**5.21 Microscope illuminator light source**, or similar high intensity incandescent spot light (for methods 2 and 3).

NOTE — A small single-filament clear glass 10 W light bulb is recommended.

**5.22 Automatic titration apparatus** (for method 1).

**5.23 Beakers**, of capacity 100 cm<sup>3</sup>, Berzelius tall form.

**5.24 Variable resistance**, for use with the light source (5.21).

## 6 Preparation of the sample

Dry an adequate amount of the sample for 1 h at a temperature of 105 ± 2 °C or 125 ± 2 °C as described in ISO 1126. Allow to cool to ambient temperature in a desiccator. Keep the dried sample in the desiccator until ready for testing.

## 7 Test conditions

The test should preferably be carried out in a room having ambient conditions of either 23 ± 2 °C and 50 ± 5 % relative humidity or 27 ± 2 °C and 65 ± 5 % relative humidity.

It is recommended that the reagents and the apparatus be allowed to attain temperature equilibrium in the room for at least 2 h before being used.

NOTE — Storage of the CTAB solution at temperatures below 22 °C will result in slow crystallization.

The testing room shall be free from fumes or vapours which could contaminate the reagents and testing equipment used and thus affect the results.

## 8 Preparation of filters

**WARNING NOTE — New batches of filters (5.9) should be evaluated to ensure normal filtration times. The maximum time taken to avoid errors should be 8 min.**

The filter discs to be used for removing the colloiddally dispersed carbon black from the depleted CTAB solutions shall be saturated with CTAB solution before use as follows:

Submerge 25 filters, one at a time, in a least 100 cm<sup>3</sup> of the CTAB solution (4.2) in the wide-mouthed jar (5.18). During this operation, remove and discard the packing papers separating the filter discs. Allow the filters to soak for at least 48 h before use. The CTAB solution used for soaking the discs shall be discarded after use. Soaked filter discs should be used within 1 month or discarded.

Some filter discs tend to curl during pre-soaking, making leak-free installation in the filter holder difficult. To prevent the filter discs from curling, a glass stopper, of nearly similar diameter and heavy enough to keep the discs flat during soaking, should be placed on top of them. This should be removed within the first 24 h.

## 9 Procedure

### 9.1 Standardization of reagents

**9.1.1** Dry an adequate amount of the standard reference black (4.9) as indicated in clause 6.

**9.1.2** Weigh, to the nearest 0,1 mg, five test portions of this dried standard reference black to cover the range 0,20 to 0,60 g in intervals of 0,10 g.

**9.1.3** Place each test portion in a 100 cm<sup>3</sup> conical flask (5.16) containing a 22 mm magnetic stirring bar (5.4) and stopper the flasks. By means of an adjustable automatic dispenser affixed to the CTAB stock solution reservoir add 30,00 cm<sup>3</sup> of CTAB solution to the flask and place the stopper in position. Immerse the flask to a depth of at least 3 cm in an ultrasonic cleaning bath modified to provide concurrent stirring, and agitate for 6 min. The water temperature in the bath should be kept between 22 and 27 °C throughout the equilibration procedure.