International Standard 6235

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Rubber, raw — Determination of block polystyrene content — Ozonolysis method

Caoutchouc brut — Détermination de la teneur en polystyrène séquencé — Méthode de l'ozonolyse

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 6235 was developed by Technical Committee ISO/TC 45, *Rubber and rubber products*, and was circulated to the member bodies in July 1979.

It has been approved by the member bodies of the following countries :

Belgium	India	Sri Lanka
Canada	Indonesia	Sweden
China	Italy	Switzerland
Czechoslovakia	Mexico	Thailand
Denmark	Netherlands	Turkey
Egypt, Arab Rep. of	Poland	United Kingdom
Germany, F. R.	Romania	USA
Greece	South Africa, Rep. of	USSR
Hungary	Spain	

The member body of the following country expressed disapproval of the document on technical grounds :

France

Printed in Switzerland

Rubber, raw — Determination of block polystyrene content — Ozonolysis method

WARNING — All recognized health and safety precautions shall be taken when carrying out the procedure specified in this International Standard.

1 Scope and field of application

This International Standard specifies a method for the determination of the long polystyrene block content of raw uncompounded styrene-butadiene rubber (SBR) and raw uncompounded blends of block SBR. It is not applicable to blends of block SBR with EPDM, IIR, CSM and other halogenated rubbers.

The method is applicable to raw, uncompounded latices of the above compositions and is suitable for rubbers having block polystyrene contents in the range from 5 to 100 % (*m/m*). Rubbers having block polystyrene contents of less than 5 % (*m/m*) may yield incorrect results unless a correction factor, based on information gained by working with such rubbers, is applied.

The method is intended for use on gel-free rubbers, but it may be used on rubbers containing gel if it has been proved that the gel does not interfere.

2 References

ISO 1407, *Rubber — Determination of solvent extract.*

ISO 4655, *Rubber — Reinforced styrene-butadiene latex — Determination of total bound styrene content.*

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

3 Principle

Rupture of the ethylenic bonds in rubbers by dissolving the rubber in dichloromethane, addition of ozone and decomposition of the ozonides using methanolic sulphuric acid solution.

4 Reactions

The reactions upon which the method is based are as follows :

4.1 Long, saturated, polystyrene blocks are not attacked by ozone, but small fragments produced by ozonolysis (aldehydes and carboxylic acids) and the relatively low molecular mass polystyrene fragments from scission within the random copolymer blocks, are soluble in methanolic sulphuric acid solution.

4.2 Relatively high molecular mass polystyrene blocks are insoluble in methanolic sulphuric acid solution.

4.3 It is possible to separate the relatively high molecular mass polystyrene blocks, which constitute the homopolymer block, from other soluble products, using methanolic sulphuric acid solution.

5 Reagents

Use only reagents of recognized analytical quality and distilled water or water of equivalent purity.

5.1 Dichloromethane.

It is essential that this reagent does not contain any impurities which could react with ozone to form an explosive mixture.

5.2 Methanol.

5.3 Potassium iodide, 3 % (*m/m*) solution.

5.4 Sulphuric acid, concentrated (ϱ = 1,84 Mg/m^3).

5.5 Ethanol-toluene azeotrope (ETA).

Mix 7 volumes of absolute ethanol with 3 volumes of toluene. Alternatively, mix 7 volumes of commercial grade ethanol with 3 volumes of toluene, and boil the mixture with anhydrous calcium oxide (quicklime) under reflux for 4 h. Then distil the azeotrope and collect the fraction with a boiling range not exceeding 1 °C, for use in the test.

5.6 Propan-2-ol.

6 Apparatus

Ordinary laboratory apparatus together with the following :

6.1 Gooch crucibles, of fritted glass, having fine porosity, and of capacity 20 to 25 cm^3, complying with the requirements of ISO 4793.

6.2 Drechsel (gas washing) bottle.

6.3 Ozone generator, capable of delivering about 2 % (*V*/*V*) of ozone.

(The actual concentration of ozone depends on the type of generator used.)

To minimize health hazards due to ozone, locate the ozone generator in a fume cupboard.

6.4 Magnetic stirrer.

6.5 Air condenser (optional).

7 Sample preparation

7.1 If the sample is a latex, prepare a dried film as specified in sub-clause 4.4 of ISO 4655[1)] and use part of this film as the test portion.

7.2 For oil-extended solid rubbers, extract with the ETA (5.5) using the apparatus specified in ISO 1407, dry and use part of this as the test portion.

7.3 In all cases, use random, unhomogenized test samples. **Do not mill the test samples before analysis.**

8 Procedure

8.1 Cut the test sample into small pieces and weigh, to the nearest 0,1 mg, 0,5 to 1,0 g of the test sample thus prepared. The mass of the test portion should be chosen according to the expected block polystyrene content.

8.2 Place the test portion in the Drechsel bottle (6.2) and add 50 cm^3 of the dichloromethane (5.1).

8.2.1 Dissolve the test portion at about 25 °C with occasional stirring and connect the Drechsel bottle inlet to the ozone generator, which is connected to the oxygen tank. Connect the Drechsel bottle outlet to the inlet of another Drechsel bottle, which contains 100 cm^3 of the potassium iodide solution (5.3).

WARNING — Ozone reacts with unsaturated compounds to yield ozonides. Ozonides are stable in dilute solutions and these solutions are not hazardous. When dried, however, the ozonides quickly decompose and may, in some cases, explode. Concentrated solutions of ozonides are also explosive.

It is necessary, therefore, when carrying out this analysis, to avoid decreasing the volume of solvent in the reaction vessel. If the level of solvent decreases, the flow of ozone must be stopped immediately and fresh solvent carefully added to the original level.

Failure to observe these guide-lines in the use of ozone, may result in explosive conditions.

8.2.2 Allow a flow of about 100 cm^3/min of oxygen, containing about 2 % (*V*/*V*) of ozone to pass through the Drechsel bottle. Stop the gas flow 15 min after a yellow colour, due to free iodine liberated from the potassium iodide, appears.

NOTE — Prolonged reaction with ozone could produce cleavage of the saturated carbon chains, and therefore adherence to the reaction time with ozone, as outlined in this International Standard, is mandatory. The use of di-*n*-butyl sulphide, which reacts with excess ozone, and a temperature of − 25 °C for the ozonolysis, has been used to reduce cleavage of the saturated carbon chains. (See *Journal of Polymer Science* 1956, vol. 22, pp. 213-216, D. Barnard.)

8.2.3 Disconnect the Drechsel bottle containing the dichloromethane solution from the ozone generator and the Drechsel bottle containing the potassium iodide solution.

8.2.4 Pour the dichloromethane solution, slowly and with constant stirring, into a 600 cm^3 beaker containing 350 cm^3 of the methanol (5.2) to which five drops of the concentrated sulphuric acid (5.4) have been added. Wash the Drechsel bottle with a few cubic centimetres of the dichloromethane and pour the washings into the beaker.

8.2.4.1 In most cases, the insoluble polystyrene will settle to the bottom of the beaker after standing overnight.

8.2.4.2 In some cases, the insoluble polystyrene does not settle so easily. When this occurs, agitate the solution, with magnetic stirring, overnight. To ensure that dichloromethane does not evaporate excessively, place the solution in a flask fitted with an air condenser.

8.2.4.3 If, after 24 h, the insoluble polystyrene has not settled to the bottom of the beaker, the solution may be centrifuged, after transferring to a suitable container.

8.3 Transfer the precipitated polystyrene quantitatively to a tared Gooch crucible (6.1) with the aid of a rubber "policeman". Wash the precipitate copiously with methanol (5.2) to remove the dichloromethane, then with 100 cm^3 of hot water to remove surfactants and electrolytes, and finally again with the methanol.

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1) Sub-clause 4.4 of ISO 4655 :

Dilute 5 g of latex with 2 to 3 cm^3 of water. Using a dropping tube, add the diluted latex to 100 cm^3 of the vigorously stirred propan-2-ol (5.6) at approximately 23 °C, allow to settle and decant the supernatant liquid. Stir vigorously with water to wash the coagulum and drain thoroughly on a Büchner funnel. Wash copiously with water. Steep overnight in cold water, rinse well with propan-2-ol, shred and dry thoroughly under vacuum at approximately 50 °C.

If the sample cannot be used immediately, store it under nitrogen in a cool, dark place.

8.4 Dry the precipitate for 2 h at 100 °C, allow to cool in a desiccator and weigh. Repeat the drying and weighing operations until the mass is constant.

8.5 Carry out two determinations on each test sample. A test result is the average of two determinations.

9 Expression of results

Calculate the block styrene content, c_b, as a percentage by mass, to the nearest 0,2 %, by the equation

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

where

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

m_1 is the mass, in grams, of the Gooch crucible and block polystyrene precipitate;

m_2 is the mass, in grams, of the Gooch crucible.

10 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) identification of the sample;

c) the results obtained for each determination;

d) the average result obtained from the two determinations on each sample;

e) the date of test.