AMD 1016 (104)

# Amendment Slip No. 1, published 5 September, 1972

## to BS 4398 : 1969

## Compounding ingredients for rubber test mixes

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## Revised text

**Contents page.** Add the following to precede ' Co-operating organizations '.

' CONTENTS

Co-operating organizations
Foreword

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5. Dibenzthiazyl disulphide (MBTS)
6. *N*-Cyclohexyl-2-benzthiazyl sulphenamide (CBS)
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8. Tetramethyl thiuram disulphide (TMTD)
9. Ethylene thiourea
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**New Clauses.** Add the following new clauses to follow Clause 9.

## 10. MAGNESIUM OXIDE

***10.1 Description.*** *The material shall be a dry, soft powder of the active type* known commercially as ' light calcined magnesia '. It shall be readily dispersible in rubber.

NOTE. Owing to the hygroscopicity of magnesium oxide, exposure to atmosphere should be avoided, and the material should be stored in sealed polyethylene liners or other suitable packages.

**10.2 Residue on sieve.** When tested by the method described in Appendix S, the material shall comply with the following requirements:

| | |
|---|---|
| Retained on 125 μm test sieve* | 0·05 % max. |
| Retained on 63 μm test sieve* | 0·20 % max. |
| Retained on 45 μm test sieve* | 0·50 % max. |

**10.3 Requirements.** The material shall conform to the following requirements when tested by the appropriate method of test.

| | | *Method* |
|---|---|---|
| Magnesium oxide | 92·0 % min. | Appendix T |
| Copper | 10 p.p.m. max. | Appendix B |
| Manganese | 50 p.p.m. max. | Appendices C and U |
| Loss on ignition | 6·0 % max. | Appendices E and V |
| Calcium oxide | 2·0 % max. | Appendix W |
| Acetic acid insolubles | 0·2 % max. | Appendix G |
| Water soluble matter | 1·0 % max. | Appendices F and X |
| Combined oxides ($R_2O_3$) | 0·2 % max. | Appendix Y |
| Iodine adsorption number | 40 min. | Appendix Z |

NOTE. An iodine adsorption number of 40 is reasonably in line with a surface area of 35 $m^2/g$ measured by the nitrogen adsorption method given in Appendix A of this standard.

## 11. COATED SULPHUR

**11.1 Description.** The material shall consist essentially of finely ground rhombic sulphur together with basic magnesium carbonate. It shall be readily dispersible in rubber.

**11.2 Sieve analysis.** When tested by a dry method described in BS 1796† the material shall meet the following requirements:

| | |
|---|---|
| Retained on 125 μm test sieve* | 0·01 % max. |
| Retained on 63 μm test sieve* | 10 % min. |

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* Complying with BS 410, ' Test sieves '.

† BS 1796, ' Methods for the use of British Standard fine-mesh test sieves '.

**11.3 Requirements.** The material shall contain 2·5 ± 0·2 % of basic magnesium carbonate and shall conform to the following requirements when tested by the appropriate method of test.

| | | *Method* |
|---|---|---|
| Ash | 1·20–1·45 % | Appendix E |
| Carbon | 0·05 % max. | BS 4113* |
| Acidity | Nil | BS 4113* |
| Matter insoluble in carbon disulphide | 2·6 ± 0·2 % | Appendix M |
| Copper | 10 p.p.m. max. | Appendix B |
| Manganese | 50 p.p.m. max. | Appendix C |

NOTES ON REQUIREMENTS

1. The carbon content of the sulphur is determined as in BS 4113* after the removal of the magnesium carbonate by treating with dilute acid followed by washing and drying.
2. The carbon disulphide insoluble fraction is the nett insoluble, and includes both the ash content of the sulphur together with the magnesium carbonate.
3. The ash value includes both the ash resulting from the sulphur and the magnesium oxide produced by calcination of the magnesium carbonate.

## 12. NAPHTHENIC OIL

**12.1 Description.** A mineral oil of which the viscosity-gravity constant (VGC) *lies between the limits 0·840 to 0·905.*

NOTE. The viscosity-gravity constant is defined as follows:

$$\mathrm{VGC} = \frac{d - 0{\cdot}24 - 0{\cdot}022 \log (V - 35{\cdot}5)}{0{\cdot}755}$$

where $d$ = relative density at 15·6 °C
and V = Saybolt universal viscosity at 99 °C.

**12.2 Requirements.** The material shall conform to the following requirements when tested by the appropriate method of test.

| | | *Method* |
|---|---|---|
| Viscosity at 99 °C | 15·4 cSt to 19·5 cSt | BS 4708† |
| Flash point (Cleveland open cup) | 216 °C min. | BS 4689‡ |
| Pour point | − 4 °C max. | BS 4452§ |
| Aniline point | 60–80 °C | BS 4715¶ |
| Refractivity intercept | 1·048–1·061 | Appendix AA |

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* BS 4113, ‘ *Methods of test for sulphur* ’.
† BS 4708, ‘ Viscosity of transparent and opaque liquids (kinematic and dynamic viscosities) ’.
‡ BS 4689, ‘ Flash and fire points by Cleveland open cup ’.
§ BS 4452, ‘ Method for determination of pour point of petroleum oils ’.
¶ BS 4715, ‘ Aniline number of petroleum products ’.

| Clay-gel analysis % by mass | | |
|---|---|---|
| Asphaltenes | 0·1 % max. | Appendix BB |
| Resins | 7·0 % max. | |
| Aromatics | 40–60 % | |
| Saturates | 55–35 % | |
| Copper | 10 p.p.m. max. | Appendix B |
| Manganese | 10 p.p.m. max. | BS 903*, Part B15 |

NOTE. 1 centistoke (cSt) = $10^{-5}$ $m^2/s$.

### 13. SRF BLACK

**13.1 Description.** Semi reinforcing black made by the furnace process.

**13.2 Availability.** Because of the impracticability of defining all the necessary properties of an SRF black to ensure adequate uniformity this compounding ingredient is available as a standard blended batch whose uniformity has been carefully controlled.

NOTE. This standard SRF black is available as BSI–SRF No. 1 Control from Philblack Limited.

**New Appendices.** Add the following new Appendices and Figures to follow Appendix R.

## APPENDIX S

### DETERMINATION OF SIEVE RESIDUE USING THE GALLIE-PORRITT APPARATUS

**S.1 Apparatus.** The apparatus consists of a metal funnel A (see Fig. 3), about 200 mm diameter, terminating at the foot in a short cylindrical outlet, in which is inserted a shallow removable cup B, on the bottom of which a wire cloth sieve C is soldered; this is 25 mm in diameter. Water under pressure is supplied by a tube D fitted with a nozzle designed to discharge a spreading jet through the sieve; the distance of the orifice from the sieve can be adjusted. The recommended minimum water pressure is 2 bar†. The tube is provided with a filter H to remove any solid particles from the water; this filter must be made from wire cloth at least as fine as sieve C, and must be sufficiently large to prevent undue loss of pressure.

A similar arrangement is provided for another tube E used to supply a gentle stream of water for wetting the powder and keeping the volume of the liquid in the funnel constant during the test.

NOTE. Details of a satisfactory, but more elaborate, apparatus are described in BS 3483, ' Methods of testing pigments for paints ', Part B4, ' Determination of residue on sieve by a mechanical threshing procedure '.

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* BS 903, ' Methods of testing vulcanized rubber ', Part B15, ' Determination of manganese '.

† 1 bar = $10^5$ $N/m^2$.

**S.2 Procedure.** Mount a sieve cup with wire cloth of the required mesh in the apparatus and allow water to flow through it for 3 min. Examine the sieve for particles; if none are observed the apparatus is ready for use.

Dry the sieve cup at 105 ± 2 °C, weigh and mount in the apparatus, holding in place by union nut G.

Weigh about 25 g of the sample accurately to 0·1 g, make into a slurry with water in a beaker, and transfer quantitively to the funnel. About half fill the funnel with water from tube E. Slowly turn the high pressure jet D on full and adjust the position of the nozzle under the liquid, in relation to the sieve, until there is little or no disturbance on the surface, and the level is, if anything, sinking. Now use the supply from E to maintain the level constant, and to wash down any solid matter adhering to the sides.

NOTE. When the best operating conditions have been so attained the discharge pipe F below the sieve is completely filled with water; increasing the length of this column of liquid by adding a length of rubber pipe improves the efficiency of the apparatus.

Take samples of the issuing water from time to time during the test, and when this is free from suspended matter, reduce the rate of flow of the jet. Wash down any residual material adhering to the sides of the funnel into the lower portion of the apparatus, and then adjust the jet to a rate which keeps the cylindrical portion full of violently agitated water. When the residual matter has been thoroughly washed in this way until the effluent runs clear (usually 3–4 min), turn off the jet and wash the grit down into the cup. Unscrew the milled union nut G, remove the discharge pipe and cup, and wash the contents of the latter with distilled water. Dry the cup and contents at 105 ± 2°C and weigh (see Note). This mass, less the initial mass of the cup, equals the mass of the sieve residue.

NOTE. Alternatively, the contents of the cup may be transferred, using a fine jet of water from a wash bottle, to a weighed watch-glass or metal dish, which is then dried as above.

**Calculation**

Percentage sieve residue, $= \dfrac{M}{S} \times 100$

where $M$ = mass of residue retained on sieve in grams,

$S$ = mass of test portion in grams.

## APPENDIX T

## DETERMINATION OF MgO CONTENT OF MAGNESIUM OXIDE

**T.1 Principle.** Volumetric titration with ethylenediamine tetraacetic acid (sodium salt). This titration gives the sum of magnesium and calcium oxides; the latter is determined separately (see Appendix W) and a corresponding correction applied.

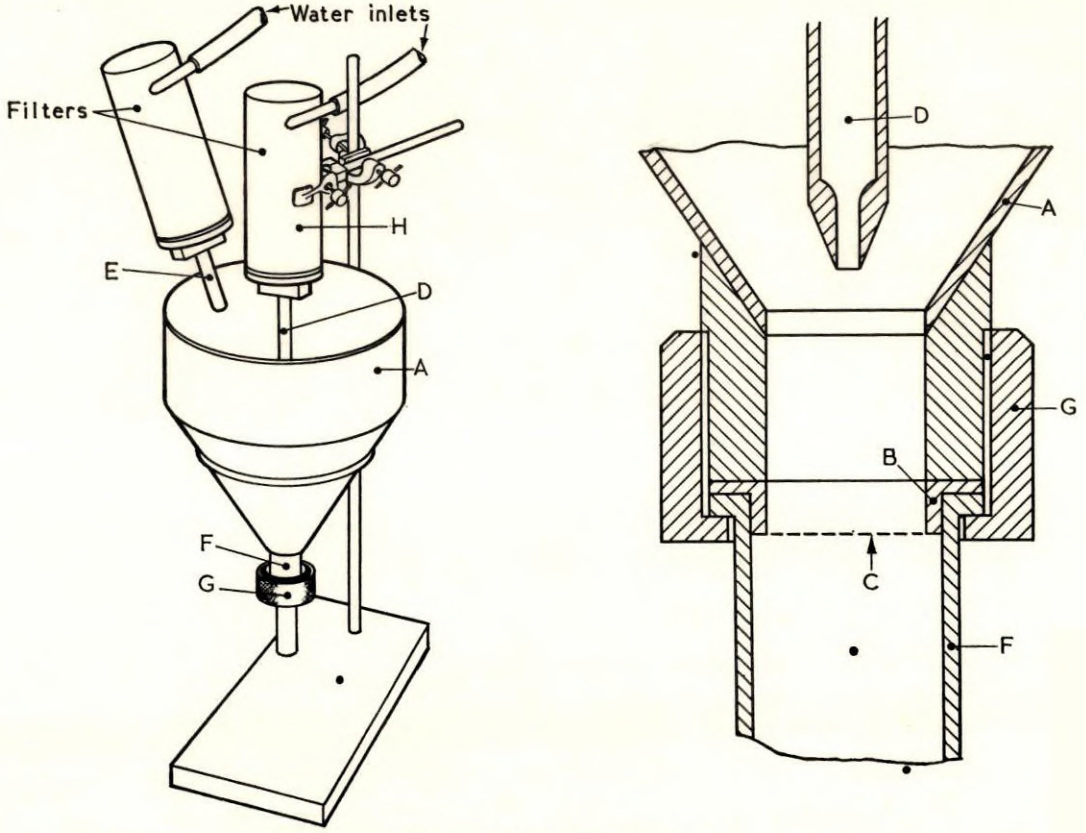

Fig. 3. Gallie-Porritt apparatus

**T.2 Reagents.** All reagents shall be of a recognised analytical quality. The water shall comply with BS 3978*.

(1) *Hydrochloric acid*, dilute. 1 volume of hydrochloric acid ($d = 1{\cdot}18$) plus 3 volumes of water.

(2) *Buffer solution, pH 10.* Dissolve 68 g of ammonium chloride in approximately 300 ml of water. Add 570 ml of ammonium hydroxide ($d = 0{\cdot}88$) and dilute to 1 litre with water.

(3) *EDTA solution* 0·01M. Dissolve 3·73 g of the di-sodium salt of ethylenediamine tetraacetic acid (EDTA) in water and dilute to 1 litre. Store in a polyethylene container. Standardize, by the procedure described below, against pure magnesium iodate.

(4) *Indicator*. Weigh 0·5 g of Mordant black 11† and dissolve in about 2 ml of hot water. Add 10 g of sodium chloride, mix thoroughly and dry at 105 ± 2 °C. When dry, add 90 g of sodium chloride and 4·5 g of hydroxylamine hydrochloride (hydroxy-ammonium chloride) and grind thoroughly.

NOTE 1. If desired the 2 ml of water and the 10 g of sodium chloride may be increased provided the total weight of sodium chloride does not exceed 100 g.

Alternatively, add 0·5 g of Mordant black 11† to 100 ml of industrial methylated spirit, warm to dissolve the dyestuff and add 4·5 g of hydroxylamine hydrochloride (hydroxy-ammonium chloride). Allow to stand overnight and filter. This indicator will not keep for more than one month.

NOTE 2. It is permissible to use commercially available indicator tablets based on the indicator specified above.

(5) *Magnesium iodate tetrahydrate* $Mg(IO_3)_2.4H_2O$.

### T.3 Procedure

**3.1 Standardization of EDTA solution.** Weigh accurately about 1·25 g of magnesium iodate tetrahydrate (mass = $M_1$), dissolve in water and dilute to 250 ml in a one-mark volumetric flask.

Pipette 25 ml of the solution into a conical flask. Dilute to approximately 100 ml with water; add 2 ml of buffer solution followed by 0·2 g or 6 drops of indicator.

Titrate with 0·01 M EDTA solution to a clear blue colour (absence of red); volume of EDTA solution used = $V_1$ml.

$$\text{Molarity of EDTA solution, } X = \frac{M_1}{4{\cdot}462\ V_1}$$

**3.2 Determination of MgO.** Weigh accurately about 0·5 g of the sample (mass = $M_2$), make into a slurry with water and dissolve by addition of a slight excess of

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* BS 3978, ' Water for laboratory use '.

† See BS 4123, ' Schedule of preferred chemical indicators '.

dilute hydrochloric acid. Warm, if necessary, to ensure complete dissolution of the magnesium oxide. Dilute to 1 litre in a volumetric flask.

Pipette 25 ml of the solution into a conical flask. Dilute to approximately 100 ml with water. Add 2 ml of buffer solution followed by 0·2 g or 6 drops of indicator. The colour of the solution should be wine-red.

Titrate with 0·01M EDTA solution to a clear blue colour (absence of red). Volume of EDTA solution used = $V_2$ ml. This titrates magnesium plus calcium ions.

**T.4 Calculation.** MgO + CaO (expressed as MgO), as % of sample = $\frac{161\cdot3\ V_2X}{M_2}$

Make an allowance for the calcium oxide content, determined gravimetrically as described in Appendix W, as follows (see Note):

Above (CaO + MgO) value = (CaO % × 0·718) = MgO, %.

NOTE. Owing to the large excess of magnesium oxide over calcium oxide, a separate determination of the latter is preferred, as opposed to EDTA titration of calcium oxide.

## APPENDIX U

## DETERMINATION OF MANGANESE IN MAGNESIUM OXIDE

Proceed by the method described in Appendix C, but with the following modification of Clause C.2.1, paragraph 1: ‘ Weigh, to the nearest 0·01 g, about 5 g of the sample and place in a conical flask. Dissolve in 20 ml of nitric acid, dilute to between 75 and 100 ml with distilled water, and boil for 5 minutes. Filter and add 5 ml of orthophosphoric acid ’.

## APPENDIX V

## DETERMINATION OF LOSS ON IGNITION OF MAGNESIUM OXIDE

Proceed by the method described in Appendix E, but with the following modifications:

1st and 3rd paragraphs: for ‘ 550 ± 25 °C ’ read ‘ 950 ± 50 °C ’.

1st paragraph, line 3: for ‘ 5 g ’ read ‘ 1 g ’.

3rd paragraph, line 2: for ‘ 30 minutes ’ read ‘ 60 minutes ’.

## APPENDIX W

### DETERMINATION OF CALCIUM OXIDE

**W.1 Principle.** Double precipitation of calcium as the oxalate and gravimetric determination after ignition to the oxide.

**W.2 Reagents.** All reagents shall be of recognized analytical quality. Water shall comply with BS 3978*.

(1) *Hydrochloric acid dilute.* 1 volume of hydrochloric acid ($d = 1{\cdot}18$) diluted with 3 volumes of water.

(2) *Ammonium chloride solution*, 10 % $m/v$.

(3) *Methyl orange indicator solution.*

(4) *Ammonium hydroxide solution*, concentrated, $d = 0{\cdot}880$.

(5) *Oxalic acid solution*, 10 % $m/v$.

(6) *Pyridine.*

(7) *Ammonium oxalate*, saturated solution.

**W.3 Procedure.** Dissolve an accurately weighed test portion ($M_1$) of about 2 g in dilute hydrochloric acid in a beaker and add 100 ml of ammonium chloride solution. Make the solution just alkaline to methyl orange with ammonia, add dilute hydrochloric acid slowly with stirring until the methyl orange just turns pink and then add 100 ml of oxalic acid solution. Make up the volume of the solution to approximately 500 ml and add pyridine with constant stirring until the solution *just turns yellow*. Then stand the beaker aside for 1½ hours.

Keep the solution as cool as possible before adding pyridine; this helps to avoid excessive precipitation of magnesium oxalate.

Filter the liquid, preferably through a filter paper†. Drain the liquid as completely as possible from the precipitate without attempting to transfer the precipitate from the filter. After filtration wash the paper once or twice to remove the magnesium salt solution, and then wash thoroughly back into the original beaker with hot dilute hydrochloric acid. After several washings of the filter with distilled water, bring the volume in the beaker to about 500 ml, add 25 ml of ammonium oxalate solution, bring the solution to the boil, make just alkaline to methyl orange with ammonia, stir thoroughly and allow to stand for not less than ½ hour.

Filter off the precipitated calcium oxalate exactly as before, re-dissolve in hydrochloric acid and precipitate once more. Finally filter off, wash thoroughly

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* BS 3978, ' Water for laboratory use '.

† A Whatman No. 30 paper is suitable.

with water and ignite to calcium oxide in a muffle furnace at 800–900 °C for not less than 2 hours. After cooling in a dessicator, weigh the calcium oxide as rapidly as possible ($M_2$) to avoid excessive exposure to the air.

**W.4 Calculation.** Calcium oxide $= \frac{M_2}{M_1} \times 100\,\%$.

## APPENDIX X

## DETERMINATION OF WATER-SOLUBLE MATTER IN MAGNESIUM OXIDE

Proceed by the method described in Appendix F, but with the following modification of the first sentence:

> ' Weigh accurately about 5 g of the sample into a 100 ml beaker and make into a slurry with 20 ml of water at a temperature of 55–60 °C.

## APPENDIX X

## DETERMINATION OF COMBINED OXIDES $R_2O_3$

**Y.1 Explanatory note.** The oxides determined by the method are those corresponding to hydroxides insoluble in ammonium chloride solution, viz, mainly ferric oxide and aluminium oxide.

**Y.2 Reagents.** All reagents shall be of recognized analytical quality. The water shall comply with BS 3978*.

(1) *Hydrochloric acid*, dilute (1 : 1). 1 volume of hydrochloric acid ($d = 1{\cdot}18$) plus 1 volume of water.

(2) *Hydrochloric acid*, dilute (1 : 3). 1 volume of hydrochloric acid ($d = 1{\cdot}18$), plus 3 volumes of water.

(3) *Nitric acid*, concentrated, $d = 1{\cdot}42$.

(4) *Ammonium chloride*.

(5) *Ammonia solution*, dilute. 1 volume of ammonia solution ($d = 0{\cdot}88$) plus 1 volume of water.

(6) *Ammonium nitrate*, 2 % *m*/*v* solution.

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* BS 3978, ' Water for laboratory use '.

**Y.3 Procedure.** Weigh accurately about 20 g of the sample ($M_1$), make it into a slurry with water and dissolve the test portion by the addition of a slight excess of the 1 : 1 hydrochloric acid. Add a few drops of nitric acid and boil for five minutes. Filter if necessary.

Add approximately 50 g of ammonium chloride and dilute to 500 ml. Precipitate the combined hydroxides from the warm, but not hot, solution by the addition of a slight excess of dilute ammonia solution. Add a small amount of filter paper pulp and allow the precipitate to settle.

Filter through a filter paper†, washing once with ammonium nitrate solution.

Dissolve the precipitate from the paper into the original beaker with hot 1 : 3 hydrochloric acid. Wash the paper thoroughly with hot distilled water.

Heat the solution of the precipitate to boiling and re-precipitate as above. Filter through a filter paper‡ and wash with ammonium nitrate solution, followed by a final washing with hot distilled water.

Transfer precipitate and paper to an ignited, weighed alumina or platinum crucible, dry, char and ignite to constant mass $M_2$ at 1100 ± 50 °C.

**Y.4 Calculation.** Percentage $R_2O_3 = \frac{M_2}{M_1} \times 100$.

## APPENDIX Z

### DETERMINATION OF IODINE ADSORPTION NUMBER OF MAGNESIUM OXIDE

**Z.1 Principle of method.** A weighed test portion is mixed vigorously with a measured volume of a standard iodine solution. The mixture is then centrifuged or filtered through a filter crucible. A measured quantity of the clear iodine solution is titrated with a standard solution of sodium thiosulphate. From this titration value and the sample mass, the iodine adsorption number of the test material is calculated.

**Z.2 Reagents.** All the reagents shall be of recognized analytical quality and the water used shall comply with BS 3978*.

(1) *Iodine solution* (0·1N). Dissolve 12·69 g of iodine in 1 litre of carbon tetrachloride. Standardize with the 0·05N sodium thiosulphate solution.

(2) *Sodium thiosulphate solution* (0·05N). Dissolve 0·992 g of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$), weighed to the nearest 0·1 mg, in

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* BS 3978, ' Water for laboratory use '.

† A Whatman No. 4 filter paper is suitable.

‡ A Whatman No. 30 filter paper is suitable.

approximately 500 ml of water in a one-litre volumetric flask. Add 5 ml of pentan-1-ol and shake the solution in the flask to mix thoroughly. Dilute to 1000 ml with water. Shake the solution in the flask vigorously to ensure uniform dilution.

(3) *Starch indicator solution* complying with BS 4123*.

### Z.3 Apparatus

(1) *Bottles*, glass, optically clear, with polyethylene or glass stoppers, about 200 ml capacity, or

(2) *Weighing bottles*, tall form, 200 ml capacity, cap style stoppers, with joint surfaces coated with silicone high vacuum grease.

(3) *Burette*, 50 ml complying with the requirements of BS 846†, Class A.

(4) *Pipettes*, 20 ml and 100 ml, complying with the requirements of BS 1583|| Class A.

(5) *Centrifuge*, capable of speeds above 1000 r.p.m., or

(6) *Filter crucibles*, porcelain, chemically inert to iodine.

(7) *Balance*, analytical; with a sensitivity of 0·1 mg.

**Z4. Procedure.** Weigh about 2 g of the sample to the nearest 0·1 mg and place in the glass bottle or weighing bottle.

Pipette 100 ml of iodine solution into the bottle and stopper immediately. Shake the bottle vigorously for 30 minutes at no less than 120 excursions per minute. Thorough mixing of the magnesia and iodine solution is necessary.

NOTE. If mechanical shakers are used, 240 vigorous excursions per minute are recommended. The Griffin flask shaker and similar equipment is suitable for this procedure.

If the bottle is shaken by hand, experience has shown that it may be necessary to cool it under running water to avoid the evaporation of the solvent and consequent build up of pressure in the bottle.

Immediately after shaking, separate the magnesium oxide from the iodine solution by centrifuging at a speed above 1000 rev/min. Immediately after centrifuging, decant the iodine solution completely, in one smooth movement into a 250 ml beaker, leaving the magnesium oxide in the bottom of the bottle.

Alternatively use a filter crucible to separate the magnesium oxide from the solution after the mixture has been allowed to stand for five minutes. Filter with light suction through the clean dry filter crucible into a clean, dry test tube (about 20 mm × 200 mm) placed under the end of a crucible holder inside a 1000 ml filtering flask. The end of the crucible holder should be above the surface of the solution in the test tube after filtering.

NOTE. In some cases the two procedures of separation do not give the same results and the procedure used should therefore be stated in the test report.

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* BS 4123, ' Schedule of preferred chemical indicators '.

† BS 846, ' Burettes and bulb burettes '.

|| BS 1583, ' One-mark pipettes '.

Immediately after decanting or filtering, pipette 20 ml of the solution into a 250 ml conical flask. Titrate the iodine solution with the sodium thiosulphate solution until a pale yellow colour remains. Add approximately 5 ml of the starch indicator solution and continue titrating until one drop of the sodium thiosulphate solution causes the blue colour to change to colourless. Read the burette to the nearest 0·1 ml.

Make a blank determination using the same reagents but omitting the magnesium oxide.

**Z.5 Expression of results.** Calculate the iodine adsorption number in milligrams of iodine per gram of magnesium oxide as follows:

$$I = (B - S)\frac{\mathrm{N}}{M} \times \frac{100}{20} \times 126{\cdot}9$$

where: $I$ = iodine adsorption number in milligrams of iodine per gram of magnesium oxide,

$B$ = volume of the sodium thiosulphate solution (in millilitres) required for titration of the blank,

$S$ = volume of the sodium thiosulphate solution (in millilitres) required for titration of the sample,

$M$ = mass of test portion (in grams),

$\mathrm{N}$ = normality of the sodium thiosulphate solution.

## APPENDIX AA

## DETERMINATION OF REFRACTIVITY INTERCEPT

The refractivity intercept of an oil is calculated from the formula

Refractivity intercept = $n_{\mathrm{D}}^{20} - 0{\cdot}5\, d^{20}$

where: $n_{\mathrm{D}}^{20}$ = refractive index for the sodium D line at 20 °C, determined as described in BS 684*,

$d^{20}$ = density at 20 °C (Mg/m$^3$), determined by Method 1 of BS 684*.

## APPENDIX BB

## ANALYSIS OF RUBBER PROCESSING OILS BY THE CLAY-GEL ADSORPTION CHROMATOGRAPH METHOD

**BB.1 Principle.** The method uses a chromatographic adsorption on clay and silica gel to split the oil into a resinous highly polar fraction containing most of

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* BS 684, ' Methods of analysis of oils and fats '.

the heterocyclic molecules, a relatively non-polar aromatic fraction and a saturates fraction containing the naphthenic and paraffinic hydrocarbons. Asphaltenes are separated as matter insoluble in n-pentane, which may also include insoluble resinous bitumens produced by the oxidation of the oil.

**BB.2 Summary of method.** The test portion is dissolved in n-pentane and the insoluble matter filtered off and weighed. The soluble part is charged into a glass percolation column containing clay in the upper section and silica gel plus clay in the lower section. The column is washed with n-pentane to collect the saturates which are not adsorbed on either the clay or silica gel under the conditions specified. The upper clay section is removed from the lower silica gel section and washed further with a 1:1 benzene-acetone mixture to collect the polar compounds, the result is adjusted to compensate for any variation in the volatiles content of the clay. The aromatics, which are adsorbed on the silica gel, are calculated by difference. When the n-pentane insoluble content is known to be less than 1 % by weight, the sample can be charged into the column without any previous treatment.

### BB.3 Apparatus

(1) *Clay-gel column*; as illustrated in Fig. 4.

(2) *Beaker*, 400 ml capacity.

(3) *Beaker*, 100 ml capacity.

(4) *Büchner filter*, glass, 60 mm diameter, 150 ml capacity fitted with a porosity 4 filter disc complying with BS 1752*.

(5) *Glass funnel*, 100 mm diameter, analytical type, complying with BS 1923†.

(6) *Aluminium foil dish*, 60 mm diameter, 16 mm deep.

(7) *Electric muffle furnace*, capable of maintaining a uniform temperature of 290 ± 15 °C.

(8) *Separating funnel*, 500 ml capacity complying with BS 2021.‡

(9) *Filter paper*, fine texture, 185 mm diameter.

(10) *Glass beads*, diameter about 3 mm.

(11) *Conical flask*, 250 ml capacity.

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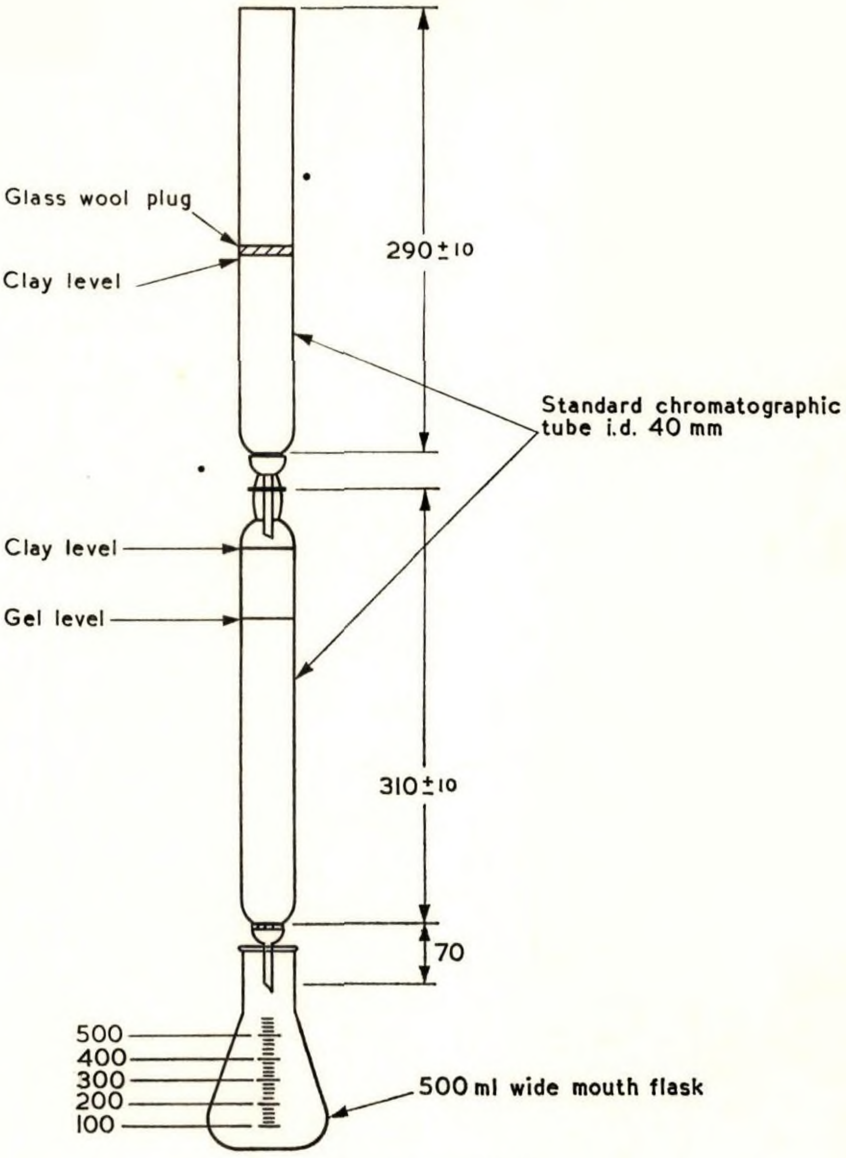
* BS 1752, ' Laboratory sintered or fritted filters '.
† BS 1923, ' Glass filter funnels '.
‡ BS 2021, ' Separating and dropping funnels '.



All dimensions in millimetres

**Fig. 4. Clay-gel column for chromatographic analysis of rubber processing oils**

**BB.4 Reagents.** The reagents used shall be of recognised analytical quality.

(1) *Acetone.*

(2) *Benzene.*

(3) *Benzene-acetone mixture* (equal volumes).

(4) *n-Pentane.*

(5) *Calcium chloride*, anhydrous granules.

(6) *Clay adsorbent*, 30–60 mesh (250–500 μm) containing 11·0–13·0 % by mass of volatiles at 290 °C. A suitable material is available from Englehard Minerals and Chemicals Division, Menlo Park, New Jersey, USA as 30–60 Mesh clay for use in ASTM method D2007.

(7) *Silica gel*, 28–200 mesh (75–550 μm), activated before use by drying at 160 °C for 8 hours; suitable materials are marketed by F. L. Cox & Co., Joseph Crosfield, and W. R. Grace (Silica Gel Division).

**BB.5 Clay volatiles correction.** Heat the aluminium foil dish in the furnace at 290 ± 15 °C for 1 hour. Cool in a desiccator and weigh to the nearest 1 mg.

Place about 5 g of clay in the dish, spread the clay over the bottom of the dish and weigh to the nearest 1 mg.

Heat the dish and contents in the furnace at 290 ± 15 °C. After 2 hours remove and cool in a desiccator. Reweigh to the nearest 1 mg and calculate the percent mass loss of the clay. This value is used to calculate the corrected polar content of the oil (see Section BB.10).

**BB.6 Sample preparation.** If the n-pentane insoluble content is known to be less than 1 % by mass, proceed with the fractionation as described in Section BB.8. If there is any uncertainty that the n-pentane insoluble content is not below 1 % by mass, determine insolubles as described in Section BB.7.

**BB.7 Determination of insolubles.** Weigh about 10 g of the sample accurately to 0·5 mg in a preweighed 250 ml conical flask. Add 100 ml of n-pentane and mix well. Warm the mixture for a few seconds in a warm water bath and swirl to assist solution. Samples having a high insoluble content may require vigorous agitation to dissolve the n-pentane soluble portion. Allow the mixture to stand about 30 minutes at room temperature.

Filter the mixture (see Note) using a 500 ml suction flask containing glass beads and the pre-weighed Büchner filter. Rinse out the flask twice using 10 ml and 20 ml of n-pentane and pour washings through the filter. Pour about 50 ml of n-pentane through the filter funnel just when the residue appears to be dry on the surface. Wash the inner walls of the filter funnel with 10–20 ml of n-pentane.

Wash the residue with a further 50 ml of n-pentane. Continue aspiration until the residue is relatively dry as shown by cracks.

NOTE. Owing to the low surface tension of n-pentane, and its consequent tendency to run down the outside of the vessel from which it is poured, pouring of solution from one vessel to another should be by decanting down a glass rod.

Transfer in portions the filtrate from the suction flask to a 250 ml conical flask and evaporate the solvent (as outlined in Section BB.9) until 35–50 ml total sample plus solvent remains. Use this recovered material, without adding additional n-pentane, as the charge to the clay gel column as described in Section BB.8.

Reassemble the Büchner filter and empty suction flask and continue aspirating air for at least 45 minutes. Remove the filter plus residue and weigh. Determine n-pentane insoluble by subtracting the mass of the empty filter.

**BB.8 Fractionation.** The chromatograph apparatus should conform as closely as possible to that shown in Fig. 4.

Pack the lower section of the adsorption column with 200 g of silica gel plus 50 g of clay, on top of the silica gel, and 100 g of clay in the upper section of the column. Tap the sections gently to allow the adsorbents to acquire a constant level in the columns. Over the top surface of the clay in the upper column place a piece of glass wool, about 25 mm loose thickness, to prevent agitation of the clay when charging with eluent solvents. Join the sections without lubricating.

If the n-pentane insoluble content has not been previously determined weigh about 10 g of the sample to the nearest 1 mg in a 100 ml beaker. Dilute with 25 ml of n-pentane and mix well to ensure a uniform solution. Add 25 ml of n-pentane to the top of the column and when nearly all the solvent has been absorbed by the clay add the diluted test portion to the column (or where insolubles have been removed as described in Section BB.7, add the recovered material). Wash the beaker (or the flask used to contain the recovered material) with n-pentane and add the washings to the column. Wash the walls of the column above the clay with n-pentane. When the washings have entered the clay add n-pentane to the column and maintain a head level above the clay to wash the saturates portion of the test material through the adsorbent. Loosen the connection joint between the two sections at the start of the eluent entering the lower section in order to promote an even percolation and prevent channelling. Fit the column sections tightly together after a head level of about 5 ml is obtained in the lower section. Collect 250 ± 10 ml of the initial n-pentane effluent from the column in a graduated pre-weighed 500 ml flask provided with glass beads (fraction 1).

Disconnect the two column sections and continue washing the upper clay section with n-pentane. During the washing maintain the n-pentane level above the clay so that it is about 25 mm when 150 ml has been collected in the receiver flask. At this point discontinue additions and allow n-pentane to essentially drain from the column. About 200 ml of n-pentane effluent should be in the receiver and should be discarded.

Charge the benzene/acetone mixture into the upper clay section. Collect 250 ml of the effluent, or until the effluent is practically colourless, in a 500 ml separating funnel. Swirl the separating funnel to assist the water to settle and stand for about 5 minutes. Discard the lower aqueous layer. Add about 10 g of anhydrous calcium chloride granules to the separating funnel and agitate for about 30 seconds. Allow to settle for about 10 minutes. Filter into a pre-weighed 400 ml beaker. Rinse the separating funnel with about 25 ml of n-pentane and filter. Wash the filter paper with about 10–15 ml of n-pentane. Add both filtrates to the mixed solvent fraction (fraction 2).

**BB.9 Removal of solvent.** Gently warm the beakers containing the two fractions (i.e. fractions 1 and 2) over a water bath at 40–60 °C. Place a nitrogen jet about 20 mm above the liquid in each beaker and adjust so that the gas cuts mildly into the surface of the liquid (see Note). When about a quarter of the solvent has evaporated increase the temperature of the bath until the water boils gently. When the solvent has nearly all evaporated place the beakers on a hotplate at low heat. Continue nitrogen sweeping over the residue surfaces while the temperature is increased; avoid overheating and do not allow the residues to smoke.

NOTE. As evaporation of pentane from open vessels involves fire and toxicity risks, it should be carried out in a fume cupboard.

When the residues are solvent-free cool to room temperature. Weigh each beaker and determine the mass of the residues.

### BB.10 Calculations

Asphaltenes, per cent by mass $= \frac{B}{A} \times 100 = G$

Saturates, per cent by mass $= \frac{C}{A} \times 100 = H$

Polar compounds, per cent by mass $= \frac{D}{A} \times 100 = E$

Polar compounds corrected (resins) per cent by mass $= \frac{6{\cdot}5 \times E}{19{\cdot}5 - F} = J$

Aromatics, per cent by mass $= 100 - (G + H + J)$