PD 4978

# Amendment No. 1, published 31 July, 1963

to B.S. 903 : Part B15 : 1963

Methods of testing vulcanized rubber

Part B15 : Determination of manganese

## Revision

**Summary.** Insert the following at the end of this clause:

'This method is not applicable to compounds containing titanium dioxide'.

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# B.S. 903 : Part B15 : 1963

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THIS BRITISH STANDARD, having been approved by the Rubber Industry Standards Committee and endorsed by the Chairman of the Chemical Divisional Council, was published under the authority of the General Council on 12th February, 1963.

B.S. 903, first published, June, 1940.
B.S. 903, first revision, October, 1950.
B.S. 903 : Part B15, first published, February, 1963.

This standard makes reference to the following British Standards:

B.S. 1752. Laboratory sintered or fritted filters.
B.S. 1792. One-mark volumetric flasks.

The following B.S.I. references relate to the work on this standard:
Committee references RUC/10 and RUC/10/5
Draft for comment CZ(RUC) 6008

## CO-OPERATING ORGANIZATIONS

The Rubber Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government department and scientific and industrial organizations:

*Federation of British Rubber and Allied Manufacturers
*Institution of the Rubber Industry
*Ministry of Aviation
Natural Rubber Bureau
*Natural Rubber Producers' Research Association
*Rubber and Plastics Research Association of Great Britain
Rubber Growers' Association
*Society of Motor Manufacturers and Traders Ltd.

The Government department and scientific and industrial organizations marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of this British Standard:

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British Rubber and Resin Adhesive Manufacturers' Association
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BRITISH STANDARD

# METHODS OF TESTING VULCANIZED RUBBER

## Part B15

## Determination of Manganese

### FOREWORD

This British Standard Method has been prepared under the authority of the Rubber Industry Standards Committee, and replaces Section 8.3 of B.S. 903 : 1950.

In the revision of B.S. 903 the methods are being published as separate parts, and chemical methods are distinguished by the letter B.

### SUMMARY

5–10 g of material is charred in a silica crucible and the carbonaceous residue heated at 550 ± 20°C in a muffle to remove all the carbon. The ash is sulphated to ensure complete removal of organic matter and fused with potassium hydrogen sulphate. After solution in dilute sulphuric acid, insoluble matter and excessive amounts of calcium sulphate are removed. Any iron present is masked by the addition of phosphoric acid and the permanganate colour developed by boiling with potassium periodate. The colour is measured photometrically and is proportional to the manganese present in the solution.

### REAGENTS

All reagents shall be of recognized analytical reagent quality and distilled water shall be used wherever water is specified.

*Stabilized water*. To approximately 1 litre of water add about 0·1 g of potassium permanganate and a few drops of sulphuric acid. Distil the water through an effective spray trap and discard the first 50 ml of distillate. Collect the rest of the distillate and store in a glass-stoppered bottle.

*Standard manganese solution*. Weigh out 0·720 g of potassium permanganate ($KMnO_4$) into a small beaker and dissolve in water containing 2 ml of sulphuric acid, $d = 1{\cdot}84$. Add a saturated solution of sulphur dioxide in water until the solution is colourless. Boil the solution vigorously for 15 minutes, cool to 20°C, transfer to a 500 ml one-mark volumetric flask and dilute to the mark with water at 20°C. Measure 10·0 ml of this solution into a 500 ml one-mark volumetric flask* and dilute to the mark with stabilized water at 20°C. This latter solution contains the equivalent of 0·01 mg Mn per ml (10 μg Mn per ml) and should be prepared just prior to use.

*Potassium permanganate*, about 0·001 N.

*Sulphuric acid*, $d = 1{\cdot}84$.

*Sulphuric acid, dilute*. Dilute 1 volume sulphuric acid, $d = 1{\cdot}84$, with 1 volume water.

*Orthophosphoric acid*, 85–90 per cent $H_3PO_4$.

*Phosphoric acid, dilute*. Dilute 1 volume orthophosphoric acid, 85–90 per cent $H_3PO_4$, with 1 volume water.

*Potassium periodate*, $KIO_4$.

*Potassium hydrogen sulphate*, fused powdered.

## PROCEDURE

Weigh accurately 5–10 g of the prepared sample (to within ten milligrammes), cut into small pieces and add the pieces separately to a heated silica crucible mounted in a hole cut in an asbestos board so that at least two-thirds of the crucible projects below the asbestos. Commence a blank determination at the same time using the same reagents and give identical treatment to the test and blank determinations. Heat the crucible and its contents with a small flame until all volatile or readily combustible material is removed. Then transfer the crucible to a furnace at a temperature of 550 ± 25°C and heat until the ash is substantially free of carbon—it may be necessary to heat overnight to achieve this with some compounded rubbers.

Allow the crucible to cool, add a little sulphuric acid, $d = 1{\cdot}84$, dropwise round the sides of the crucible, in amount just sufficient to moisten the residue. Deliver the acid from a dropping pipette made to deliver small drops 0·01–0·02 ml in volume. Carefully heat the crucible so that copious evolution of sulphuric trioxide occurs, until the acid is driven off and fuming ceases, then heat more strongly for a few minutes longer. If the ash is not clean repeat this process until all organic matter is destroyed. Finally moisten with a little sulphuric acid and gently ignite until evolution of fumes almost but not quite ceases. Avoid strong ignition in order to retain the ash in the form of sulphate.

Add 5 g of potassium hydrogen sulphate and fuse cautiously at first, gradually increasing the temperature to a moderate red heat, until a clear melt is obtained or until no further reaction on the ash occurs and any insoluble matter is dispersed in the melt. When the amount of ash is large the quantity of potassium hydrogen sulphate may have to be increased, by adding a gram at a time and reheating, in order to complete the reaction easily and quickly. However, it is not advisable to exceed 10 g of potassium hydrogen sulphate as potassium

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* B.S. 1792, ' One-mark volumetric flasks '.

salts may crystallize out later in the procedure (see note). Allow the crucible and its contents to cool. Add 2 ml of dilute sulphuric acid and 15 ml of water to the contents, and heat until the cake dissolves or is completely loosened from the walls of the crucible.

NOTE. When the quantity of potassium hydrogen sulphate required to obtain completion of the reaction has been established for a particular class of compound, that amount of sulphate can be added in one lot to further samples of the same material so that the time of fusion is kept to a minimum.

Completely transfer the contents of the crucible to a 100 ml beaker and heat until all soluble matter is dissolved. Cool to 10°C, filter through a sintered glass filter (porosity Grade 3)*, and wash out the beaker with a few ml of water passing the washings through the filter to wash the residue. Transfer the filtrate and washings to a 100 ml conical flask. Adjust the volume of the filtrate to approximately 40 ml with water, add 4 ml of dilute phosphoric acid and mix well. If the solution is coloured yellow by the presence of iron and the solution is not completely decolorized by the phosphoric acid, add more phosphoric acid, 1 ml at a time, until all the iron is complexed and the solution is colourless when cold. Add 0·3 g of potassium periodate, raise to the boil, boil gently for 10 minutes and keep above 90°C for a further 10 minutes to ensure full development of the permanganate colour. Cool, transfer to a 50 ml one-mark graduated flask and dilute to 50 ml at 20°C using stabilized water, and mixing well. The permanganate colour is stable for a long time and any sign of fading indicates incomplete removal of either organic matter or chloride. If necessary clear the coloured solution and the reagent blank determination also by centrifuge.

Rinse out the optical cells with dilute potassium permanganate, then with stabilized water and finally with the test solution. Measure the optical density of the test solution against the reagent blank solution as a reference solution by means of a spectrophotometer set at a wavelength of 525 mμ using 4 cm cells; alternatively use a photoelectric absorptiometer with suitable filters. From the observed optical density and the calibration graph of the instrument obtain the concentration of the manganese in the test solution.

## PREPARATIION OF CALIBRATION GRAPH

Add 0, 2·0, 4·0, 6·0, 8·0 and 10·0 ml of standard manganese solution containing 10 μg of manganese per ml of 5·0 ml of diluted sulphuric acid contained in a 100 ml conical flask and dilute to 25–30 ml with stabilized water. Add 4 ml of dilute phosphoric acid, mix well, add 0·3 g of potassium periodate and continue as described for the test solution. Determine the optical density of the solutions containing the standard amounts of manganese using the solution containing no added manganese as reference solution, at a wavelength of 525 mμ using 4 cm cells. Plot the relationship between the weight of manganese in microgrammes and the optical density.

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* B.S. 1752, 'Laboratory sintered or frittered filters'.

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