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BRITISH STANDARD 903: 1950

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METHODS OF TESTING VULCANIZED

RUBBER

BRITISH STANDARDS INSTITUTION

BRITISH STANDARD
METHODS OF TESTING
VULCANIZED
RUBBER

B.S. 903 : 1950

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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 31st October, 1950.

First published, June, 1940
First revision October, 1950

The Institution desires to call attention to the fact that this British Standard does not purport to include all the necessary provisions of a contract.

In order to keep abreast of progress in the industries concerned, British Standards are subject to periodical review. Suggestions for improvements will be recorded and in due course brought to the notice of the committees charged with the revision of the standards to which they refer.

A complete list of British Standards, numbering over 1600, indexed and cross-indexed, for reference, together with an abstract of each standard, will be found in the Institution's Yearbook, price 5s. post free.

This British Standard requires reference to the following:—

- B.S. 148. Insulating oils for electrical purposes.
- B.S. 358. Rules for the measurement of voltage with sphere-gaps.
- B.S. 410. Test sieves.
- B.S. 600. Application of statistical methods to industrial standardization and quality control.
- B.S. 690R. Quality control charts.
- B.S. 871. Abrasive papers and cloths for general purposes.
- B.S. 872. Abrasive papers and cloths (technical products).
- B.S. 1008. Guide for quality control and control chart method of analysing data.
- B.S. 1428. Micro-chemical apparatus.

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CO-OPERATING ORGANIZATIONS

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

Board of Trade

- British Rubber Development Board
- *British Rubber Producers' Research Association
- *Federation of British Rubber Manufacturers' Associations
- *Institution of the Rubber Industry
- *Ministry of Supply
- *Research Association of British Rubber Manufacturers
- *Rubber Growers' Association

The Government departments 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 :—

Admiralty

- Air Ministry
- Association of British Chemical Manufacturers
- British Chemical Plant Manufacturers' Association
- British Electrical and Allied Industries Research Association
- British Railways
- British Rubber Adhesive Manufacturers' Association
- Department of the Government Chemist
- General Post Office
- Institute of Brewing
- ~~Institute of Food Science and Technology~~
- Institution of Chemical Engineers
- Institution of Gas Engineers
- Institution of Mechanical Engineers
- Institution of Mechanical Engineers (Automobile Division)
- Institution of Municipal Engineers
- Institution of Water Engineers
- London Advisory Committee for Rubber Research (Ceylon and Malaya)
- Ministry of Health
- Ministry of Works
- National College of Rubber Technology
- National Physical Laboratory
- Royal Institute of Chemistry of Great Britain and Ireland
- Rubber Trade Association of London
- Society of Motor Manufacturers and Traders

BRITISH STANDARD

METHODS OF TESTING
VULCANIZED RUBBER

FOREWORD

B.S. 903 : 1950

1. This British Standard has two main purposes :

- (i) to provide standardized methods of analysis and test for use in British Standards for rubber products, thus avoiding the confusion that has been found to arise if each product committee sets up its own methods.
- (ii) to provide a set of reliable methods for use by all those concerned with the analysis and testing of vulcanized rubber ; it is hoped in this way to encourage uniformity of practice in analysis and testing, and so make the results obtained more useful.

2. The following major changes have been made in this revision as compared with the original (1940) issue :—

- (i) the scope has been widened to include synthetic rubbers as well as natural rubber ; this standard now comprises methods for examining both soft and hard (ebonite type) vulcanizates made from natural rubber, butadiene-styrene copolymers, butadiene-acrylonitrile copolymers, chloroprene polymers and copolymers, isobutene-diene copolymers (Butyl rubber), and thioplasts, though it is not implied that every test described is appropriate or suitable for all types of vulcanizate.
 - (ii) many additional tests not in general use have been introduced.
 - (iii) each method or group of closely related methods is now in effect a self-contained document and is accordingly given a distinctive number appended to the main number '903' ; thus 'Tension stress-strain test' is designated 'B.S. 903 Part 15.'
3. Throughout this document the word 'rubber,' where not qualified by the adjective 'natural,' means any or all of the types of rubber enumerated in paragraph 2 (i).
4. The present issue does not include all the test procedures for which standardization is desirable, because some require further investigation before reliable standard techniques can be recommended. In view of the urgent need for a revision of B.S. 903 to meet the demands of rubber manufacturers and users, it has been thought best to defer inclusion of these still debatable procedures until they have been further studied.

The procedures reserved for further consideration are :—

Chemical

Determination of styrene (in synthetic rubbers).

Unsaturation by iodine value (in synthetic rubbers) (the following may be consulted for existing methods : (1) Kemp and Peters, *Ind. Eng. Chem. (Anal.)*, 1943, 15, 453; (2) Lee, Kolthoff and Mairs, *J. Polymer Sci.*, 1948, 3, 60).

Identification of synthetic rubbers (the following may be consulted for existing methods : (1) Ministry of Supply, Admiralty ; Services' Rubber Investigations, Users' Memorandum No. U9A ; (2) A.S.T.M. Standards on Rubber Products, 1949).

Determination of zinc.

Glue (direct determination on total fillers).

Physical

Experimental mixing and vulcanizing.

Dynamic fatigue.

Dynamic modulus.

Rubber-to-metal adhesion.

Flexing test for ply-separation of rubber/fabric articles.

Exposure (ozone) cracking.

Shear stress-strain test.

Effect of swelling liquids on mechanical properties.

Permittivity and power factor at 50 c/s.

Water absorption of ebonite.

Tension strength of ebonite.

Hardness of ebonite.

'Cold flow' of ebonite.

Brush-discharge test for ebonite.

Measurement of compression strength of ebonite (to supplement the proof test given in this issue).

5. The methods here described are precision standards of reference, and it is not intended that all the refinements of detail shall be applied in day-to-day routine test work, or in every product specification.

6. In view of the rapid developments that are taking place in rubber testing, the methods will be kept continuously under review in order that they may be brought up to date as occasion requires.

7. It is intended that each method shall, where appropriate, eventually be accompanied by data showing the degree of reproducibility of the results, and it has already been possible to include such information for some of the methods. (See also note on 'Reproducibility of Results' below.)

8. The particular forms of test apparatus specified in this standard have been selected because they are known to give reliable results ; consideration will be given, however, to any proposals submitted to the British Standards Institution regarding alternative or improved forms of apparatus.

REPRODUCIBILITY OF RESULTS

Some of the test specifications contain a final section on the magnitude of the test errors which are likely to be encountered in good practice. This has been included because it enables a laboratory to determine whether its test procedures are grossly less accurate than the standard which is reasonably attainable. It should be pointed out that in the majority of cases information is given only for the error of test, and not for the variation between different laboratories, or between repeat mixings, etc. ; these sources of variation are, however, usually much larger than the error of test. In addition, there is a practical difficulty in defining the error of test because non-destructive tests, which generally permit several determinations to be made on one test piece, can often be made to have relatively small error compared with similar tests which require replicate test pieces for assessing the error. Flex-cracking or abrasion tests form an intermediate case, because several readings can be obtained from one test piece even though the test is destructive in nature. Where it is necessary to make a distinction the following terms will be used : *test measurements* are the individual results from non-destructive tests, e.g. a single indentation reading ; *test results* are individual results from destructive tests, e.g. a tension strength result from one ring or dumb-bell, or the mean of a series of test measurements made on one test piece, e.g. the mean of four indentation measurements on one test piece ; *mean (or median) results* are the mean (or median) of a number of test results and are therefore subject to the variation between different test pieces.

In some cases the error of test is expressed by its characteristic standard deviation (for definitions of this and other statistical terms see Ref. 2, page 53), but in the majority of cases the standard deviation (S.D.) is proportional to the mean value of the property being measured, and is hence not truly characteristic ; in these cases it is replaced by the percentage coefficient of variation (C. of V.).

It is hoped that the values given in the different sections will encourage each testing laboratory to investigate its own accuracy of testing, as this will provide a much fuller understanding of the information which can be derived from comparative tests. The details of statistical procedures which need to be used in calculating the errors of test are given in Refs. 1-3, while a bibliography of many of the recent papers on the use of statistical methods is given in Ref. 4.

References

1. B.S. 609, 'The application of statistical methods to industrial standardization and quality control' (a very full account).
2. B.S. 600R, 'Quality control charts.' (A shortened version of B.S. 600.)
3. B.S. 1008, 'Guide for quality control and control chart method for analysing data.'
4. R. G. Newton, 'The Meaning of Test Results,' *Proc. Second Rubber Technology Conference, London, 1948*, pp. 233-243; I.R.W., 1948, 119, 335.

Sup. B 315-1958

B.S. 903, Part 1

B.S. 903 : Part 1 : 1950

PREPARATION OF SAMPLE AND
CONDITIONING OF TEST PIECES

SECTION 1.1 DEFINITIONS

- Lot.** The whole of the material whose composition or properties it is desired to know.
- Sample.** That part of the lot which is abstracted to represent the lot.
- Test portion.** The weighed portion of the sample on which a chemical analysis is carried out.
- Test piece.** An appropriately shaped piece taken from the sample for use in a physical or electrical test.

SECTION 1.2

PREPARATION OF SAMPLE FOR CHEMICAL ANALYSIS

1.21 General precautions. Care shall be taken that the sample is fully representative of the lot. Thus, if it is desired to deduce the composition of the original mix, any surface bloom shall be incorporated, but if the composition of the bulk of the article is required, bloom shall be excluded. In the case of large articles, several pieces of approximately equal size shall be taken from widely separated positions, and the report shall indicate the method of taking the sample and the positions from which the pieces are taken.

1.22 Soft vulcanized rubber. The sample shall be comminuted, e.g. by cutting up with scissors, rasping on a rapidly rotating rasp, or grinding in a coffee mill or other suitable grinder, so that substantially the whole (approximately 99 per cent) will pass a B.S. 10 mesh test sieve*, or alternatively shall be sheeted to a thickness not exceeding 0.5 mm. by passing between the cold tightly-closed differential rolls of a laboratory mill. The type of grinder or mill used is immaterial provided the sample does not become contaminated or unduly heated. Any iron particles present in the comminuted or sheeted material shall be removed by a magnet.

1.23 Elponte. The sample shall be rasped to a powder which will pass a B.S. 44 mesh test sieve*. The powder shall be treated with a magnet to remove any iron particles.

1.24 Rubberized fabric. The sample used for analysis shall comprise several pieces taken diagonally, preferably from selvage to selvage, so that each

* B.S. 410, 'Test sieves.'

piece includes different warp and weft threads. If possible some of the rubber shall be separated from the fabric without wetting, but if a liquid has to be used, the fabric side shall be wetted with just sufficient chloroform or carbon tetrachloride to swell the rubber; exposure to the vapour is often sufficient, and is preferable to wetting. The swollen rubber shall be completely dried in air at room temperature and treated as described in Clause 1.22.

If it is impossible to separate sufficient rubber from the fabric, the material shall be cut into small pieces and analysed as a whole. In this case the proportion by weight of fabric in the material shall, where possible, be determined by one of the following methods and allowed for in calculating the results:—

- (a) Mechanical stripping.
 - (b) Swelling with a solvent followed by mechanical stripping or scraping.
 - (c) Disintegration of the rubber by a high-boiling solvent.
- Method (a) is preferred; Method (c) is the least reliable owing to the danger of filters from the rubber being retained in the fabric.

SECTION 1.3

PREPARATION OF SAMPLE (SOFT RUBBER) FOR

PHYSICAL TESTS

1.31 Removal of fabric. If fabric is attached to or embedded in the rubber it shall be removed before cutting the test pieces or making the tests. The method of removal shall preferably avoid the use of a swelling agent, but benzene, chloroform or carbon tetrachloride may be employed if necessary.

1.32 Adjustment of thickness. The sample, after removal of any fabric as described in Clause 1.31 shall, if necessary, be brought to a uniform thickness not above the specified maximum, preferably by a rapidly rotating abrasive wheel (a wheel 6 in. in diameter running at about 1400 r.p.m. is suitable) or a machine using an endless band of abrasive cloth; in either case a fine abrasive (No. 60 to 80 grit) shall be used for finishing off the surface. Undue heating of the rubber shall be avoided. Cloth-marked surfaces shall be made smooth in the same manner except (i) for the test for equilibrium water vapour absorption, (ii) for the test for electrical surface resistivity, for which the original surface shall be tested, (iii) for the test for ply separation (adhesion), and (iv) when the rubber is less than $\frac{3}{32}$ in. thick (0.8 mm.).

The surfaces produced by this buffing treatment lead to slightly lower values for tension strength and breaking elongation than those with a smooth mould finish, the magnitude of the effect depending on the type

of rubber. Clothmarking, if not removed, has a similar but greater effect on these properties.

Samples that have been buffed shall be conditioned as described in Clause 1.444 before test pieces are cut.

SECTION 1.4

CONDITIONING OF TEST PIECES FOR PHYSICAL TESTS

(Applicable to soft rubber and ebonite unless otherwise stated.)

1.41 Storage of samples and test pieces. The properties of vulcanized rubber change continuously with time, these changes being particularly rapid during the first 24 hours after vulcanization. Tests should therefore be carried out not less than 24 hours after vulcanization, and for accurate comparisons between different rubbers it may be necessary to ensure that these are tested at substantially the same interval after vulcanization.

1.42 Protection against light. Samples and test pieces shall be protected from light as completely as possible.

1.43 Aged test pieces. Test pieces that have been subjected to accelerated ageing shall be tested between 16 and 96 hours after removal from the ageing oven or pressure vessel.

1.44 Temperature and period of conditioning for mechanical tests (soft rubber).

1.441 For the tests described in B.S. 903/15 (Tension stress-strain test), B.S. 903/16 (Tension set), B.S. 903/17 (Compression stress-strain), B.S. 903/18 (Compression set), B.S. 903/19 (Hardness), B.S. 903/21 (Creep and stress relaxation), B.S. 903/24 (Abrasion resistance), and B.S. 903/25 (Tear strength), the test pieces (except as noted below in Clauses 1.443 and 1.444) shall be kept at a temperature of $20 \pm 2^\circ\text{C}$. for a period of not less than 12 hours immediately prior to being measured, marked (if necessary) and tested. This 12-hour period may be part of the 24 hours referred to in Clause 1.41 or the 16 to 96 hours referred to in Clause 1.43. If the surfaces of the test piece require buffing (as, for example, in B.S. 903/22, Resilience), this shall be carried out before the conditioning at $20 \pm 2^\circ\text{C}$.

1.442 For other mechanical tests at room temperature (i.e. in the region of 20°C .) the test pieces shall be conditioned as follows:—

- Durometer indentation (B.S. 903/20): at least 1 hour at $20 \pm 5^\circ\text{C}$.
- Resilience (B.S. 903/22) } See Methods of test.
- Resistance to low temperature (B.S. 903/23) }
- Resistance to flex-cracking and cut growth
- (B.S. 903/26): at least 1 hour at $20 \pm 5^\circ\text{C}$.
- Ply separation (adhesion)
- (B.S. 903/31): at least 24 hours at $20 \pm 5^\circ\text{C}$.

1.443 Test pieces to be tested at temperatures other than 20°C. (as may be required, e.g. for Compression set, B.S. 903/18; Hardness, B.S. 903/19; Durometer indentation, B.S. 903/20; Creep and stress relaxation, B.S. 903/21; Resilience, B.S. 903/22; Tear strength, B.S. 903/25; Resistance to flex-cracking and cut growth, B.S. 903/26) shall be conditioned for one hour at the test temperature. If, prior to testing, they are transferred from the conditioning chamber to a sample holder, they shall be maintained at the test temperature for a further five minutes before measurements are made.

1.444 Samples which have been buffed by the method described in Clause 1.32 shall be conditioned at $20 \pm 2^\circ\text{C}$. for at least 12 hours before the test pieces are cut. If the tests are to be made at a temperature in the region of 20°C., the test pieces may be marked, measured and tested immediately, but in any case they shall be kept at $20 \pm 2^\circ\text{C}$. until tested. If the test is at a temperature other than 20°C., the test pieces (after any necessary marking and measuring) shall be conditioned as described in Clause 1.443. In all cases the testing shall be carried out within 72 hours of buffing.

1.45 Temperature and period of conditioning for mechanical tests (ebonite). For all the tests except water vapour absorption the test pieces shall be subjected to a controlled atmosphere of relative humidity 30–75 per cent and temperature $20 \pm 5^\circ\text{C}$. for 18–24 hours. Each test piece shall be tested in this atmosphere, or the test started within three minutes of removal therefrom.

1.46 Temperature and period of conditioning for electrical tests. For tests of electric strength (B.S. 903/32), electrical surface and volume resistivity (B.S. 903/33), permittivity and power factor (B.S. 903/34) each test piece shall be wiped carefully with absorbent paper or, where suitable, with a cloth moistened with petroleum ether or pure benzene.

The test pieces shall then be preconditioned in an atmosphere of relative humidity 30–75 per cent and temperature $20 \pm 5^\circ\text{C}$. for 18–24 hours. Each test piece shall be tested in this atmosphere, or within three minutes of removal therefrom, except for the measurement of surface and volume resistivity (B.S. 903/33), for which tests a further conditioning at 65 ± 5 per cent relative humidity and $22 \pm 2^\circ\text{C}$. is required, and power factor and permittivity (B.S. 903/34), for which a further conditioning at $22 \pm 2^\circ\text{C}$. is required.

A relative humidity of 65 ± 5 per cent may be obtained by the use of lumps of a suitable salt* which shall be sprinkled with water occasionally. The surface of the salt shall be moist but care shall be taken that the lumps are not wholly covered by water. To ensure that the relative

* Suitable salts for giving 65 per cent relative humidity are (a) sodium nitrate, (b) ammonium nitrate, (c) cobalt chloride, (d) an equilibrium mixture of sodium chloride and sodium nitrate.

humidity of the controlled atmosphere is maintained at the correct value, the air shall be circulated inside the chamber. The surface of the salt shall be large per unit volume of air space, otherwise the rate of attainment of equilibrium is very slow. The apparatus described below has been found satisfactory in maintaining the relative humidity of the controlled atmosphere at a constant figure.

The chamber consists of a cubical box with sides 24 in. (610 mm.) long. The floor of the box is nearly covered by a tray containing lumps of the salt which are occasionally sprinkled with water as indicated above. The test pieces to be conditioned are placed on a shelf half-way up the box. Air is circulated by a small fan over the tray, up through holes cut at two corners of the shelf, over the test pieces and down through holes at the opposite corners of the shelf. The humidity of the air, which may be measured by wet-and-dry-bulb thermometers if the velocity of the air past them is greater than three metres per second, attains a constant value, unless the prevailing conditions are extreme, in about three minutes after the box has been closed and the fan has been started. As an alternative to wet-and-dry-bulb thermometers, which require a known air velocity, a dew-point thimble may be inserted in the box and used when the fan is not working; with either method, a window is necessary to avoid opening the box.

1.47 Mechanical conditioning. The modulus of rubber test pieces is markedly dependent on their previous mechanical history, and it may therefore be necessary to carry out a further modulus test after a suitable mechanical conditioning.

The ultimate tension properties (i.e. tension strength and elongation at break) are generally not largely affected by stretching the test piece before the test; however, the modulus may be considerably different for a long period after any preliminary straining. This difference, which appears as a softening, depends upon the nature of the rubber, the magnitude of the preliminary straining, and the period which elapses before the test is performed. Repeated stretching increases this softening but by far the largest contribution is given by the first stretch.

The conditioning should be similar to the type of deformation encountered in service; if this is not known, the test pieces shall be strained at the standard rate of stretching (18–20 in. per minute) to 50 per cent of the elongation at break, held at this elongation for 5 seconds, and then released; one minute after release the test piece shall be stretched again to break, the usual measurements being made of the modulus or the elongation(s) at constant load(s). For dumb-bell test pieces the original gauge marks are used for these measurements.

Mechanical conditioning is usual in compression stress-strain tests, especially on manufactured articles, and a recommended treatment is described in Clause 17.51 of B.S. 903, Part 17, relating to that test.

Supp. B 31.5.1958

B.S. 903, Part 2: EXTRACTION METHODS

This part includes methods for the following determinations:—

- Section 2.1 Acetone extract.
- Section 2.2 Unsaponifiable matter in acetone extract.
- Section 2.3 Paraffin wax and ceresin.
- Section 2.4 Chloroform extract.
- Section 2.5 Alcoholic potash extract.

SECTION 2.1 ACETONE EXTRACT

2.11 Explanatory note. Acetone completely extracts (provided extraction is sufficiently prolonged) the following common ingredients, amongst others:—certain non-rubber constituents of the crude rubber (fatty acids, quebrachitol, sterols, etc., from natural rubber, and emulsifying agents, anti-oxidants, and other similar materials used in making synthetic rubbers), some resins, sulphur, mineral oils, wool grease, saponifiable waxes, paraffin wax, ceresin, pine tar, and some dyestuffs, organic accelerators and anti-oxidants and/or their decomposition products.

Acetone incompletely extracts:—fatty oils, oxidized (blown) fatty oils, vulcanized fatty oils (rubber substitutes), mineral rubber (bitumen), oxidized rubber, and some of the polymer from vulcanized thioplasis (for the latter it is therefore preferable to use light petroleum b.p. 80–100°C. in place of acetone).

2.12 Reagent.

Acetone. The acetone used for this determination shall be substantially free from water and polymers of acetone, and shall be of recognized analytical reagent quality.

2.13 Apparatus. The extraction apparatus shall be of the reflux type with the condenser placed immediately above the cup which holds the rubber. The cup shall be of the siphon type and situated in the vapour of the boiling solvent.

All-glass apparatus is preferable, but a chromium-plated metal condenser is permissible. There shall be no cork, rubber or similar material from which soluble matter may be extracted. It is convenient for the extraction vessel to be of a size that will permit it to be weighed directly, otherwise the solution containing the extract shall be transferred to a small flask for evaporation, drying and weighing. A suitable type of apparatus is shown in Fig. 2.1; a heat exchanger is interposed between the condenser and the extractor to ensure that the liquid falling into the extraction cup is substantially at its boiling point.

2.14 Procedure. The sample may be either comminuted or sheeted as described in B.S. 903, Part 1, Section 1.3, and shall be protected from light

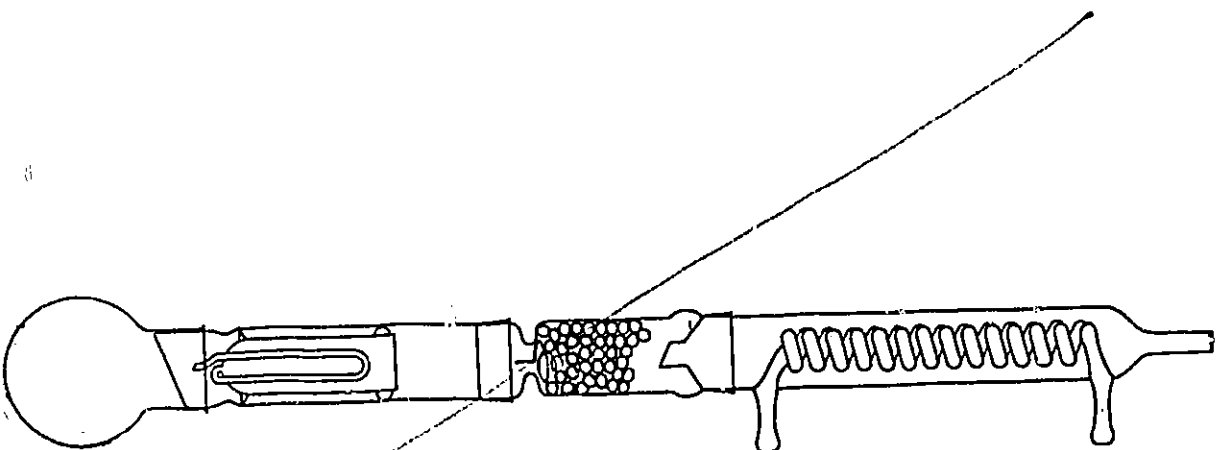


Fig. 2.1 Extraction apparatus

B.S. 903, Part 2: EXTRACTION METHODS

This part includes methods for the following determinations:—

- Section 2.1 Acetone extract.
- Section 2.2 Unsaponifiable matter in acetone extract.
- Section 2.3 Paraffin wax and ceresin.
- Section 2.4 Chloroform extract.
- Section 2.5 Alcoholic potash extract.

SECTION 2.1 ACETONE EXTRACT

2.11 Explanatory note. Acetone completely extracts (provided extraction is sufficiently prolonged) the following common ingredients, amongst others:—fatty non-rubber constituents of the crude rubber (fatty acids, quebrachitol, sterols, etc., from natural rubber, and emulsifying agents, anti-oxidants, and other similar materials used in making synthetic rubbers), some resins, sulphur, mineral oils, wool grease, saponifiable waxes, paraffin wax, ceresin, pine tar, and some dyestuffs, organic accelerators and anti-oxidants and/or their decomposition products.

Acetone incompletely extracts:—fatty oils, oxidized (blown) fatty oils, vulcanized fatty oils (rubber substitutes), mineral rubber (bitumen), oxidized rubber, and some of the polymer from vulcanized thioplasmas (for the latter it is therefore preferable to use light petroleum b.p. 80–100°C. in place of acetone).

2.12 Reagent.

Acetone. The acetone used for this determination shall be substantially free from water and polymers of acetone, and shall be of recognized analytical reagent quality.

2.13 Apparatus. The extraction apparatus shall be of the reflux type with the condenser placed immediately above the cup which holds the rubber. The cup shall be of the siphon type and situated in the vapour of the boiling solvent.

All-glass apparatus is preferable, but a chromium-plated metal condenser is permissible. There shall be no cork, rubber or similar material from which soluble matter may be extracted. It is convenient for the extraction vessel to be of a size that will permit it to be weighed directly, otherwise the solution containing the extract shall be transferred to a small flask for evaporation, drying and weighing. A suitable type of apparatus is shown in Fig. 2.1; a heat exchanger is interposed between the condenser and the extractor to ensure that the liquid falling into the extraction cup is substantially at its boiling point.

2.14 Procedure. The sample may be either comminuted or sheeted as described in B.S. 903, Part 1, Section 1.2, and shall be protected from light

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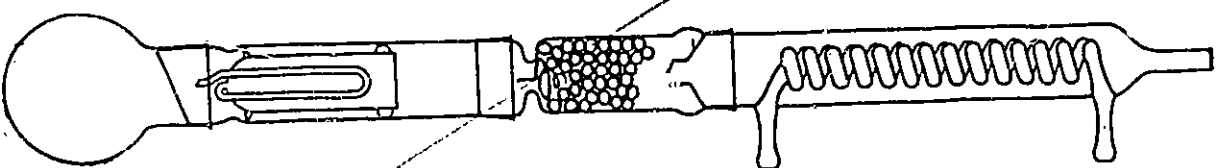


Fig. 2.1 Extraction apparatus

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until the analysis is completed. For referee purposes comminute the sample by rasping.

If the sample has been comminuted, place a weighed test portion (2 g. to 4 g.) in an acetone-extracted paper linbale.

If the sample has been sheeted, wrap loosely a weighed test portion (2 g. to 4 g.) in filter paper or de-sized linen, previously acetone-extracted, so that no two portions of the surface of the sheet come into contact with each other.

Insert the test portion, prepared as described, in the extraction cup, and pour sufficient acetone into the extraction vessel to fill the extraction cup about twice. Subject the test portion to at least 80 hot extractions during a continuous period of not less than 8 or more than 16 hours in the case of soft rubber, and to at least 160 hot extractions during a continuous period of not less than 16 or more than 40 hours in the case of ebontle.

Distill the acetone from the soluble matter in a weighed vessel, preferably the extraction vessel, and as soon as all the acetone has been removed, dry the extract at 70–75°C. for one hour; cool in a desiccator and weigh.

For precise work or for referee purposes carry out a blank determination, using the same quantities of reagents and the same conditions of test, and apply a corresponding correction to the main result.

2.15 Expression of results. The weight of the extract (corrected if necessary as described above), expressed as a percentage of the weight of the test portion, shall be taken as the 'acetone extract.'

SECTION 2.2

UNSAFONIFIABLE MATTER IN ACETONE EXTRACT

2.21 Explanatory note. The unsafonifiable portion of the acetone extract includes unsafonifiable non-rubber constituents of the crude rubber, and any mineral oil, paraffin wax, ceresin, mineral rubber (bitumen) and any unsafonifiable oxidation products of the rubber that are present in the extract.

2.22 Reagents.

Acetone.

Alcoholic potassium hydroxide solution: 5.6 g. KOH in 100 ml.

Ethyl ether: freed from peroxides is essential to avoid risk of explosion in distillation.

NOTE: All reagents used should be of recognized analytical reagent quality, and distilled water should be used wherever water is specified.

2.23 Procedure. To the vessel containing the dried acetone extract add 25 ml. of alcoholic potassium hydroxide solution. Boil under a reflux condenser for two hours and then evaporate to dryness on a water bath. Transfer to a separating funnel, using about 50 ml. of water, followed by

25 ml. of ethyl ether. After extraction, separate the ether layer and continue to extract the aqueous layer with small additional portions of ether until the extracts are colourless. Wash the combined ether extracts repeatedly with half their volume of water until the washings are no longer alkaline to litmus, and distil off most of the ether. To remove the last traces of water, add about 4 ml. of acetone and carefully evaporate on a water bath, blowing out the vapour with a gentle current of air. Repeat the acetone treatment if traces of water still remain (as indicated by mistiness on the sides of the flask); dry the flask and residue for one hour at 70–75°C., cool in a desiccator and weigh.

Carry out a blank determination using the same quantities of reagents and the same conditions of test, and apply a corresponding correction to the main result.

2.24 Expression of results. The corrected weight of the extract, expressed as a percentage of the weight of the test portion, shall be taken as the 'unsafonifiable matter in the acetone extract.'

SECTION 2.3 PARAFFIN WAX AND CERESIN

2.31 Reagents.

Chloroform.

Ethyl alcohol, absolute.

Ethyl alcohol, 95 per cent.

NOTE: All reagents used should be of recognized analytical reagent quality.

2.32 Procedure. Boil the unsafonifiable matter from the acetone extract for 30 minutes with 50 ml. of absolute alcohol under reflux. (If insoluble matter remains, filter while hot.) Cool the solution, and finally keep it for one hour at –5°C. Filter off the paraffin wax and ceresin which have separated out, the funnel being surrounded by the cooling mixture to avoid a rise of temperature. Wash the material on the filter with 100 ml. of 95 per cent ethyl alcohol, previously cooled to –5°C., and then dissolve it off the filter by washing with a total of about 30 ml. of hot chloroform in four or five portions, collecting the solution in a small weighed flask. Distill the chloroform from the solution, dry the residue for one hour at 70–75°C., cool in a desiccator and weigh. This residue consists of paraffin wax and ceresin, and may contain sulphur.

To determine the correction for the solubility of the wax in alcohol use a residue obtained in, and follow exactly the method employed in, the previous operation. The difference between the weights of residue obtained in the two operations is the weight of paraffin wax and/or ceresin soluble in the volume (150 ml.) of alcohol used, under the conditions of the estimation. This weight is added to the weight of residue obtained in the first operation.

2.33 Expression of results. The corrected weight of residue, expressed as a percentage of the weight of the test portion, shall be taken as 'paraffin wax and ceresin.'

SECTION 2.4 CHLOROFORM EXTRACT

2.41 Explanatory note. Chloroform will extract from soft vulcanized rubber, previously subjected to extraction with acetone, about half the mineral rubber (bitumen) which remains after acetone extraction. As a small amount of the rubber may be extracted, a small chloroform extract (e.g. not exceeding 4 per cent calculated on the rubber content in the case of natural rubber) does not necessarily indicate the presence of bitumen; the latter can, however, usually be recognized by its dark colour. Chloroform extraction should not be applied to thioplasts owing to their relatively high solubility.

2.42 Reagent.

Chloroform.

Note. This should be of recognized analytical reagent quality.

2.43 Procedure. Determine the chloroform extract immediately after the acetone extraction, without drying the acetone extracted rubber. To do this replace the extraction vessel used for the acetone extraction by one containing sufficient chloroform to fill the extraction cup approximately twice, and extract the rubber with this solvent for four hours or until the liquid flowing from the siphon is colourless, whichever is the longer. The rate of distillation of the chloroform shall be such that at least ten hot extractions occur per hour. Distil off the chloroform and dry the extract for one hour at 70–75°C., cool in a desiccator and weigh.

2.44 Expression of results. The weight of the extract expressed as a percentage of the weight of the test portion shall be taken as the 'chloroform extract.'

SECTION 2.5 ALCOHOLIC-POTASH EXTRACT

2.51 Explanatory note. The alcoholic-potash extraction is made on rubber previously extracted with acetone and/or chloroform; if the determination of acetone extract is not required, the rubber may be extracted directly with chloroform; if the acetone extract is required and mineral rubber (bitumen) is known to be absent, the chloroform extraction may be omitted. The alcoholic-potash extract consists of the fatty acids derived from saponifiable constituents of the vulcanized rubber, so far as these remain after the previous extraction(s). The most important of these constituents are: vulcanized oils (rubber substitutes), fatty oils, oxidized

(blown) oils, and oxidized rubber. The alcoholic-potash extract is usually taken as an index of the amount of the vulcanized-oil substitutes present in the rubber. The method is not applicable to thioplasts since they are attacked by potassium hydroxide.

2.52 Reagents.

Acetone.

Alcoholic potassium hydroxide solution; 5.6 g. KOH in 100 ml.

Ethyl alcohol 95 per cent.

Ethyl ether; freedom from peroxides is essential to avoid risk of explosion during distillation.

Hydrochloric acid, concentrated, sp. gr. 1.18.

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

2.53 Procedure. Dry the rubber from the acetone or chloroform extraction at room temperature in a vacuum. It is essential that exposure of the dried extracted rubber to the air should be kept as short as possible. Place the rubber in a 200 ml. flask and add 50 ml. of alcoholic potassium hydroxide solution; boil under a reflux condenser for four hours, using a ground glass joint to connect the condenser to the flask.

Decant the solution through a filter and collect the filtrate in a porcelain basin. Wash the rubber with two 25 ml. portions of hot alcohol and then thoroughly with hot distilled water, decanting the washings through the filter and collecting with the main filtrate.

Evaporate the combined filtrate and washings to dryness on a boiling water bath and dissolve the residue in 50 ml. of distilled water. Transfer the solution to a separating funnel and carefully add concentrated hydrochloric acid until the liquid is slightly acid. Allow the solution to cool.

Extract the acidified liquid completely with three 25 ml. portions of ethyl ether and wash the combined ether extracts with distilled water until the washings are no longer acid when tested with methyl orange.

Transfer the ether solution to a weighed flask and distil off most of the ether. To remove the last traces of water, add about 4 ml. of acetone and carefully evaporate on a water bath, blowing out the vapour with a gentle current of air. Repeat the acetone treatment if traces of water still remain (as indicated by mistiness on the sides of the flask); dry the flask and residue for one hour at 70–75°C., cool in a desiccator and weigh.

Carry out a blank determination using the same quantities of reagents and the same conditions of test, and apply a corresponding correction to the main result.

2.54 Expression of results. The corrected weight of the extract expressed as a percentage of the weight of the original test portion, shall be taken as the 'alcoholic-potash extract.'

Supp. B. 36-10-1958

B.S. 903, Part 3 : SULPHUR DETERMINATIONS

This part includes methods for the following determinations :—

Section 3.1 Total sulphur.

3.12 Carius method.

3.13 Fusion method.

3.14 Combustion method.

Section 3.2 Extractable sulphur.

3.22 Bromine method.

3.23 Nitric acid method.

3.24 Copper spiral method.

Section 3.3 Rubber-combined sulphur.

Section 3.4 Sulphur in total fillers.

Section 3.5 Sulphide sulphur.

SECTION 3.1 TOTAL SULPHUR

3.11 General explanation. 'Total sulphur' ideally denotes the total amount of sulphur, in whatever form, contained in the sample.

The percentages of total sulphur as determined by the three recommended methods should agree within the usual limits of experimental error, except when the sample contains certain fillers, notably lithopone and barium and calcium sulphates, the sulphur in which may or may not be included in the result according to the method used.

3.12 Carius method.

3.121 SUMMARY AND EXPLANATORY NOTE. The rubber is oxidized by heating with fuming nitric acid under pressure in a sealed tube. After dilution and removal of any insoluble matter, the sulphuric acid in the liquid is precipitated as barium sulphate, which is filtered off and weighed. The result will not include the sulphur contained in barium sulphate present as such or in lithopone. It will include the sulphide sulphur present in lithopone, and the sulphur present as calcium sulphate in quantities likely to be met with in practice.

Some analysts add picric acid solution immediately before the precipitation of barium sulphate. This is permissible if preferred, except for referee purposes when it shall be omitted. If used, add 10 ml. of a saturated aqueous solution of picric acid after dilution of the solution containing sulphate. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution, proceeding as in Clause 3.123.

3.122 REAGENTS.

Barium chloride solution, 10 g. in 100 ml. water.

Hydrochloric acid, concentrated, sp. gr. 1.18.

Nitric acid, fuming, sp. gr. 1.50.

Sodium chloride.

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

3.123 PROCEDURE. Introduce, by means of a long-stemmed funnel, 5 ml. of fuming nitric acid into a bomb-tube 18-24 in. in length and sealed at one end. Withdraw the funnel carefully so as to avoid wetting the side of the tube.

Cautiously slide into the bomb-tube a small ignition tube containing about 0.2 g. of the sample (0.1 g. in the case of ebonite or thioplasts), taking care that at this stage the rubber does not come into contact with the acid.

Seal the open end of the bomb-tube in a blow-pipe flame by the usual technique, and allow to cool. When cold, place the tube in a bomb-furnace. Raise the temperature of the furnace gradually, over a period of three hours, to 230°C., and maintain this temperature for a further three hours.

Allow the tube to cool in the furnace, and when cold release the pressure by carefully heating the tip until the glass is softened and becomes perforated by the escaping gases. Remove the tube from the furnace and open it by making a deep file scratch round the glass and applying the end of a glass rod, heated to redness.

Wash the contents of the bomb-tube into a 600 ml. beaker, add 0.5-1.0 g. of sodium chloride and evaporate nearly to dryness. Add 10 ml. of concentrated hydrochloric acid and evaporate to dryness. Repeat the operation with a further 10 ml. of acid. Take up the residue in 200 ml. of hot water, containing 1 ml. of concentrated hydrochloric acid, filter off any insoluble matter and wash with hot water. Dilute the filtrate and washings (or the unfiltered solution if clear) to 300-350 ml. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution. Continue to boil the liquid for 5-10 minutes and allow to stand for at least one hour at 90-100°C.

Filter through a sintered glass or silica crucible (porosity No. 4) which has been previously washed, dried, and weighed. After the filtration wash the crucible and the precipitate with hot water until the washings are free from chloride, dry at 110°C. for one hour, cool in a desiccator and weigh.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

3.124 EXPRESSION OF RESULTS.

$$\text{Percentage of total sulphur} = \frac{B \times 13.73}{W}$$

where
 B = Corrected weight of barium sulphate, in grammes,
 W = Weight of test portion, in grammes.

3.13 Fusion method.

3.131 SUMMARY AND EXPLANATORY NOTE. The sample is treated with nitric acid-bromine mixture and after evaporation of the acid, the dried residue is fused with an excess of anhydrous sodium carbonate. The melt is leached out with water, the residue filtered off, and the filtrate acidified to decompose the excess of carbonate and evaporated to dryness to precipitate silica. The residue is extracted with water, and after filtration the sulphate present in the filtrate is precipitated as barium sulphate which is weighed. The result will include all the sulphur present as lithopone and barium and calcium sulphates.

Some analysts add picric acid solution immediately before the precipitation of barium sulphate. This is permissible if preferred, except for referee purposes when it shall be omitted. If used, add 10 ml. of a saturated aqueous solution of picric acid after dilution of the solution containing sulphate. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution, proceeding as in Clause 3.133.

3.132 REAGENTS.

Barium chloride solution; 10 g. in 100 ml. water.

Hydrochloric acid, concentrated, sp. gr. 1.18.

Methyl orange, 1 g. in 100 ml. water.

Nitric acid-bromine mixture; nitric acid, sp. gr. 1.42, saturated with bromine.

Potassium nitrate.

Sodium carbonate, anhydrous.

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

3.133 PROCEDURE. Place 0.5 g. of the sample (or 0.1 g. in the case of ebonite or thioplasts) in a 75 ml. porcelain crucible, add 2-3 g. of potassium nitrate and 15 ml. of nitric acid-bromine mixture and cover with a small clock-glass.

Heat gently on a water bath until the reaction commences, remove from the bath until the first vigorous reaction has subsided, and then continue to heat for one hour or until the rubbier has completely disintegrated and no globules of sulphur are visible in the liquid. Remove the clock-glass, rinse it with the minimum quantity of water, and evaporate the contents of the crucible to dryness on the water bath.

Moisten the dry residue with 1-2 ml. of water and, using a stout glass rod rounded at the end, break up the mass and mix intimately with 5 g. of anhydrous sodium carbonate. Transfer the contents of the crucible to a 75 ml. nickel crucible using small pieces of moistened filter paper to transfer any material adhering to the porcelain crucible or to the glass rod.

Heat gently in a sulphur-free flame or at the mouth of an electric furnace to char the organic matter; subsequently heat more strongly until the contents of the crucible fuse, and maintain in this state for several minutes. Allow to cool, place the crucible on its side in a 250 ml. beaker, cover with hot water and set aside on a boiling-water bath or hot plate until the melt has completely disintegrated.

Remove the crucible and rinse thoroughly with hot water. Filter the extract into a 600 ml. beaker, wash the residue with hot water until the washings are neutral, collecting the washings with the main filtrate. Allow to cool.

Neutralize the filtrate by the careful addition of concentrated hydrochloric acid using methyl orange as indicator, and add 5 ml. of acid in excess. Evaporate to dryness, allow to stand for one hour on the water bath, and repeat the evaporation after the further addition of 10 ml. of acid. Add 1 ml. of concentrated hydrochloric acid to the dried residue followed by 150 ml. of water, and boil for several minutes. Filter if necessary. Dilute the solution to 300-350 ml.

Heat the solution to boiling, and while hot, add slowly a slight excess of hot barium chloride solution. Continue to boil the liquid for 5-10 minutes and allow to stand for at least one hour at 90-100°C.

Filter through a sintered glass or silica crucible (porosity No. 4) which has previously been washed, dried and weighed. After the filtration wash the crucible and the precipitate with hot water until the washings are free from chloride, dry at 110°C. for one hour, cool in a desiccator and weigh.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

3.134 EXPRESSION OF RESULTS.

$$\text{Percentage of total sulphur} = \frac{B \times 13.73}{W}$$

where
 B = Corrected weight of barium sulphate, in grammes,
 W = Weight of test portion, in grammes.

3.14 Combustion method.

NOTE. The micro-combustion method for the determination of sulphur described in B.S. 1428* (in preparation) is acceptable as an alternative.

3.141 SUMMARY AND EXPLANATORY NOTE. The sample is burnt in a rapid stream of oxygen, the resulting sulphur dioxide is oxidized by

* B.S. 1428, 'Micro-chemical apparatus.'

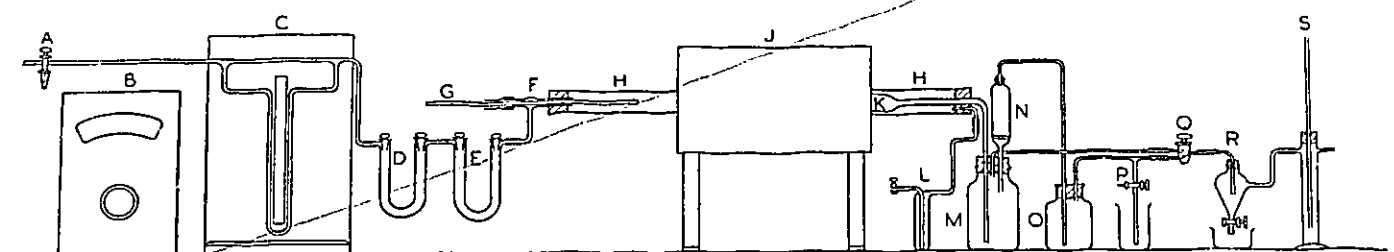


Fig. 3.1 Apparatus for the determination of total sulphur by the combustion method

hydrogen peroxide, and the resulting sulphuric acid is titrated with standard alkali.

This semi-micro method occupies a total time of about one hour, but requires special apparatus. Modified procedures are necessary if the sample contains chlorine compounds or acrylonitrile copolymers.

Provided the temperature of the furnace is 1350° C. or over, the result will include all inorganically combined sulphur likely to be present (i.e. all except alkali sulphate). If alkali or alkaline earth sulphates, and alkali or alkaline earth salts (e.g. carbonates) which would give sulphates under the experimental conditions stated, are absent, the temperature of the furnace can be reduced to 1000° C.

3.142 REAGENTS.

Hydrogen peroxide solution : 3 g. H_2O_2 in 100 ml.

Indicator solution : 0.125 g. methyl red and 0.083 g. methylene

blue in 100 ml. alcohol.

Magnesium perchlorate ('anhydrous').

Oxygen.

Silica powder.

Soda-lime, preferably a self-indicating type.

Sodium hydroxide, 0.02N solution (also 0.1N solution for

ebonite or thioplasts).

Zinc oxide.

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

3.143 APPARATUS. The assembly of the apparatus recommended is shown in Fig. 3.1. The following approximate dimensions are preferred.

F. Entry tube

G. Silica rod

H. *Combustion tube

*Liner

*Combustion boat

J. Electric combustion furnace

K. Silica exit tube

M. First absorbing vessel

N. Second absorbing vessel

O. Third absorbing vessel

* This apparatus shall withstand a temperature of 1500° C.

Oxygen shall be fed from a cylinder via the three-way tap A to a calibrated flow-meter C thence through the U-tubes D packed with soda-lime and E packed with magnesium perchlorate (anhydrous) to the entry tube T-piece F, which passes through a one-hole rubber bung into a combustion tube H containing a liner. A silica rod G (by which the boat can be propelled along the combustion tube) slides in the straight arm of the T-piece F. The joint between the rod and tube shall be sealed with a short rubber sleeve.

The combustion tube H shall rest in the combustion furnace J which shall be fitted with automatic temperature control so that the required temperature (1375°C . or 1000°C .; see Clause 3.141) can be maintained within $\pm 25^{\circ}\text{C}$.

The exit end of the combustion tube shall be closed by a rubber bung through which passes a silica tube K, expanded at its inner end to clear the bore of the combustion tube by about 1 mm., and bent vertically downwards at the other end to enter the first absorbing vessel M. The second absorbing vessel N shall consist of a sintered glass filter (porosity 3), mounted vertically over the vessel M. Finally the exit gases shall pass into a third absorbing vessel O and be drawn off by means of a suction pump. The bung at the exit end of the combustion tube shall be pierced by a fine adjustable air-leak, admitting air through an Arnold bubbler L. This ensures that the products of combustion enter the silica exit tube, and do not accumulate behind its expanded end.

A mercury release valve S shall be incorporated, if necessary, to neutralize fluctuations in the suction pump, and a water trap R between the mercury valve and the absorption train ensures that the vacuum line is free from water. Suction shall be applied through two three-way taps Q and P which are manipulated either to provide a gaseous stream through the system or to transfer the contents and necessary washings from the second and third absorption vessels to the first vessel M prior to the final titration.

3.144 PROCEDURE. Weigh approximately 0.1 g. (0.05 g. in the case of ebouite or thioplasts) of the rasped sample into the combustion boat, and cover with silica (freshly ignited in a sulphur-free atmosphere). If barium sulphate is present sprinkle the rubber with 0.05 g. of zinc oxide followed by a layer of silica.

Neutralize 150 ml. of 3 per cent hydrogen peroxide solution with 0.02 N sodium hydroxide solution, using approximately 0.2 ml. of indicator solution and taking the grey colour as the neutral point. Distribute the neutralized solution in the absorption train as follows:—

70 ml. in the first vessel M, 30 ml. in the second vessel N and 50 ml. in the third vessel O. Assemble the absorption train quickly to ensure that the solution in the vessel N does not percolate into the lower vessel, and connect to the exit end of the combustion tube.

Switch on the current to the electric furnace. Connect the exit arm of the U-tube E to the side arm of the entry tube T-piece F, and the air leak at the exit end to the Arnold bubbler. Turn the three-way tap A so that the flow-meter tube is open to the atmosphere. Open the taps on the U-tubes D and E, and apply suction gradually to the system so that air is drawn through the whole apparatus at 550 ml/min. as indicated by the flow meter. Adjust the air-leak bubbler to pass approximately 0.25 ml. every second. Turn the lower three-way tap P so that the vacuum is released to atmosphere, the setting of the pump remaining unchanged.

Disconnect the purifying train by detaching the exit end of the U-tube E from the side-arm of the T-piece F. Turn the three-way tap A so that oxygen is connected to the purifying train, and adjust the supply of oxygen so that the rate of flow is 500 ml. per minute. To ensure a steady stream of oxygen a pressure of at least 50 lb./sq. in. should be shown on the pressure gauge of the cylinder.

When a temperature of 1375°C .* has been attained in the furnace, remove the bung and fitting at the entry end of the combustion tube, reverse the three-way tap P on the absorption train so that air is again drawn through the combustion tube and absorption train and insert the boat in the mouth of the combustion tube. Close the combustion tube with the entry fitting and connect the side-arm of the T-piece F to the exit end of the U-tube E which is still passing oxygen at 500 ml. per minute.

By means of the silica rod propel the boat towards the middle of the furnace, at about 1 cm./min., moving in approximately 1 cm. steps, until a bright flash indicates that combustion has commenced. At the same time a pink coloration of the indicator in the hydrogen peroxide solution shows that the absorption of acid gases is taking place. Slowly advance the boat into the hottest zone of the furnace, and continue the combustion, maintaining the temperature at $1375^{\circ} \pm 25^{\circ}\text{C}$. until white fumes cease to be evolved (approximately a further 20 minutes), when the colour in the third absorption vessel O should begin to fade, indicating that most of the carbon dioxide has been removed from the solution.

Switch off the furnace current, disconnect the U-tube E from the T-piece F, at the same time reducing the vacuum slightly to prevent aeration of the absorbing solutions becoming too violent. Turn off the supply of oxygen and close the taps on the U-tubes D and E. Slowly withdraw the absorption train with air still passing, and disconnect the air-leak tube.

When the indicator in the last absorbing vessel O is completely bleached, i.e. when all carbon dioxide has been removed from the solution by aeration, reverse the lower three-way tap P so as to release the suction to atmosphere, and cork the expanded end of the exit adapter. Reverse the three-way tap Q and thus withdraw the solutions from the second and third absorbing vessels to the first vessel M, and after a brief draining,

* Or 1000°C . (see Clause 3.141).

rinse the last two absorption vessels with three 20 ml. portions of water from the beaker by operating the three-way tap P.

When the last rinsing has been well drained through the sintered glass filter, again open the tap P and reverse the tap Q. This returns the absorption train to atmospheric pressure, when the cork may be withdrawn from the exit adaptor.

Detach the first absorbing vessel from the rest of the assembly and twice rinse the inside and outside of the exit tube with water, adding the rinsings to the bulk of the solution. Titrate with 0.02N (0.1N for ebontic or thioplasts) sodium hydroxide solution.

3.145 EXPRESSION OF RESULTS.

$$\text{Percentage of total sulphur} = \frac{V \times 0.032}{W}$$

where V = Volume of 0.02N NaOH, in ml.

W = Weight of test portion, in grammes.

3.146 SPECIAL PROCEDURE FOR RUBBERS CONTAINING CHLORINE; ERROR DUE TO NITRILE NITROGEN.

Chlorine. The final titration with sodium hydroxide solution is followed by a Volhard titration with silver nitrate and potassium thiocyanate. From the chloride content thus determined a correction for the corresponding amount of hydrochloric acid is subtracted from the alkali titration value.

Nitrile nitrogen. This invalidates the final titration, and a method for the determination of sulphuric acid in such cases has still to be worked out.

References.

1. R. Belcher and C. E. Spooner, *Fuel*, 1941, 20, 130.
2. *Idem*, *J. Chem. Soc.*, 1943, 313.
3. *Idem*, *Ind. Chem.*, 1943, 19, 653.

SECTION 3.2 EXTRACTABLE SULPHUR

3.21 General explanation. A sulphur determination is made on the matter extracted from the rubber by acetone. Depending on the method used, the result of this determination (of the 'free sulphur') usually represents an intermediate value between the following two extremes: (i) the elemental sulphur extractable by boiling acetone (true free sulphur), and (ii) the total sulphur (elemental and combined) in the extract. It is not yet known precisely what forms of sulphur are included in the sulphur as determined by the three methods described in Sections 3.22, 3.23 and 3.24. The bromine and nitric acid methods give similar results for sulphur in the acetone extract of factice (either brown or white), but it is not known how much of this is combined sulphur.

3.22 Bromine method.

3.221 SUMMARY AND EXPLANATORY NOTE. The acetone extract is oxidized by bromine in presence of water, and the resulting sulphuric acid is precipitated as barium sulphate, which is weighed. This method gives all the elemental sulphur, and part, but not all, of the sulphur in sulphur-containing accelerators; it is not known whether the result includes any combined sulphur from other sources, e.g. sulphur reaction products of rubber 'resins'.

Some analysts add picric acid solution immediately before the precipitation of barium sulphate. This is permissible if preferred, except for referee purposes, when it shall be omitted. If used, add 10 ml. of a saturated aqueous solution of picric acid after dilution of the solution containing sulphate. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution, proceeding as in Clause 3.223.

3.222 REAGENTS.

Barium chloride solution; 10 g. in 100 ml. water.

Bromine.

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

3.223 PROCEDURE. Extract a weighed test portion of the rubber with acetone by the method described in B.S. 903, Part 2, Section 2.1; add to the dried extract 50 ml. of water and 2 ml. of bromine, and cover with a watch glass. Allow the vessel to stand for at least 30 min. in a water-bath at about 70°C., then remove the watch glass and heat cautiously without boiling until the solution is almost colourless. Filter the solution and dilute to 250 ml. with water. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution. Continue to boil the liquid for 5–10 min. and allow to stand for at least one hour at 90–100°C.

Filter through a sintered glass or silica crucible (porosity No. 4) which has previously been washed, dried, and weighed. After the filtration wash the crucible and the precipitate with hot water until the washings are free from chloride, dry at 110°C. for one hour, cool in a desiccator and weigh.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

3.224 EXPRESSION OF RESULTS.

$$\text{Percentage of extractable sulphur} = \frac{B \times 13.73}{W}$$

where B = Corrected weight of barium sulphate, in grammes.

W = Weight of test portion, in grammes.

3.23 Nitric acid method.

3.231 SUMMARY AND EXPLANATORY NOTE. The acetone extract is oxidized by heating with nitric acid and potassium chlorate. The resulting sulphuric acid is precipitated as barium sulphate, which is weighed. This method gives all the elemental sulphur, part or all of the sulphur from sulphur-containing accelerators (usually a higher proportion than by the bromine method), and part, but not all, of the sulphur that has entered into combination with rubber 'resins'.

Some analysts add picric acid solution immediately before the precipitation of barium sulphate. This is permissible if preferred, except for referee purposes, when it shall be omitted. If used, add 10 ml. of a saturated aqueous solution of picric acid after dilution of the solution containing sulphate. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution, proceeding as in Clause 3.233.

3.232 REAGENTS.

Barium chloride solution : 10 g. in 100 ml. water.

Hydrochloric acid, concentrated, sp. gr. 1.18.

Nitric acid, concentrated, sp. gr. 1.42.

Potassium chlorate

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

3.233 PROCEDURE. Extract a weighed test portion of the rubber with acetone by the method described in B.S. 903, Part 2, Section 2.1. To the vessel containing the dried extract add 30 ml. of concentrated nitric acid, cover with a watch glass, and heat on a steam bath for four hours, or for a longer period if necessary, until most of the organic matter is destroyed. After the first hour add, at intervals and in small portions, 2.5 g. of potassium chlorate in order to accelerate oxidation. Do not allow the temperature to rise sufficiently to melt the sulphur into globules, as these oxidize extremely slowly. Evaporate the liquid to dryness, add 3 ml. of concentrated hydrochloric acid, and again evaporate to dryness; repeat the evaporation with further 3-ml. portions of hydrochloric acid until no more brown fumes are evolved when the hydrochloric acid is added. Dissolve the residue in a mixture of 50 ml. of hot water and 1 ml. of concentrated hydrochloric acid, filter, and dilute to 250 ml. with water. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution. Continue to boil the liquid for 5-10 minutes and allow to stand for at least one hour at 90-100°C.

Filter through a sintered glass or silica crucible (porosity No. 4) which has previously been washed, dried and weighed. After the filtration wash the crucible and the precipitate with hot water until the washings are free from chloride, dry at 110°C. for one hour, cool in a desiccator and weigh.

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Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

3.234 EXPRESSION OF RESULTS.

where $\text{Percentage of extractable sulphur} = \frac{B \times 13.73}{W}$

B = Corrected weight of barium sulphate, in grammes.

W = Weight of test portion, in grammes.

3.24 Copper spiral method.

3.241 SUMMARY AND EXPLANATORY NOTE. The rubber is extracted with boiling acetone, as in the normal estimation of acetone extract, except that a spiral of clean copper gauze is placed in the flask containing the acetone. The copper reacts with the extracted sulphur and certain compounds containing labile sulphur, forming copper sulphide. When extraction is complete the spiral is removed and the acetone filtered to collect any loose copper sulphide. The spiral and filter paper are then treated with hydrochloric acid, and the resulting hydrogen sulphide passed through cadmium acetate solution. The cadmium sulphide formed is determined iodometrically. This method is commonly regarded as giving elemental sulphur only, but too high a result may be obtained in the presence of compounds containing co-ordinated sulphur, such as tetramethyl thiuram disulphide.

3.242 REAGENTS.

Acetone.

Cadmium acetate solution : 25 g. cadmium acetate, 25 g. sodium acetate, and 100 ml. glacial acetic acid, made up to 1000 ml. with water.

Hydrochloric acid, dilute : 1 vol. of concentrated acid (sp. gr. 1.18) to 1 vol. of water.

Iodine solution, approx. 0.1N.

Sodium thiosulphate solution, standard, 0.1N.

Starch solution.

NOTE. All reagents used should be of recognized analytical reagent quality.

3.243 APPARATUS ; PREPARATION OF SPIRAL. The spiral shall be made from about 5 g. of 40-60 mesh copper gauze cut into a 1 cm. wide strip, which shall be loosely rolled up to form a spiral approximately 2 cm. in diameter, the turns being conveniently held in place by a loop of copper wire.

The surface of the copper shall be chemically clean and to ensure this the spiral shall be thoroughly washed immediately before use in strong hydrochloric acid until it has a bright and untarnished appearance. If badly tarnished the copper shall be briefly immersed in dilute nitric acid. All traces of acid shall be removed by washing with distilled water and finally with acetone.

35

C 2

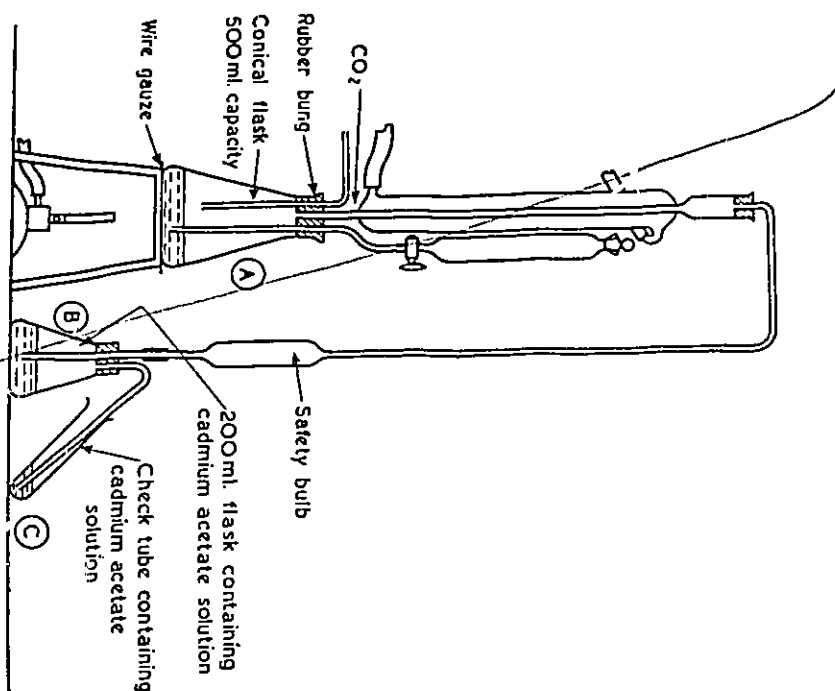


Fig. 3.2 Apparatus for the determination of extractable sulphur by the copper spiral method

The assembly of the apparatus is shown in Fig. 3.2. The rubber stopper in flask A shall be well boiled in 10 per cent sodium hydroxide solution and then in dilute hydrochloric acid before it is used.

3.244 PROCEDURE. Extract a weighed test portion of the rubber with acetone as described in B.S. 903, Part 2, Section 2.1, but with modifications in procedure as follows—

Place the specially prepared copper spiral (for the preparation of which see Clause 3.243) together with the acetone in the extraction vessel, and extract for four hours, or longer if the extract coming from the siphon is still coloured after this time. At the end of the extraction period pour off the acetone through a filter paper (to collect any loose particles of copper sulphide) and wash thoroughly both the spiral and the filter with hot acetone. Transfer the spiral and the filter paper and its contents to flask A, see Fig. 3.2. Introduce an excess (100–150 ml.) of cadmium acetate solution into flask B, and also fill the check tube C with the same solution so that the end of the exit tube is covered. Pass a current of carbon dioxide through the apparatus to sweep out most of the air and adjust the rate of flow to give about two bubbles per second through the liquid in flask B.

Run in 100 ml. of dilute hydrochloric acid from the funnel, heat to boiling, and continue to boil gently for one hour. The hydrogen sulphide evolved is absorbed in flask B, giving a yellow precipitate of cadmium sulphide. Disconnect the flask from the delivery tube, stop the current of carbon dioxide and remove the check tube. The solution in the check tube should be clear; if any precipitate has formed in it, repeat the determination using a greater volume of solution in flask B.

Add a measured volume (v ml.) of iodine solution to flask B so that excess of iodine is present, and allow the iodine to react with any precipitate adhering to the entry tube. When the precipitate has dissolved completely, remove and rinse the tube and titrate the excess of iodine with standard sodium thiosulphate solution using starch as indicator in the usual manner.

Determine the concentration of the iodine solution, in terms of millilitres of standard thiosulphate solution, by titrating v ml. iodine solution with standard sodium thiosulphate solution.

The difference between the volume of sodium thiosulphate solution used in the standardization and that used in the determination is equivalent to the iodine which has reacted with the cadmium sulphide.

3.245 EXPRESSION OF RESULTS.

$$\text{Percentage of extractable sulphur} = \frac{0.16 \times V}{W}$$

where V = Volume of 0.1 N thiosulphate, in millilitres,

W = Weight of test portion, in grammes.

SECTION 3.4 SULPHUR IN 'TOTAL FILLERS'

Some analysts add picric acid solution immediately before the precipitation of barium sulphate. This is permissible if preferred, except for reference purposes when it shall be omitted. If used, add 10 ml. of a saturated aqueous solution of picric acid after dilution of the solution containing sulphate. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution, proceeding as in Clause 3.43.

3.42 Reagents.

Barium chloride solution; 10 g./in 100 ml. water.

Hydrochloric acid, concentrated sp. gr. 1.18.

Methyl orange, 1 g. in 100 ml. water.

Sodium carbonate, anhydrous

NOTE: All reagents used should be of recognized analytical reagent quality, and distilled water should be used wherever water is specified.

3.4.44 Expression of results.

$$\text{Percentage of sulphur in total fillers} = \frac{B \times 13.73}{\dots}$$

where B = Corrected weight of barium sulphate, in grammes.
 W = Weight of test portion, in grammes

3.52 Reagents.

1 vol. of water.

Iodine, approx. 0.1 N solution.

Sodium thiosulphate, 0.1 N standard solution

NOTE. All reagents used should be of recognized analytical reagent quality

3.54 Procedure. Weigh an amount of the dried acetone-extracted rubber (1.0000 g) (1.0000 g) of the original sample (1.0000 g).

3.5.4 Procedure. Weigh an amount of the dried acetone-extracted rubber equivalent to a known weight (between 1 and 2 g.) of the original sample, and transfer it to flask A (Fig. 3.2). Introduce an excess (100–150 ml.) of cadmium acetate solution into flask B and fill the check tube C with the same solution so that the end of the exit tube is covered. Pass a current of carbon dioxide through the apparatus to sweep out most of the air and adjust the rate of flow to give about two bubbles per second through the liquid in flask B.

Run in 100 ml. of dilute hydrochloric acid from the funnel and heat to boiling; continue to boil gently for one hour. The hydrogen sulphide evolved is absorbed in flask B, giving a yellow precipitate of cadmium sulphide. Disconnect the flask from the delivery tube, stop the current of carbon dioxide and remove the check tube. The solution in the latter should be clear; if any precipitate has formed in it, repeat the determination using a greater volume of solution in flask B.

Determine the concentration of the iodine solution, in terms of millilitres of standard thiosulphate solution, by titrating v ml. of iodine solution with standard sodium thiosulphate solution.

used in the standardization and that used in the determination is equivalent to the iodine which has reacted with the cadmium sulphide.

3.55 Expression of results.

$$\text{Percentage of sulphide sulphur} = \frac{0.16 \times V}{W}$$

where

V = Volume of 0.1 N thiosulphate, in millilitres.

W = Weight of test portion, in grammes.

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RUBBER (POLYMER) DETERMINATIONS

This part includes methods for the following determinations:—

Section 4.1 Calculation of rubber content.

Section 4.2 Natural rubber hydrocarbon (direct determination).

Section 4.3 Nitrogen (for acrylonitrile copolymers).

Section 4.4 Chlorine (for chloroprene polymers and copolymers).

Section 4.5 Isobutene-diene (Butyl) rubber.

Section 4.6 Thioplast rubbers.

The direct methods (Sections 4.2–4.6) are in general preferred to the indirect method by calculation (Section 4.1).

No method is included for butadiene-styrene copolymers because there is at present no satisfactory method for the direct determination of these copolymers. Should a satisfactory method be developed, an addendum to this standard will be issued, drawing attention to the method.

SECTION 4.1 CALCULATION OF RUBBER CONTENT

The rubber content may in general be determined by difference as follows:—

$$\text{Rubber content} = [100 - (\text{acetone extract} + \text{chloroform extract} + \text{alcoholic-potash extract} + \text{total fillers} + \text{rubber-combined sulphur})]$$

where the acetone, chloroform and alcoholic-potash extracts are determined as described in B.S. 903, Part 2, the 'total fillers' as described in B.S. 903, Part 5, and the rubber-combined sulphur as described in B.S. 903, Part 3, and all the results are expressed as percentages of the rubber sample prepared in accordance with B.S. 903, Part 1, Section 1.2.

This gives the content of polymer which has been rendered insoluble by vulcanization. To obtain the corresponding figure for the crude rubber, a correction depending on the type of rubber shall be applied; for natural rubber a multiplier factor of 1.03 is appropriate. (This factor allows for the natural rubber resins, which are here classed as 'rubber' and normally represent about 3 per cent of *Hevea* rubber. The proteins normally present in raw natural rubber are here included as 'polymer'.)

This 'difference' method is not applicable to thioplasts.

SECTION 4.2 NATURAL RUBBER HYDROCARBON (DIRECT DETERMINATION)

4.21 Summary. The rubber is oxidized by a mixture of chromic and sulphuric acids under such conditions that for each 4 isoprene units in the rubber hydrocarbon 3 molecules of acetic acid are produced. The acetic acid is removed by steam distillation and estimated by titration with alkali. Corrections have to be applied for certain interfering substances commonly present in vulcanized rubbers.

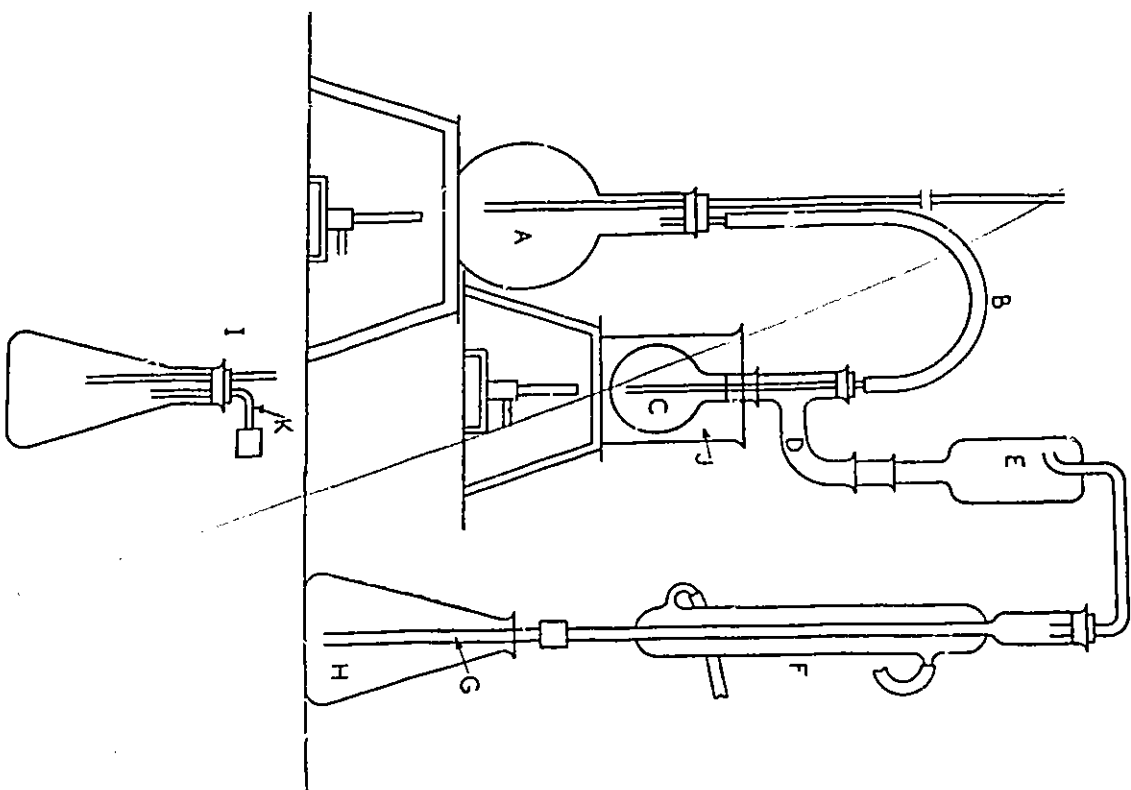


Fig. 4.1 Apparatus for the determination of natural rubber hydrocarbon

4.22 Reagents.

Chromic acid oxidation mixture. Dissolve 200 g. chromic anhydride in 500 ml. water, add 150 ml. of sulphuric acid (concentrated, sp. gr. 1.84) and mix the solutions well.

Phenolphthalein, 0.2 g. in 100 ml. alcohol.

Sodium hydroxide, 0.1N solution.

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

4.23 Apparatus. A diagram of the apparatus required is shown in Fig. 4.1. The use of rubber connections shall be avoided where they might come in contact with the oxidation mixture.

4.24 Procedure. Extract (as described in B.S. 903, Part 2, Section 2.1, Acetone extract, Section 2.4, Chloroform extract, and, if facies is present, Section 2.5, Alcoholic-polish extract) a sufficient amount of the rubber sample to contain approximately 0.3 g. of rubber hydrocarbon. Omit the chloroform extraction in the case of poorly vulcanized rubbers. Dry the extracted rubber in an oven at 70–100°C. for one hour.

Place 700 to 900 ml. of water in the steam-generating flask A. Place sufficient water in the receiving flask H to cover the end of the entry tube. Mark the outside of the oxidation flask C at a point indicating the liquid level when the flask contains 75 ml. Transfer 50 ml. $\pm$ 1 ml. of the chromic acid oxidation mixture to the oxidation flask. Lift the steam-tube B and insert the extracted rubber. Replace the steam-tube and tighten the connection. Heat the beaker J of water surrounding the oxidation flask to boiling, continue boiling for one hour, and then remove the flask to boiling, continue boiling for one hour, and then remove the beaker and burner. During the oxidation period heat the steam-generating flask A, with the stopper removed, until the contents are boiling. Replace the stopper and outlet tube B in the mouth of the steam-generating flask and pass steam through the oxidation flask. When the volume of liquid in the oxidation flask has increased to approx. 75 ml., place the burner under it and adjust the flame to maintain the liquid at approximately this volume. Continue the distillation until 500 ml. are collected in the receiving flask H. This operation should take about 30 minutes. Remove the burners and immediately remove the receiving flask H and the entry tube G. Rinse the tube with water, catching the rinsings in the receiving flask.

Adjust the temperature of the liquid in the receiving flask to 25°C. $\pm$ 5°C., insert the aeration assembly I into the receiving flask as shown in the figure and attach tube K to a vacuum line. Draw a stream of air through the liquid for 30 minutes at approximately 2 litres per minute. Remove the vacuum line and loosen the aeration assembly I. Rinse the aeration assembly with distilled water and collect washings in the flask. Add phenolphthalein indicator and titrate with 0.1N sodium hydroxide. In the presence of chloroprene polymers or copolymers or other

chlorine-containing materials, add neutral potassium iodide to the distillate after aeration and titrate any iodine which may be liberated with neutral sodium thiosulphate before proceeding with the alkali titration.

Carry out a blank determination using the same quantities of reagents and the same conditions of test. The sodium hydroxide titration value should not exceed 0.2-0.3 ml. Apply a corresponding correction to the main result.

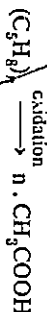
4.25 Expression of results.

Percentage of rubber hydrocarbon = $\frac{0.908 \times V}{W}$

where V = Corrected volume of NaOH, in millilitres.

W = Weight of test portion, in grammes.

This calculation is based on the observation that under the above conditions 75 per cent yield is obtained in the reaction



using purified rubber. To calculate the results on the basis of crude rubber, apply a suitable correction for non-rubber constituents. Smoked sheet may be assumed to contain 93.0 per cent of rubber hydrocarbon and pale crepe 93.5 per cent.

4.26 Corrections for other organic substances present. Allowance must be made for the presence of other rubbers because most of them, when oxidized with chromic acid, give some acid volatile in steam, as also does cellulose. The appropriate corrections given in Table 4.1 should be subtracted. Mineral rubber (bitumen), if not completely removed by the prior extraction with chloroform, leads to too high a result. Interference from other materials such as fat, etc., is negligible because the rubber has been extracted as described in Section 4.24. Polyisobutene, which is unlikely to be met in a vulcanized compound, also interferes by protecting the rubber from attack; it is, however, extractable by chloroform as described in B.S. 903, Part 2, Section 2.4.

TABLE 4.1

Material	Correction as rubber hydrocarbon
Cellulose	0.02 x cellulose content
Gutta percha or balata	1.0 times gutta percha or balata content (i.e. it behaves as if it were natural rubber)
Thiokol RD	0.18 times Thiokol RD content
Neoprene FR	0.12* times neoprene FR content
Perbunan or Hycar OR-15	0.015-0.02 times Perbunan or Hycar OR-15 content
GR-S	0.05 times GR-S content
Neoprene GN	0.03* times neoprene GN content

* After allowance has been made for the halogen acids.

4.27 Correction for combined sulphur. Sulphur when combined lowers the apparent rubber hydrocarbon content. A correction can be made for this from the graph shown in Fig. 4.2. This is essential for ebonites, but for normal soft vulcanizates the correction is small and may usually be neglected.

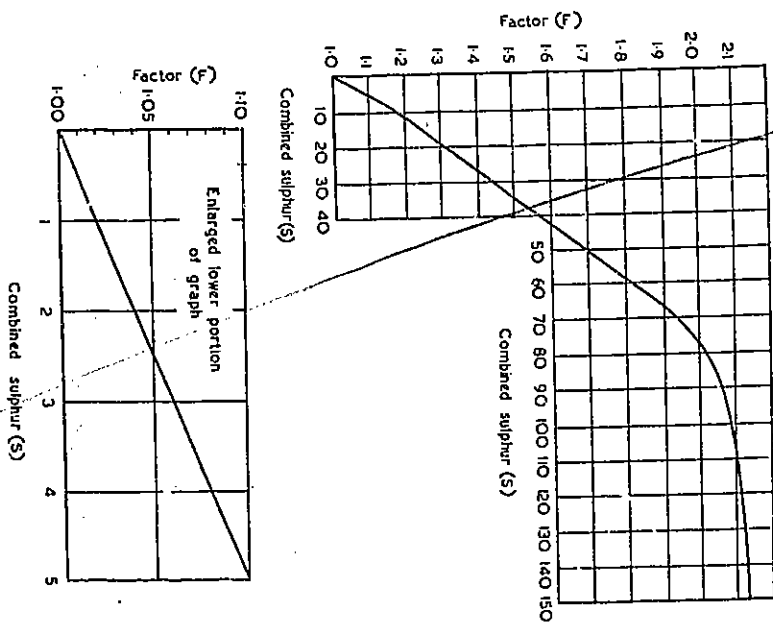


Fig. 4.2 Average correction factor for combined sulphur

To apply this correction the rubber-combined sulphur is determined as described in B.S. 903, Part 3, Section 3.3, and expressed as a percentage (S) of the rubber hydrocarbon (R) determined as described in Clauses 4.24 and 4.25 above. From Fig. 4.2 the factor (F) corresponding to this value of (S) is read off; the true rubber hydrocarbon content is then given by $R \times F$.

References.

I. E. Khernskova and E. Korsunskaya. *Kauchuk i Rezina* (U.S.S.R.), 1937, 39, 7.

2. V. L. Burger, W. E. Donaldson, and J. A. Baly. *A.S.T.M. Bull.*, 1943, No. 120, 23.
3. W. C. Wake. *I.R.I. Trans.*, 1945, 21, 158.

SECTION 4.3. NITROGEN (FOR ACRYLONITRILE COPOLYMERS)

4.31 Summary and explanatory note. The method described is a form of the Kjeldahl method. The rubber is oxidized by heating with a mixture of potassium sulphate and concentrated sulphuric acid plus a catalyst, thereby converting nitrogen compounds into ammonia, which is then estimated by making the reaction mixture alkaline, distilling off the ammonia, absorbing this in boric acid solution, and titrating with hydrochloric acid.

The nitrogen content of a vulcanized rubber sample can be used to determine how much acrylonitrile is present in the vulcanized polymer, provided the sample does not contain other nitrogen compounds insoluble in acetone and chloroform. As the acrylonitrile content of commercial synthetic rubbers varies (see table below), this result does not immediately give the amount of such rubber in the sample unless the type of rubber present is known; if the sample contains only one type of rubber some indication of which type is present may be obtained by the swelling-ratio test (Ref. 1).

In the absence of other nitrogen compounds in the extracted rubber, the acrylonitrile content is given by $3.79 \times$ nitrogen content.

The following table gives the typical nitrogen contents of commercial acrylonitrile copolymer rubbers:—

TABLE 4.2

Rubber	Nitrogen, per cent
Thiokol RD	4 (approx.)
Butaprene NF	5.7
Butaprene NM	6.8
Perbunan (Paracril)	7.5
Hycar OR-25	8.0
Chemigum I	8.0
Butaprene NA	9.7
Butaprene NX	10.5
Hycar OR-15	11.0
Hycar OR-5	13.5

4.32 Reagents.

Boric acid solution. Dissolve 40 g. of boric acid in water, warming if necessary, and make up the volume to 2 litres. Add 20 ml. of indicator solution and mix well. The solution keeps for at least three months without deterioration.

Copper sulphate ; or selenium and mercuric acetate.

Hydrochloric acid, 0.1N solution.

Indicator solution ; 0.125 g. methyl red and 0.083 g. methylene blue in 100 ml. alcohol.

Potassium sulphate, anhydrous.

Sodium hydroxide solution ; 40 g. in 100 ml. water.

Sulphuric acid, concentrated, sp. gr. 1.84.

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

4.33 Procedure. Weigh accurately about 1 g. of the sample and extract with acetone and chloroform as described in B.S. 903, Part 2, Sections 2.1 and 2.4.

Remove the excess solvent from the extracted rubber by drying at 70–100°C. for about one hour, then transfer to a clean, dry 250 ml. Kjeldahl flask. Add 10 g. of anhydrous potassium sulphate, 0.5 g. of copper sulphate or of selenium plus mercuric acetate, and finally 25 ml. of concentrated sulphuric acid.

(NOTE. Alternatively a larger flask, 800–1000 ml., may be used, so as to avoid the need for subsequent transference of the contents to a second flask.)

Heat the flask over a bunsen flame, gently at first until the initial reaction has subsided, and then more strongly until the solution is almost boiling. Continue heating at this temperature until the liquid becomes clear and pale green in colour. Heat for a further 45 minutes and allow to cool. Dilute the liquid cautiously with water and transfer to a round-bottomed litre flask. Wash out the Kjeldahl flask several times with further quantities of water and add the washings to the main liquid. Dilute to about 600 ml. and add a few pieces of porous pot to prevent bumping.

Fit the litre flask with a two-holed rubber bung carrying a tap funnel and a splash head, the other end of the splash head being attached to a vertical water-cooled condenser. Measure into a 750 ml. conical flask 50 ml. of the boric acid solution and then place the flask under the condenser in such a manner that the end of the exit tube is below the surface of the solution. Cool the flask in a bath of ice water.

Add to the liquid in the litre flask, by means of the tap funnel, an excess of 40 per cent sodium hydroxide solution. Heat to boiling and continue to boil vigorously until about 300 ml. of distillate has collected in the conical receiver, and in any case for not less than 40 minutes, by

which time the distillate from the condenser should no longer colour a Brilliant Yellow paper. Disconnect the condenser and receiver from the remainder of the apparatus, and rinse the inner and exit tubes of the condenser with water, collecting the rinsings in the receiver. Titrate the ammonia in the liquid with 0.1*N* hydrochloric acid.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final titre obtained above.

4.34 Expression of results.

$$\text{Percentage of nitrogen} = \frac{V \times 0.140}{W}$$

where V = Corrected titre of 0.1*N* hydrochloric acid, in millilitres.
 W = Weight of test portion, in grammes.

Reference.

I. L. F. C. Parker. *J.S.C.I.*, 1945, 64, 65.

SECTION 4.4
CHLORINE (FOR CHLOROPRENE POLYMERS AND COPOLYMERS)

4.41 Summary and explanatory note. The method described is the Carius method, in which the rubber is oxidized by heating with fuming nitric acid and silver nitrate under pressure in a sealed tube, whereby the chlorine present is converted into silver chloride, which is filtered off from the diluted reaction mixture and weighed.

The chlorine content of a vulcanized rubber sample can be used to determine how much chloroprene is present in the vulcanized polymer, provided the sample does not contain other chlorine compounds insoluble in acetone. As the chlorine content of commercial synthetic rubbers varies (see table below), this result does not immediately give the amount of such rubber in the sample, unless the type of rubber present is known; if the sample contains only one type of rubber, some indication of which type is present may be obtained by the swelling-ratio test (Ref. 1).

In the absence of other chlorine compounds in the extracted sample, the chloroprene content is given by $2.49 \times$ chlorine content.

The following table gives the typical chlorine content of commercial chloroprene rubbers :—

TABLE 4.3

Rubber	Chlorine, per cent
Neoprenes CG, GN, and KNR	37-38
Neoprenes G and GN-A	38
Neoprene E	38-39
Neoprene FR	29
" IL.S*	32-33
" Z†	30
"	32

* Also contains 4 per cent of nitrogen.
† Also contains 3 per cent of nitrogen.

4.42 Reagents.

Ammonia solution ; 10 g. NH_3 in 100 ml.

Nitric acid, fuming, sp. gr. 1.50.

Nitric acid, dilute ; 1 vol. concentrated acid (sp. gr. 1.42) to 5 vols. water.

Silver nitrate.

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

4.43 Procedure. Introduce into a bomb-tube, 18-24 in. in length and sealed at one end, 1 g. of silver nitrate and then, by means of a long-stemmed funnel, 5 ml. of fuming nitric acid. Withdraw the funnel carefully so as to avoid wetting the side of the tube.

Cautiously slide into the bomb-tube a small ignition tube containing about 0.2 g. of the sample, taking care that at this stage the sample does not come into contact with the acid.

Seal the open end of the bomb-tube in a blow-pipe flame by the usual technique and allow to cool. When cold place the tube in a bomb furnace. Raise the temperature of the furnace gradually, over a period of three hours, to 230°C. and maintain this temperature for a further three hours. Allow the tube to cool in the furnace, and when cold release the pressure by heating the tip carefully until the glass is softened and becomes perforated by the escaping gases. Remove the tube from the furnace, and open it by making a deep file scratch round the glass and applying the end of a glass rod, heated to redness.

Wash the contents of the bomb-tube into a 600 ml. beaker ; add 10 per cent ammonia solution until the liquid is alkaline, and then add 20 ml. in excess. Warm the solution on a water bath for 30 minutes, stirring occasionally, and filter. Wash the filter paper with hot water until free from chloride, collecting the washings with the main filtrate.

To the combined filtrate and washings add dilute nitric acid until the solution is just acid and then add 5 ml. in excess. Heat the solution almost to boiling, stirring constantly, and maintain this temperature until the precipitate has coagulated and the supernatant liquid is clear.

Note. During this and subsequent operations, the precipitate of silver chloride should be protected as much as possible from bright light.

Allow the solution to stand for one or two hours, and then filter through a sintered glass or silica crucible (porosity No. 4) which has previously been washed, dried and weighed. Wash the crucible and precipitate with water acidified with a few drops of nitric acid until the filtrate gives no turbidity on the addition of a few drops of hydrochloric acid. Dry at 130–150°C. for one hour, cool in a desiccator and weigh.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

4.44 Expression of results.

$$\text{Percentage of chlorine} = \frac{S \times 24.74}{W}$$

where S = Corrected weight of silver chloride, in grammes.

W = Weight of test portion, in grammes.

Reference.

1. L. F. C. Parker. *J.S.C.I.*, 1945, 64, 65.

SECTION 4.5 ISOBUTENE-DIENE (BUTYL) RUBBER

4.51 Summary. The method consists of a preliminary degradation of the rubber with nitric acid, followed by light petroleum extraction of the degraded product, the extracted matter being dried and weighed as polyisobutene.

4.52 Reagents.

Light petroleum, b.p. 40–60°C.

Methylated spirit.

Nitric acid, concentrated, sp. gr. 1.42.

Sodium carbonate, anhydrous.

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

4.53 Procedure. Cut the sample sufficiently small to pass a B.S. 10 mesh sieve* (the material should *not* be buffed or rasped). Weigh about 0.25–0.5 g. into a sintered glass or silica crucible (porosity No. 2) and boil under reflux with concentrated nitric acid, the crucible being supported on a glass stand which should raise it about 4 cm. from the bottom of the tube, as shown in Fig. 7.1 (see p. 59); use sufficient nitric acid to flood the sintered disc.

After 10 minutes allow the crucible to drain out of contact with the hot acid, then wash it at the filter pump with two washings each of 25 ml. of water, followed by two similar washings of aqueous methylated spirit and one of methylated spirit, and suck dry. Wipe the outside of the crucible free from spirit, and return it to the same or a similar apparatus, this time with another glass stand bringing the crucible 5 cm. higher in the tube, * B.S. 410, 'Test sieves.'

and extract with light petroleum for two hours. (Place a few pieces of porous pot in the tube to prevent bumping.) Repeat the acid digestion, washing, and subsequent extraction with light petroleum *twice*, making a *total of three* treatments.

Combine the three lots of light petroleum extract obtained, and add a small quantity (approx. 0.5–1.0 g.) of anhydrous sodium carbonate. After leaving to stand for 10 or 15 minutes, filter the liquid through a fluted filter paper (Whatman No. 1) and wash the latter carefully, particularly at the edges, with a fine stream of boiling light petroleum. This washing is important; about 50–70 ml. of light petroleum are required to wash the paper free from polyisobutene; incomplete washing will be detected by the stickiness of the edges of the filter paper. Disil off excess light petroleum (when the liquid bulk is reduced it may be advantageous to transfer it, again with hot washing, to a smaller flask to facilitate weighing). Evaporate just to dryness on a hot plate, transfer to an oven at 70–75°C., and dry to constant weight.

Note. The above procedure has been devised for vulcanizates containing carbon black. With vulcanizates free from black, satisfactory results have been obtained with only one nitric acid digestion (of 40 minutes duration) and one extraction (preferably overnight) with light petroleum.

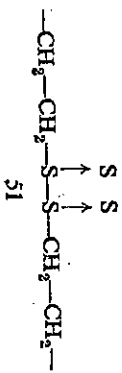
4.54 Expression of results. The extract shall be expressed as a percentage of the weight of the test portion, to give the polyisobutene content of the original sample; *or* the extract shall be multiplied by 1.03 and expressed as a percentage of the weight of the test portion, to give the percentage of Butyl rubber in the original sample.

Reference.

P. D. Galloway and W. C. Wake, *Analyst*, 1946, 71, 505.

SECTION 4.6 THIOPLAST RUBBERS

4.61 Summary and explanatory note. The determination of non-extractable sulphur by the method set out in B.S. 903, Part 3, Section 3.3 will enable the amount of thioplast in the sample to be determined if unambiguous results have been obtained from qualitative tests, i.e. if the type of thioplast is known, but not otherwise. Conversely, the type can be determined from the quantitative data only if the total amount of thioplast present is known. Mixtures of thioplasts are sometimes used for processing reasons and in case of difficulty the labile sulphur should be determined. The labile sulphur is that attached by co-ordinate covalecencies to other sulphur atoms, as shown below, and it can be estimated by the direct method here described, which consists in allowing the labile sulphur to react with sodium sulphite to form sodium thiosulphate, which is determined iodometrically.



The results obtained by this method are not very uniform and this is probably because mixtures of materials are used in the commercial preparation. Also, most thioplasts contain more non-extractable sulphur, present in various forms, than their alleged constitution allows.

The following table shows typical results of the distribution of sulphur in some thioplasts:—

TABLE 4.4

Thioplast	Total sulphur, per cent	Sulphur in acetone extract, per cent	Labile sulphur, per cent	Per cent ethylene tetrasulphide calculated from labile sulphur content
Thiokol A	79.8	11.4	37.9	53.1
" AZ	84.1	7.3	36.6	89.6
" F	54.9	0.5	0	0
" FA	45.1	0.5	0	0
" N	68.5	3.0	6.2	13.8

These figures show that the presence of tetrasulphide polymer is clearly demonstrated from the labile sulphur content, but in the presence of mixed polymers it is doubtful whether the accuracy of estimation is better than 5–10 per cent.

4.62 Reagents.

Sodium sulphite solution, 10 gr. in 100 ml. water.

Formaldehyde solution, 40 g. in 100 ml. (Formalin).

Acetic acid, 20 ml. diluted to 100 ml. with water.

Iodine, 0.1*N* solution.

Ice.

Note. All reagents used should be of recognized analytical reagent quality.

4.63 Procedure. Extract a weighed amount, about 0.1 g., of the rubber with acetone by the method described under B.S. 903, Part 2, Section 2.1. When the extraction is complete, transfer the rubber, without drying, to a beaker and cover with 100 ml. of sodium sulphite solution. Leave standing overnight and then boil for 12 hours. Cool the solution and add 10 ml. of formaldehyde solution followed by 40 ml. of acetic acid.

Titrate the solution against iodine in the usual way except that the temperature should be kept below 5°C. by the addition of ice.

4.64 Expression of results.

$$\text{Percentage of labile sulphur} = \frac{0.321 \times V}{W}$$

where V = Volume of 0.1*N* iodine, in millilitres.

W = Weight of test portion, in grammes.

If it is assumed that all the labile sulphur is derived from ethylene tetrasulphide polymer, then:

$$\text{Percentage of ethylene tetrasulphide polymer} = \frac{0.782 \times V}{W}$$

Reference.

L. F. C. Parker. *I.R.J.*, 1945, 108, 387.

B.S. 903, Part 5 : TOTAL FILLERS

SECTION 5.1 SUMMARY AND EXPLANATORY NOTE

The dissolution of a vulcanized rubber in a high boiling-point solvent followed by dilution and filtration enables the total insoluble solid fillers of the rubber to be determined in one operation. The most important of these fillers are mineral fillers, carbon black, graphite, and cellulosic fibres. Constituents such as elemental sulphur, mineral rubber, and resins will in general not be included in total fillers.

Various combinations of solvent and diluent have been used for this purpose, e.g. if natural rubber only is present nitrobenzene and acetone, or decahydronaphthalene ('dekalin') and light petroleum (boiling range 40–60°C.) have been found satisfactory. With oil-resisting rubbers containing acrylonitrile the latter combination is useless, and with Butyl rubber the former is unsatisfactory. The combination given in Section 5.2 below is known to dissolve the existing synthetic rubbers as well as natural rubber. The process is essentially oxidative, and care must be taken throughout the dissolution to ensure that air has access to the contents of the flask.

SECTION 5.2 METHOD

5.21 Reagents.

Carbon tetrachloride.

Chloroform (if preferred to carbon tetrachloride as a diluent).

p-Dichlorobenzene.

Note. All reagents used should be of recognized analytical reagent quality.

5.22 Procedure. For precise work weigh out a 1 g. test portion of the rubber and extract with acetone as described in B.S. 903, Part 2, Section 2.1. Acetone extract; for ordinary purposes the prior extraction of the test portion with acetone may be omitted. Place the test portion (without drying) in a 750 ml. conical flask, loosely closed by a glass bulb, add 10 ml. of carbon tetrachloride and heat on a hot plate over which is placed a sheet of asbestos paper to avoid local over-heating. Continue the heating until much of the liquid has evaporated; then add 100 g. of *p*-dichlorobenzene and continue heating at about 170–180°C. Remove the bulb from time to time to permit access of air, and for G.R.-S or Butyl rubber vulcanizates blow a few puffs of air occasionally into the flask over the surface of the liquid; this is best accomplished by a small rubber bulb attached to a glass tube. Continue the heating until dissolution is com-

ple; the time required for this varies from about 30 minutes for natural rubber to 1-3 hours for GR-S. Cool to below the boiling point of the diluent (chloroform or carbon tetrachloride), add 100 ml. of the diluent, and allow to stand for several hours for the residue to settle. Settling may be accelerated by centrifuging.

Decant the supernatant liquid and filter through a weighed sintered glass crucible of suitable porosity, or through a filter paper if the sulphur content of the fillers is to be determined (see B.S. 903, Part 3, Section 3.4) : wash the residue with warm diluent, followed by a small quantity of acetone. Dry at 70-75°C., cool in a desiccator and weigh.

If nitrobenzene or decahydronaphthalene is used as solvent (see Section 5.1) the procedure is essentially the same except that (i) the preliminary heating with carbon tetrachloride is omitted, (ii) 40 ml. of the solvent is used and the mixture is heated to boiling, (iii) the diluent is acetone or light petroleum, respectively.

5.23 Expression of results. The weight of the insoluble residue, expressed as a percentage of the weight of the test portion, shall be taken as the 'total fillers.'

SECTION 6.1 SUMMARY AND EXPLANATORY NOTE

A small weighed test portion of the comminuted sample is first ignited gently to decompose the rubber and remove volatile matter, and then to red heat to incinerate all organic matter. The residue consists principally of the non-volatile mineral fillers, or their decomposition products, together with their reaction products with sulphur and/or oxygen. The temperature of final ignition is not critical between 500°C. (dull red) and 800°C. (red). Below 500°C., however, decomposition of certain mineral fillers, e.g. calcium carbonate, may be incomplete and variable results may be obtained. For arbitration purposes a temperature of 600 ± 25°C. shall be used.

SECTION 6.2 METHOD

6.21 Apparatus.

Silica (or porcelain) crucible, Form B, capacity 30 ml. approx.

Asbestos board, approx. 4 in. (10 cm.) square and ¾ in. (0.6 cm.) thick with hole in centre to support crucible.

Muffle furnace with pyrometer and indicator for control of temperature.

6.22 Procedure. Weigh 2 g. of the comminuted sample into the 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 spurning occurs. When the rubber is completely decomposed to a charred mass, raise the temperature of the crucible to red heat either over the bunsen burner or after transferring the crucible to a muffle furnace. Continue the heating until the ash is free from specks of carbon and then cool in a desiccator over fused calcium chloride and weigh. Repeat the heating, cooling, and weighing until a constant weight is obtained.

6.23 Expression of results. The weight of ash obtained shall be expressed as a percentage of the weight of the test portion.

903 B14:64

B.S. 903, Part 7: CARBON BLACK

This standard includes two methods applicable respectively to different types of rubber:

- Section 7.1. Carbon black in rubbers other than isobutene-diene (Butyl) rubber.
Section 7.2. Carbon black in isobutene-diene (Butyl) rubber.

SECTION 7.1

CARBON BLACK IN RUBBERS OTHER THAN ISOBUTENE-DIENE (BUTYL) RUBBER

7.1.1 Summary. The rubber is heated with nitric acid of such strength as to oxidize all the organic matter but not the free carbon. The insoluble residue of carbon (with or without mineral matter) is separated, washed with acetone and chloroform to remove residual organic matter, and then heated in a current of oxygen to burn the carbon to carbon dioxide, which is absorbed in soda-lime and weighed. This method determines all forms of amorphous free carbon such as that in channel black, furnace black, acetylene black and lamp black, as well as graphite.

7.1.2 Reagents.

- Acetone.*
Carbon tetrachloride.
Chloroform.
Calcium chloride, anhydrous.
Kieselguhr.
Nitric acid, concentrated, sp. gr. 1.42.
Nitric acid, dilute; 3 vols. concentrated acid to 1 vol. water.
Potassium hydroxide solution; 25 g. in 30 ml. water.
Soda-lime.

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

7.1.3 Procedure. Extract a 0.5-1.0 g. test portion of the rubber with acetone, as described in B.S. 903, Part 2, Section 2.1; dry the extracted test portion, and treat cautiously with 50 ml. of dilute nitric acid, finally warming at 90-100°C. for one hour. Add about 0.2 g. of ignited finely-divided kieselguhr and disperse it thoroughly by heating the mixture a few minutes longer. Cool the beaker and contents, add 10-20 ml. of carbon tetrachloride, and agitate thoroughly to mix it with the nitric acid. Filter by decantation through an ignited silica filtering crucible (porosity No. 3) containing a thin pad of kieselguhr. Wash the residue with 30 ml. of boiling concentrated nitric acid and then several times with boiling water. Transfer all residues to the crucible and wash finally with a boiling mixture

of acetone (2 vols.) and chloroform (1 vol.) until the washings are colourless. Dry the crucible and its contents at 200-250°C. to a constant weight.

Transfer the contents of the crucible carefully to a combustion boat; insert this in a hard glass combustion tube about 13 mm. internal diameter and 20-30 cm. long. Pass oxygen, freed from carbon dioxide by passing it through soda-lime tubes, through the combustion tube to displace the air. Heat cautiously the part of the tube containing the boat, while the oxygen passes at a slow rate (not more than 20 ml/min.), and lead the issuing gases through a U-tube filled with granulated anhydrous calcium chloride (previously treated with carbon dioxide and then freed from excess gaseous carbon dioxide by a current of dried air). Finally lead the gases through a weighed absorption tube containing soda-lime (preferably of the self-indicating type), followed by a drying agent or a separate drying tube. Continue the heating until all the carbon has been burnt. Continue passing the oxygen for 10 minutes longer to displace the carbon dioxide. Disconnect the soda-lime tube, allow it to cool, and re-weigh it. The increase in weight is the weight of carbon dioxide produced by the burning of the carbon.

7.1.4 Expression of results.

$$\text{Percentage of free carbon} = \frac{27.27 \times C}{W}$$

where C = Weight of carbon dioxide, in grammes.

W = Weight of test portion, in grammes.

For rubbers which do not contain any filler that loses water on ignition (e.g. clay), it is sufficient for less exact work to ignite the crucible in which the carbon black has been filtered off and dried, and to assume that the loss in weight equals the weight of carbon. This procedure tends to give high figures, owing to the difficulty of removing all volatile matter prior to ignition.

SECTION 7.2

CARBON BLACK IN ISOBUTENE-DIENE (BUTYL) RUBBER

7.2.1 Summary. The method depends upon degrading the copolymer to polyisobutene by heating with concentrated nitric acid. The polyisobutene is then extracted from the carbon black by means of light petroleum.

7.2.2 Reagents.

- Light petroleum, b.p. 40-60°C.*
Methylated spirit.
Nitric acid, concentrated, sp. gr. 1.42.

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

7.23 Procedure Cut the sample sufficiently small to pass a B.S. 10 mesh sieve* (the material should *not* be buffed or rasped). Weigh about 0.25–0.5 g. into a sintered glass crucible (porosity No. 2), and boil under reflux with concentrated nitric acid, the crucible being supported on a glass stand which should raise it about 4 cm. from the bottom of the tube, as shown in Fig. 7.1 use sufficient nitric acid to flood the sintered disc.

After 10 minutes allow the crucible to drain out of contact with the hot acid, then wash it at the filter pump with two washings, each of 25 ml. of water, followed by two similar washings of aqueous methylated spirit and one of methylated spirit, and suck dry. Wipe the outside of the crucible free from spirit, and return it to the same or a similar apparatus, this time with another glass stand bringing the crucible 5 cm. higher in the tube, and extract with light petroleum for two hours. (Place a few pieces of porous pot in the tube to prevent bumping.) Repeat the acid digestion, washing, and subsequent extraction with light petroleum *twice*, making a *total of three* treatment. (If desired, combine the three lots of extraction liquid and determine the polyisobutene content by the method described in B.S. 903, Part 4, Clause 4.53.)

Dry the crucible and its contents to constant weight at 260–250°C. Then burn the carbon to carbon dioxide, as described in Clause 7.13 above.

7.24 Expression of results.

$$\text{Percentage of carbon black} = \frac{27.27 \times C}{W}$$

where

C = Weight of carbon dioxide, in grammes.

W = Weight of test portion, in grammes.

For rubbers which do not contain any filler that loses water on ignition (e.g. clay), it is sufficient for less exact work to ignite the crucible in which the carbon black has been filtered off and dried, and to assume that the loss in weight equals the weight of carbon. This procedure tends to give high figures, owing to the difficulty of removing all volatile matter prior to ignition.

Reference.

P. D. Galloway and W. C. Wake, *Analyst*, 1946, 71, 505.

* B.S. 410, 'Test sieves.'

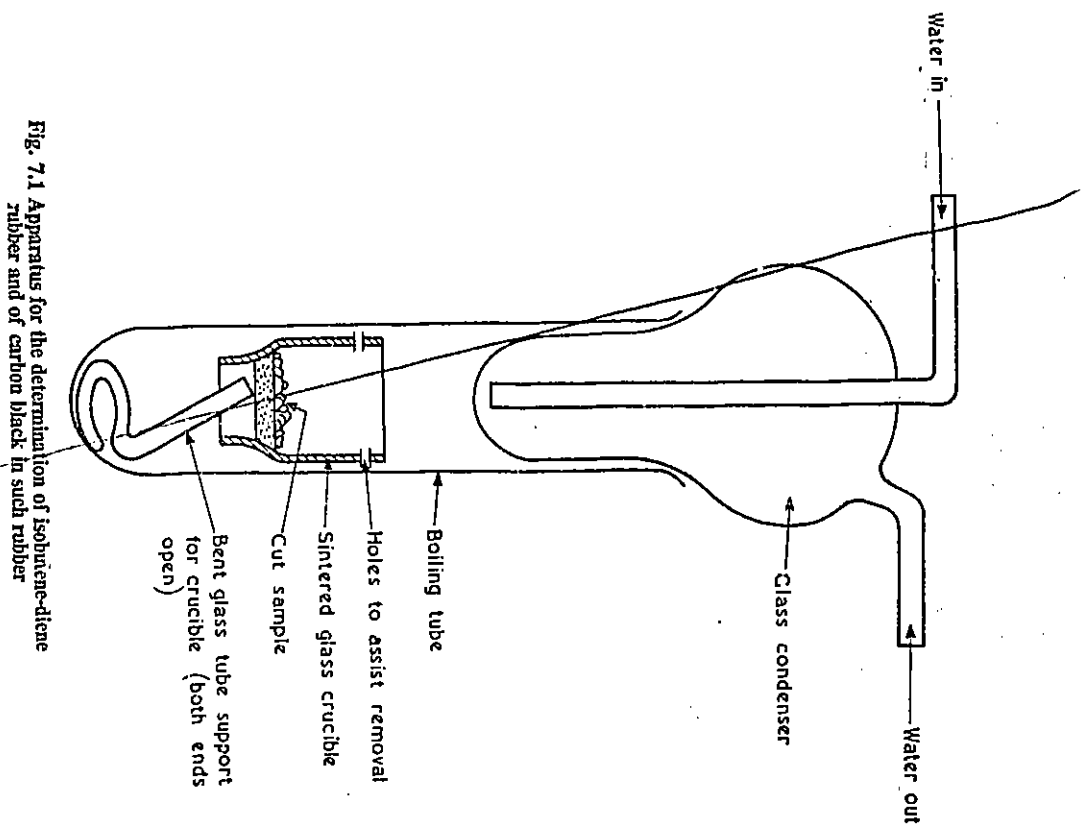


Fig. 7.1 Apparatus for the determination of isobutene-diene rubber and of carbon black in such rubber

B.S. 903, Part 8

ANTIMONY, COPPER, AND MANGANESE

This standard includes methods for the following determinations :—

Section 8.1. Antimony.

Section 8.2. Copper.

Section 8.3. Manganese.

The wet oxidation process used to destroy organic matter and obtain the solution ready for the determination of the metals is included in Section 8.1.

SECTION 8.1 ANTIMONY

8.11 Wet oxidation.

8.111 SUMMARY. The rubber is heated with a mixture of nitric and sulphuric acids to oxidize the organic matter and obtain a solution containing the metal(s) to be estimated.

Experience has shown that concentrated nitric acid of analytical reagent quality frequently requires redistillation. This need for exceptional care arises from the fact that the weight of nitric acid used may be several times that of the test portion of rubber. Care must also be taken to ascertain that the sulphuric acid is of the proper standard of purity.

8.112 REAGENTS.

Hydrogen peroxide solution : 30 g. H_2O_2 in 100 ml. ('100-volume' solution).

Nitric acid, concentrated, sp. gr. 1.42, redistilled from an all-glass apparatus.

Nitric acid, dilute : 30 vols. concentrated redistilled acid plus 70 vols. water.

Sulphuric acid, concentrated, sp. gr. 1.84.

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

8.113 PROCEDURE. Weigh accurately 0.5–1 g. of the sample* into a 100 ml. Kjeldahl flask of resistance glass or silica, and add 10 ml. of dilute nitric acid (20 ml. for the determination of copper). With many rubbers, particularly GR-S, 10 ml. of concentrated acid may safely be added at this stage, with considerable saving of time.

As soon as any vigorous initial reaction subsides, heat gently until further vigorous reaction ceases, and then cool. Add slowly 5 ml. of concentrated sulphuric acid (10 ml. for the determination of copper) at such a rate as not to cause excessive frothing or heating, 5–10 minutes usually

* 2 g. for the determination of manganese, or 5 g. for the determination of copper.

being required, and then heat until the liquid darkens in colour appreciably, i.e. begins to char. Then add concentrated nitric acid slowly in small portions to the hot solution, heating between each addition until darkening again takes place. Heating should not be so strong that charring is excessive, and a small amount of free nitric acid must be present throughout the procedure. Continue this treatment until the solution fails to darken in colour and remains pale yellow on prolonged heating. Note the total amount of nitric acid used. Finally clarify the solution by boiling with successive additions, a few drops at a time, of a mixture of equal volumes of hydrogen peroxide solution and concentrated nitric acid. Allow to cool somewhat and dilute with 10 ml. of water. The solution should be quite colourless, or faintly yellow if much iron is present. Boil down again until white fumes appear, allow to cool, add a further 5 ml. of water, boil for five minutes and cool.

8.12 Determination of Antimony.

8.121 SUMMARY. The antimony in the solution obtained by wet oxidation of the rubber is reduced to the trivalent state by sulphur dioxide, excess of the latter boiled off, and the antimony determined by titration with iodine.

8.122 REAGENTS.

Ammonium hydroxide, concentrated aqueous solution, sp. gr. 0.880.

0.880.

Citric acid solution : 25 g. in 100 ml. water.

Hydrochloric acid, concentrated, sp. gr. 1.18.

Hydrochloric acid, dilute : 1 vol. concentrated acid (sp. gr. 1.18) to 1 vol. water.

Hydrochloric acid – bromine mixture : dilute hydrochloric acid saturated with bromine.

Iodine, 0.1 N solution.

Nitric acid, concentrated, sp. gr. 1.42.

Sodium bicarbonate.

Sodium sulphite, anhydrous.

Starch solution.

Sulphuric acid, concentrated, sp. gr. 1.84.

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

8.123 PROCEDURE. To the solution obtained by wet oxidation, as described in Clause 8.11 above, add 15 ml. of dilute hydrochloric acid, boil, cool, then pass the solution through a No. 1 Whatman filter paper and wash with dilute hydrochloric acid. In the absence of iron and chromium cool the solution to 20°C. and then dilute to 100 ml. with dilute hydrochloric acid. Use this solution for the estimation of antimony and reject any residue. Call this solution A. If iron or chromium is present,

then after filtration dilute to 150 ml. with water instead of hydrochloric acid; warm, and precipitate the antimony with hydrogen sulphide. Filter and transfer the filter paper and precipitate of antimony sulphide to a Kjeldahl flask; add 15 ml. of concentrated sulphuric acid, place a funnel in the neck of the flask, and heat until the solution is colourless. Add 15 ml. of dilute hydrochloric acid to the cooled solution, boil, cool, and then pass the solution through a No. 1 Whatman filter paper, wash with dilute hydrochloric acid, cool the solution to 20°C. and dilute to 100 ml. with dilute hydrochloric acid. Call this solution A1.

Transfer solution A or A1, obtained as above, to a 500 ml. conical flask; add hydrochloric acid – bromine mixture until the solution is coloured, heat to boiling, and if the yellow colour disappears add more hydrochloric acid – bromine mixture until the hot solution is slightly coloured.

Add 1 g. of anhydrous sodium sulphite and boil until the sulphur dioxide is expelled (test with potassium dichromate paper). Cool the solution, add 40 ml. of citric acid solution and a piece of litmus paper, and dilute with 100 ml. of water. Make the solution slightly alkaline with ammonium hydroxide solution and then slightly acidify with hydrochloric acid. Cool thoroughly and dissolve 4 g. of sodium bicarbonate in the solution. Immediately titrate with 0.1N iodine solution until a faint yellow colour persists in the solution.

Confirm the end point by adding a little freshly prepared starch solution. A faint blue colour should be obtained which is much intensified by the addition of a further drop of 0.1N iodine solution. Starch solution shall on no account be added until the yellow iodine end point has been obtained.

8.124 Expression of results.

$$\text{Percentage of antimony} = \frac{0.6088 \times V}{W}$$

where

V = Volume of 0.1N iodine required, in millilitres.

W = Weight of test portion, in grammes.

SECTION 8.2 COPPER

8.21 Wet oxidation. A weighed test portion (about 5 g.) of the rubber shall be subjected to wet oxidation by the procedure described in Clause 8.11 above.

8.22 Determination of copper.

8.221 SUMMARY. The copper in the solution obtained by wet oxidation of the rubber is converted into copper diethylthiocarbamate, which is determined either colorimetrically or photometrically.

8.222 REAGENTS.

Ammonium hydroxide, concentrated aqueous solution, sp. gr. 0.880.

Citric acid solution.

Citric acid solution, 25 g. in 100 ml. water.

Copper sulphate, standard solution. Dissolve 0.3928 g. of copper sulphate pentahydrate in 0.1N sulphuric acid and dilute with this to 1 litre. Before use dilute 10 ml. of this solution to 100 ml. with water. Then 1 ml. $\equiv$ 0.00001 g. copper.

Sodium diethylthiocarbamate solution, 0.2 g. in 100 ml. water; this solution must be freshly prepared and filtered.

Sodium sulphate, anhydrous.

Sulphuric acid, dilute; 1 vol. concentrated acid (sp. gr. 1.84) to 7.5 vols. water.

Sulphuric acid, concentrated, sp. gr. 1.84.

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

8.223 PROCEDURE. Filter the solution obtained from the wet oxidation (Clause 8.11) through a No. 1 Whatman filter paper into a 100 ml. standard flask, washing with small amounts of water; dilute to the mark at 20°C. and mix well. Call this solution B. A blank solution also is required and is prepared by adding 10 ml. of concentrated sulphuric acid, and the same amounts of nitric acid and hydrogen peroxide solution as were used in the oxidation of the sample, to a 100 ml. Kjeldahl flask and boiling the mixture down to fuming. Allow to fume for about 20 minutes and evaporate twice with 5 ml. portions of water. Finally cool, dilute with 25 ml. of water, boil, cool, transfer to a 100 ml. standard flask and dilute to the mark at 20°C. Call this solution C.

Measure 80 ml. of solution B into a 250 ml. beaker ('beaker X'). Add, with stirring, a slight excess of ammonium hydroxide solution, heat to boiling and boil gently for one minute. Then filter through an open-texture filter paper and collect the filtrate in a second 250 ml. beaker ('beaker Y').

When filtration is complete, pierce the tip of the filter paper with a pointed glass rod, and by means of a jet of hot water delivered from a wash-bottle, wash the precipitate back into beaker X. Finally, wash the filter with 20 ml. of dilute sulphuric acid, and stir the contents of the beaker until the precipitate has redissolved. Cool, and then add, with stirring, a slight excess of ammonium hydroxide solution. Heat to boiling, boil gently for one minute, and filter as before, collecting the filtrate in beaker X. Wash the precipitate and filter several times with hot water, and add the washings to the combined filtrates. Add dilute sulphuric acid to the combined filtrates until the liquid is acid, then add 8 ml. of citric acid solution.

If the portion of solution B taken for analysis is known to contain less than 0.1 g. of iron, the above double precipitation with ammonia may be omitted. It is sufficient to add 8 ml. of citric acid solution to it before proceeding with the analysis.

To the solution obtained by either of the above procedures, add ammonium hydroxide solution in slight excess, and then transfer to a 250 ml. conical separator. Add 10 ml. of sodium diethyldithiocarbamate solution and mix by swirling. Add 10 ml. of chloroform, stopper the funnel, and shake vigorously for about 30 seconds. Allow the two liquids to separate and then run off the chloroform layer into a clean 100 ml. conical flask containing about 1 g. of anhydrous sodium sulphate. Repeat the extraction with two further 10 ml. portions of chloroform, running the extracts into the same conical flask. The final extract should be colourless or nearly so. If it is not, repeat the process with further 5 ml. portions of chloroform, as necessary. Swirl the contents of the conical flask to assist the removal of traces of water, allow to settle, and carefully decant the liquid into a 50 ml. Nessler cylinder if the test is to be completed colorimetrically, or into a 50 ml. standard flask if it is to be completed photometrically. Wash the residue of sodium sulphate by decantation with small portions of chloroform, and add these to the Nessler cylinder or standard flask. Dilute to 50 ml. with further chloroform in either case, and mix well.

Treat an 80 ml. portion of solution C in exactly the same way as solution B, using the same batch of reagents. Determine the copper in the 80 ml. extract from B ('test solution') and the extract from C ('blank solution') either colorimetrically or photometrically.

8.2231 Colorimetric determination. Prepare a series of standards by adding 2.0, 4.0, 6.0 and 8.0 ml. of standard copper sulphate solution to 25 ml. of water. Add a slight excess of ammonium hydroxide solution and 10 ml. of sodium diethyldithiocarbamate solution, and then extract the copper complex with chloroform as described above. Transfer the chloroform solutions to 50 ml. Nessler cylinders, dilute each to the mark with chloroform, and compare the yellowish brown colours with that of the test solution in order to determine the approximate copper content of the latter.

Then prepare in the same way a second series of standards whose copper contents differ in amounts equivalent to 0.5 ml. of standard copper sulphate solution, and which cover a range that includes the test solution. Compare the colours with that of the test solution in order to determine more precisely its copper content.

If the colour of the test solution is equivalent to more than 10 ml. of standard copper solution, then it will be too deep for accurate matching, and an aliquot portion which on dilution to 50 ml. with chloroform has an intensity of colour less than this must be used for the comparison.

Carry out a similar determination on the 'blank solution' and apply the resulting correction to the result obtained above.

Instead of using a standard series of solutions, the colour of the test solution may be matched against standard glass colour disks in a suitable instrument such as a comparator, the blank solution being placed in the compartment under the colour disk. The reading corresponding to the matching disk then gives directly the number of micrograms of copper present in the sample.

8.2232 Photoelectric (absorptometric) determination. For this determination a photoelectric absorptometer is used.

Prepare a series of standards by adding 0, 0.5, 1.0, 2.0, 3.0 and 4.0 ml. of standard copper sulphate solution to 25 ml. of water. Extract the copper exactly as described in Clause 8.2231, finally diluting each dried chloroform extract to 50 ml. in a measuring flask. Measure the optical density of each chloroform extract on the absorptometer, at 50 ml. dilution, using a cell of 4 cm. optical depth and suitable blue filters, against the first solution (containing no added copper) as reference solution. Plot a graph with parts per million of copper (or micrograms copper, if preferred) as abscissa, and optical densities as ordinates. With a reliable instrument and suitable filters the curve is a straight line. It may be considered valid for about six months, when it should be checked.

Similarly, measure the optical density of the test solution, against the blank solution as reference solution, and obtain from the graph the copper content of the sample, corresponding to this reading.

References.

1. N. Strathford, P. F. Wyatt and F. G. Kershaw, *Analyst*, 1945, 70, 232-246.
2. H. J. Vaughan, *The Use of the Spekker Photoelectric Absorptometer in Metallurgical Analysis*. Institute of Chemistry Publication, 1941.

SECTION 8.3 MANGANESE

8.31 Wet oxidation. A weighed test portion (about 2 g.) of the rubber shall be subjected to wet oxidation by the procedure described in Clause 8.11 above.

8.32 Determination of manganese.

8.321 Summary. The manganese in the solution obtained by wet oxidation of the rubber is oxidized to permanganate by means of potassium periodate, and the permanganate determined either colorimetrically or photometrically.

8.322 REAGENTS

Hydrogen peroxide solution: 30 g. H_2O_2 in 100 ml. ('100-volume' solution).

Manganese standard solution. Measure 50.0 ml. of 0.1N potassium permanganate solution into a 250 ml. beaker, add a few drops of dilute sulphuric acid (1 vol. concentrated acid to 1 vol. water). Heat to boiling and then add a saturated solution of sulphur dioxide in water, drop by drop, until the solution is just decolorized. Boil for 15 minutes and add 5 ml. of dilute sulphuric acid. Cool and transfer the solution to a 500 ml. measuring flask, dilute to the mark with water at 20°C. and mix well. Call this solution X; 1 ml. of solution X $\equiv$ 0.0001 g. manganese. Prepare this solution freshly at least once a month.

Measure 100.0 ml. of solution X into a 500 ml. measuring flask, dilute to the mark with water at 20°C. and mix well. Call this solution Y; 1 ml. of solution Y $\equiv$ 0.00022 g. manganese. Solution Y shall be freshly prepared as required.

Nitric acid, concentrated, sp. gr. 1.42.

Phosphoric acid, sp. gr. 1.75.

Potassium periodate.

Potassium permanganate.

'Stabilized' water. Assemble a distillation apparatus consisting of a round-bottomed litre flask connected via an efficient splash head to a Liebig condenser with standard ground glass joints. Introduce 500-600 ml. of ordinary distilled water into the flask, add about 0.1 g. of potassium permanganate previously dissolved in 5 ml. of water and a few drops of dilute sulphuric acid, and distil carefully into a clean receiver, rejecting the first 50 ml. of distillate and taking care that there is no carry-over by splashing or otherwise of liquid from the flask.

Sulphuric acid, concentrated, sp. gr. 1.84.

Sulphuric acid, dilute: 1 vol. concentrated acid to 1 vol. water.

Note. All reagents used should be of recognized analytical reagent quality. Distilled water should always be used except when 'stabilized' water is specified.

8.323 PROCEDURE. Filter the solution obtained from wet oxidation (Clause 8.11) through a No. 1 Whatman filter paper into a 100 ml. standard flask, washing with small amounts of water, dilute to the mark at 20°C. and mix well. Call this solution D.

A blank solution also is required and is prepared by adding 5 ml. of concentrated sulphuric acid, and the same amounts of nitric acid and hydrogen peroxide solution as were used in the oxidation of the sample, to a 100 ml. Kjeldahl flask and boiling the mixture down to fuming. Allow to fume for about 20 minutes and evaporate twice with 5 ml. portions of water. Finally cool, dilute with 25 ml. of water, boil, cool,

transfer to a 100 ml. standard flask and dilute to the mark at 20°C. Call this solution E.

Transfer 50 ml. of solution D and 50 ml. of solution E to two separate 100 ml. conical flasks; add 2 ml. of phosphoric acid and evaporate to fuming. Treat with a few drops of concentrated nitric acid and hydrogen peroxide solution to make sure that all traces of organic matter have been destroyed, and evaporate the solution twice to fuming after adding 10 ml. of 'stabilized' water each time. Dilute to 25 ml. with 'stabilized' water, add 0.2 g. of potassium periodate, boil for one minute, and then heat at about 90°C. for five minutes. Cool to room temperature, adjust the volume to 25.0 ml. with 'stabilized' water, and mix well; the solution so obtained from D is the 'test solution' and that from E is the 'blank solution'. Complete the determination either colorimetrically or photometrically as soon as possible.

8.3231 Colorimetric determination. Prepare a series of standards as follows: Measure 0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml. of standard manganese solution Y into 100-ml. conical flasks, add 4 ml. of dilute sulphuric acid and 2 ml. of phosphoric acid and evaporate to fuming. Add a few drops of a mixture of equal volumes of concentrated nitric acid and hydrogen peroxide solution, and continue as described above for solutions D and E, finally diluting to 25 ml. with 'stabilized' water.

Transfer the test, blank and standard solutions to 25 ml. or 50 ml. matched Nessler cylinders, and compare visually in the usual way. Deduct the blank reading from the test reading, and calculate, from the number of micrograms of manganese found, the manganese content of the sample.

8.3232 Photometric (absorptometric) determination. For this determination a photoelectric absorptometer is used.

Prepare a standard series by measuring 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml. of standard manganese solution Y and continuing as described in clause 8.3231 above, finally diluting to 25 ml. with 'stabilized' water in measuring flasks. Measure the optical density of each solution on the absorptometer, at 25.0 ml. dilution, using a cell of 4 cm. optical depth, and suitable green filters, against the first solution (containing no added manganese) as reference solution. Plot a graph with parts per million (or micrograms, if preferred) of manganese as abscissae and optical densities as ordinates. It may be considered valid for about six months, when it should be checked.

Similarly, measure the optical density of the test solution against the blank solution as reference solution, and obtain from the graph the manganese content of the sample, corresponding to the observed reading.

B.S. 903, Part 9 : CARBONATE

SECTION 9.1 SUMMARY

The acetone-extracted rubber is treated with hydrochloric acid ; the carbon dioxide evolved is drawn in a current of air through a purifying train and is finally absorbed in soda-lime contained in a previously weighed tube, the increase in weight of the tube being taken as the weight of carbon dioxide evolved.

SECTION 9.2 METHOD

9.21 Reagents.

Soda-lime, preferably of a self-indicating type.

Hydrochloric acid, dilute; 1 vol. concentrated acid (sp. gr. 1.18) to 1 vol. water.

Copper sulphate, saturated aqueous solution.

Silver nitrate solution; 2 g. in 100 ml. water.

Silica gel.

Note. All reagents used should be of recognized analytical reagent quality.

9.22 Apparatus. A diagram of the apparatus is shown in Fig. 9.1. It shall consist of a 300 ml. flask fitted with an upright condenser and a dropping funnel, the stem of which shall reach nearly to the bottom of the flask. An absorption tube A packed with soda-lime shall be connected to the dropping funnel. The top of the condenser shall be connected to an absorption train as follows:—

B₁, B₂ 2 absorption bottles containing copper sulphate solution.

C An absorption bottle containing silver nitrate solution.

D₁, D₂ 2 U-tubes packed with silica gel.

E A U-tube packed with soda-lime and having a thick layer of silica gel over the soda-lime in the outlet limb.

The absorption train shall be connected to a water pump through an absorption tower packed with silica gel.

9.23 Procedure. Test the apparatus and determine the blank of the apparatus before performing any estimation. It is essential to re-determine the blank when any of the absorbents have been renewed. It is desirable to confirm the blank should the apparatus have been standing idle for some time even though the system has been sealed from the atmosphere by adjustment of the stop-cocks.

To determine the blank of the apparatus the procedure is as follows:—

Weigh the absorption tube E before assembling the apparatus as described. Close taps *a* and *e*, remove the soda-lime tube A from the

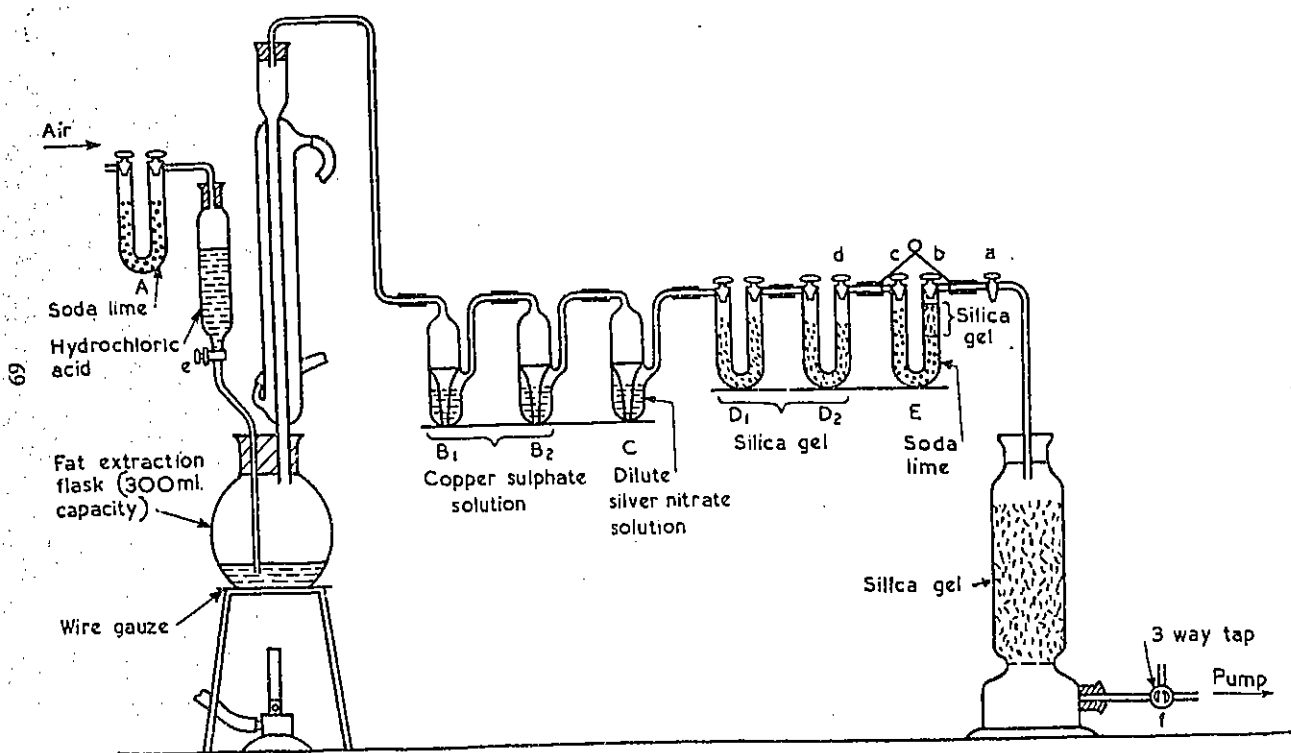


Fig. 9.1 Apparatus for the determination of carbonate

dropping funnel and pour 100 ml. of dilute hydrochloric acid into the latter. Replace the soda-lime tube A. On opening tap *e* liquid should not flow into the flask. Open tap *a* and connect the apparatus to the pump, adjusting tap *f* so that a current of air at the rate of two bubbles per second is drawn through the apparatus. Heat the acid in the flask with a small flame and continue to draw air through the apparatus for one hour. Disconnect the pump by closing tap *f* and, when bubbling of air through the liquid in the flask has ceased, close taps *a* and *e* to isolate the apparatus. Close taps *c* and *d* to seal the absorption tube E, disconnect and weigh. The increase in weight of the absorption tube should not exceed 1 mg.

In the main determination extract 1 g. of the sample with acetone as described in B.S. 903, Part 2, Section 2.1, Acetone extract. Dry in air at 70–100°C., and introduce into the 300-ml. flask. The subsequent operations are as described above in the determination of the 'blank' for the apparatus.

Deduct the increase in weight of the absorption tube in the determination of the 'blank' from that obtained in the main determination, to obtain the corrected weight of carbon dioxide.

9.24 Expression of results. The result for the determination of carbonate shall be reported as the corrected weight of carbon dioxide expressed as a percentage of the weight of the original (unextracted) test portion.

See *Hand 3*

B.S. 903 : Part 10 : 1950

B.S. 903, Part 10 : GLUE

SECTION 10.1 EXPLANATORY NOTE

Glue is sometimes incorporated in natural rubber vulcanizates in order to improve oil-resistance. With oil-resisting synthetic rubbers the older method of determining glue by determination of nitrogen is no longer applicable, and in qualitative and quantitative analysis care must be exercised to avoid confusion of nitrogen-containing acrylonitrile or cyanoprene copolymers and natural rubber compounds containing glue.

Glue will probably be less used in the future, but it may still be necessary to make an estimation. If it is known that the mix is based on natural rubber exclusive of other polymers, then estimation of nitrogen by the method described below is possible.

This method is a form of the Kjeldahl method. The rubber is oxidized by heating with a mixture of potassium sulphate and concentrated sulphuric acid plus a catalyst, thereby converting nitrogen compounds into ammonia, which is then estimated by making the reaction mixture alkaline, distilling off the ammonia, absorbing this in a boric acid solution, and titrating with hydrochloric acid.

SECTION 10.2 METHOD

10.21 Reagents.

Boric acid solution. Dissolve 40 g. of boric acid in water, warming if necessary, and make up the volume to 2 litres. Add 20 ml. of indicator solution and mix well. The solution keeps for at least three months without deterioration.

Copper sulphate; or selenium and mercuric acetate.

Hydrochloric acid, 0.1 N solution.

Indicator solution: 0.125 g. methyl red and 0.083 g. methylene blue in 100 ml. alcohol.

Potassium sulphate, anhydrous.

Sodium hydroxide solution: 40 g. in 100 ml. water.

Sulphuric acid, concentrated, sp. gr. 1.84.

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

10.22 Procedure. Weigh accurately about 1 g. of the sample and extract with acetone and chloroform as described in B.S. 903, Part 2, Sections 2.1 and 2.4.

Remove the excess solvent from the extracted test portion by drying at 70–100°C. for about one hour, then transfer to a clean, dry, 250 ml. Kjeldahl flask. Add 10 g. of anhydrous potassium sulphate, 0.5 g. of copper sulphate or selenium and mercuric acetate, and finally 25 ml. of concentrated sulphuric acid.

NOTE. Alternatively, a larger flask, 800–1000 ml., may be used so as to avoid the need for a subsequent transference of the contents to a second flask.