METHODS OF TESTING VULCANIZED RUBBER

PART B13. DETERMINATION OF ASH AND ZINC OXIDE

B.S. 903 : Part B13 : 1964

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This standard makes reference to the following British Standard:

B.S. 903. Methods of testing vulcanized rubber.
Part B1. Preparation of material for chemical analysis.

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The following B.S.I. references relate to the work on this standard:
Committee references RUC/10, RUC/10/5
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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
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BRITISH STANDARD

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SECTION 1. SUMMARY AND EXPLANATORY NOTE

A small portion of the sample is first heated gently to decompose the rubber and remove volatile matter, and is then heated to incinerate the remaining organic matter. The residue consists of the non-volatile mineral fillers, or their decomposition products, together with their reaction products with sulphur. The partial pressure of carbon dioxide from calcium carbonate balances that in the atmosphere at 520°C but at this temperature the complete elimination of carbon takes a long time. Natural clays lose all their water before 550°C is reached although some prepared aluminium silicates hold water and release it only slowly below 600°C. The presence of heavy metals increases the tendency of calcium carbonate to lose carbon dioxide. The temperature for ashing must, therefore, be a compromise chosen to give a reasonably rapid incineration of carbon with minimal changes in the mineral residue. For referee purposes this is fixed at 550°C but for routine purposes may with advantage be lowered to 520°C in the presence of whiting or calcium carbonate, or raised to 620°C in the presence of some prepared aluminium silicates.

The above method, ash by direct ignition, is suitable for most rubbers but not for polychloroprene rubber for which the ash by sulphation method should be followed. In this, acid decomposition of the rubber precedes ignition and converts oxides and carbonates into sulphates and thus prevents the loss of volatile chlorides.

Polychloroprene rubber will, in general, contain appreciable quantities of zinc and magnesium oxides and the decomposition temperatures of the sulphates formed determine the conditions for the final ashing. Because of the high decomposition temperature of calcium sulphate, this method is not suitable for compounds containing calcium carbonate or lime. In the method a weighed portion of the rubber in a silica crucible is heated with concentrated sulphuric acid. The crucible is first heated gently to decompose the rubber at about 550°C. The temperature is then raised until all the free acid has been removed, and finally to between 950°C and 980°C to reduce the sulphates to oxides. The crucible is allowed to cool in a desiccator, weighed, and the percentage ash is calculated.

When zinc oxide is to be determined, the ash obtained by direct ignition is extracted with dilute acid and, after removal of any metals of the copper and iron groups, the solution is used for the titration of zinc with EDTA. With polychloroprene rubber the higher temperature of heating necessary to obtain the zinc and magnesium in the form of oxides leads to the formation of zinc silicate from which the zinc is not fully recoverable by acid extraction. In these rubbers, therefore, the zinc must be determined on a mineral residue which has been heated to a temperature not exceeding 550°C and whose weight is therefore not significant for ash determination.

SECTION 2. ASH BY DIRECT IGNITION

2.1. Apparatus. *Silica (or porcelain) crucible*, squat form, capacity 30 ml approximately.

Asbestos board, approximately 10 cm square and 0·6 cm thick with a hole in the centre to support the crucible so that approximately two thirds of its depth protrudes below the board.

Muffle furnace with pyrometer and thermostat for control of temperature.

2.2. Procedure. Weigh to an accuracy of 0·01 g about 1 g of the sample, prepared as described in B.S. 903, Part B1*, into the ignited and weighed crucible and rest this in the hole in the asbestos board. Heat gently over a small bunsen flame so that the rubber does not ignite and no spurting occurs. When the rubber is completely decomposed to a charred mass, transfer the crucible to the muffle furnace at a temperature of 550 ± 25°C. Continue the heating until the ash is free from specks of carbon, cool in a desiccator and weigh. Repeat the heating, cooling and weighing until the change in weight on further heating for 20 minutes does not exceed 1 mg.

2.3. Expression of results

$$\text{Total ash} = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \text{ per cent}$$

where W_1 = weight of crucible,
W_2 = weight of crucible and test portion,
W_3 = weight of crucible and ash.

SECTION 3. ASH BY SULPHATION

This method is not suitable for rubbers containing calcium carbonate or lime.

3.1. Apparatus

Silica crucible, squat form, nominal capacity 50 ml.

Asbestos board, approximately 10 cm square and 0·6 cm thick, with a hole in the centre to support the crucible so that two-thirds of its depth protrude below the board.

Muffle furnace, with pyrometer and thermostat for control of temperature.

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* B.S. 903, ' Methods of testing vulcanized rubber ', Part B1, ' Preparation of material for chemical analysis '.

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

3.3. Procedure. Weigh, to an accuracy of 0·01 g, about 1 g of the sample, prepared as described in B.S. 903, Part B1*, into the ignited and weighed crucible. Carefully add 5 ml of concentrated sulphuric acid to cover the test portion and rest the crucible in the hole in the asbestos board which is supported on a stand. Heat gently over a very small bunsen flame so that the rubber does not ignite and the minimum of spurting occurs. During the initial reaction the mixture in the crucible swells and it may be necessary to remove the flame for a time to prevent undue spurting. After this period continue heating over a small flame to volatilize excess sulphuric acid. It may be necessary to increase the flame towards the end of this operation.

When all the sulphuric acid has been removed transfer the crucible to the muffle furnace at 950° to 980°C for 2 hours†. Cool the crucible in a desiccator to room temperature and weigh to the nearest milligramme.

Return the crucible to the muffle furnace and heat at 950° to 980°C for 30 minutes. Cool in a desiccator and weigh. If the loss in weight is more than 1 mg, repeat the heating, cooling and weighing operations until the loss in weight in any 30 minute heating period is less than 1 mg.

3.4. Expression of results

$$\text{Total ash} = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \text{ per cent}$$

where W_1 = weight of crucible,
W_2 = weight of crucible and test portion,
W_3 = weight of crucible and ash.

SECTION 4. ZINC OXIDE

4.1. Reagents. All reagents used shall be of recognized analytical reagent quality, and demineralized water shall be used whenever water is specified.

NOTE. Demineralized water may be prepared either by distillation or by the use of ion-exchange materials. Experience has indicated that the purity of the water may influence the stability of the blue colour obtained in the final titrations and special care shall be taken to ensure freedom from traces of iron and other metals. Instability of colour or failure to obtain a clear blue when titrating the blank may be an indication that further purification of the water used is necessary.

Hydrochloric acid, concentrated, $d = 1{\cdot}18$.

Hydrogen sulphide.

Nitric acid, concentrated, $d = 1{\cdot}42$.

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* B.S. 903, ' Methods of testing vulcanized rubber ', Part B1, ' Preparation of material for chemical analysis '.

† Under these conditions of heating 4 hours is usually necessary to convert magnesium sulphate to magnesium oxide in the absence of zinc oxide. If zinc oxide is known to be present, or if magnesium compounds are known to be absent, the heating time can be substantially reduced.

Ammonium chloride, solid.

Ammonia solution, $d = 0{\cdot}910$.

Ammonium nitrate, 2 per cent aqueous solution.

Ammonium chloride buffer solution. Dissolve 67·5 g of ammonium chloride in water, add 720 ml of ammonia solution and dilute to 950 ml with water. Add to this solution, 0·616 g of magnesium sulphate ($MgSO_4 . 7H_2O$) and 0·93 g of solid EDTA dissolved in 50 ml of water.

Indicator solution. Dissolve by warming 0·5 g of Eriochrome Black T or Solochrome Black WDFA in 100 ml of industrial methylated spirits* and add 4·5 g of hydroxylamine hydrochloride. Allow to stand over-night and centrifuge or filter. This indicator solution should not be kept for more than one month.

EDTA solution, 0·01*M*. Dissolve 3·72 g of disodium dihydrogen ethylenediaminetetra-acetate dihydrate in water and make up to 1 litre. Standardize as follows. Prepare a standard zinc solution by dissolving 0·814 g of ignited zinc oxide in the minimum quantity of hydrochloric acid (1 volume concentrated acid + 1 volume water), and making up to 1 litre with water. Pipette 10 ml of this standard zinc solution into a 250 ml conical flask. Add 100 ml of water, 5 ml of ammonium chloride buffer solution and 6–8 drops of indicator solution. Titrate with the EDTA solution until the colour changes from wine-red to clear blue. Carry out a blank determination on the reagents omitting the standard zinc solution, and from the corrected titration calculate the weight of zinc oxide equivalent to 1 ml of the EDTA solution.

Potassium cyanide, 5 per cent aqueous solution.

4.2. Procedure.

4.2.1. ***For rubbers which do not contain chlorine.*** Add 3 ml of hydrochloric acid to the ash as obtained under Clause 2.2 above, and evaporate to dryness on a boiling water bath. At the same time commence a blank determination in a second crucible using the same reagents and giving identical treatment to both test and blank determinations. Add a further 2 ml of hydrochloric acid, warm and wash the contents of the crucible into a 250 ml beaker. Dilute with water to about 50 ml, boil for 10 minutes and filter while still hot.

Test a small portion of the filtrate with hydrogen sulphide. If a precipitate forms, pass the gas into the whole of the hot filtrate, filter off the precipitate, wash with water saturated with hydrogen sulphide and boil the filtrate and washings to expel dissolved gas. If there is no precipitate, boil the small test portion until it is free from hydrogen sulphide and return it to the bulk solution.

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* It should be noted that the use of industrial methylated spirits is governed by the Methylated Spirits Regulations, 1952 (S.I. 1952, 2230).

Add 2 drops of nitric acid and boil the solution for a few minutes. To the boiling solution add 2 g of ammonium chloride and then make alkaline with the ammonia solution. Continue to boil for 2 or 3 minutes, then filter off any iron and aluminium hydroxides precipitated. If more than a trace of iron or aluminium is present, redissolve the precipitate in hydrochloric acid and re-precipitate by addition of ammonium chloride and ammonia solution.

Filter the hot solution through paper, wash with hot ammonium nitrate and add the filtrate and washings to those from the first precipitation. If necessary, boil the solution in order to reduce its volume to 80–85 ml, and then dilute to 100 ml in a volumetric flask.

Pipette 10 ml of the test solution into a 250 ml conical flask. Add 100 ml of water, 5 ml of ammonium chloride buffer solution and 6–8 drops of indicator solution. Titrate with EDTA solution until the colour changes from wine-red to clear blue. Carry out also a titration on 10 ml of the blank solution. Denote the corrected titration by T_1.

Pipette a further 10 ml of the test solution into a 250 ml conical flask. Add 100 ml of water, 5 ml of ammonium chloride buffer solution, 6–8 drops of indicator solution and 10 ml of potassium cyanide solution. Titrate with EDTA solution until the colour changes from wine-red to clear blue. Carry out also a titration on 10 ml of the blank solution. Denote the corrected titration by T_2.

4.2.2. *For polychloroprene rubbers.* Prepare an ash as described under Section 3, but do not weigh the crucible and proceed to the stage at which free sulphuric acid is fumed off at a temperature of 350°C. Then transfer to a muffle furnace at a temperature of 550 ± 25°C. Continue the heating until the ash is free from specks of carbon, and cool in a desiccator.

From this point continue the determination as described in 4.2.1, beginning with the addition of 3 ml of hydrochloric acid.

4.3. Expression of results

$$\text{Zinc oxide} = \frac{(T_1 - T_2) \times 81{\cdot}4 \times M}{W} \text{ per cent}$$

where T_1, T_2 = titrations as stated in the text,
M = the molarity of the EDTA solution,
W = weight in grammes of the test portion.