

BRITISH STANDARD 4398 : 1969

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METRIC UNITS

**SPECIFICATION FOR
COMPOUNDING INGREDIENTS
FOR RUBBER TEST MIXES**

BRITISH STANDARDS INSTITUTION

SPECIFICATION FOR
COMPOUNDING INGREDIENTS
FOR RUBBER TEST MIXES

BS 4398 : 1969

Price 12/- net

BRITISH STANDARDS INSTITUTION

INCORPORATED BY ROYAL CHARTER

BRITISH STANDARDS HOUSE, 2 PARK ST., LONDON, W.1

TELEGRAMS: STANDARDS LONDON W1

TELEPHONE: 01-629 9000

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THIS BRITISH STANDARD, having been approved by the Rubber Industry Standards Committee, was published under the authority of the Executive Board on 10th January, 1969.

SBN: 580 00437 6

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.

A complete list of British Standards, numbering over 5000, fully indexed and with a note of the contents of each, will be found in the British Standards Yearbook, price 15s. The BS Yearbook may be consulted in many public libraries and similar institutions.

This standard makes reference to the following British Standards:

BS 410. Test sieves.

BS 593. Laboratory thermometers.

BS 684. Methods of analysis of fats and fatty oils

BS 684 : Section 1.1. Determination of litre weight in air

BS 684 : Section 1.2. Determination of refractive index

BS 684 : Section 1.6. Determination of titre

BS 684 : Section 2.6. Determination of saponification value

BS 684 : Section 2.7. Determination of unsaponifiable matter

BS 684 : Section 2.10. Determination of acidity, acid value and mineral acidity

BS 684 : Section 2.13. Determination of iodine value

BS 684 : Section 2.35. Analysis by gas-liquid chromatography of methyl esters of fatty acids.

BS 903. Methods of testing vulcanized rubber.

Part A 9. Determination of abrasion resistance.

Part B 15. Determination of manganese.

BS 1225. Recommended methods for polarographic and spectrographic analysis of high purity zinc and zinc alloys for die casting.

BS 1673. Methods of testing raw rubber and unvulcanized compounded rubber.

Part 2. Chemical analysis of raw natural rubber.

BS 1752. Laboratory sintered or fritted filters.

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

BS 3406. Methods for the determination of particle size of powders.

Part 4. Optical microscope method.

BS 3472. Raw styrene-butadiene rubbers (1500 series).

2 A



BS 3630. Methods for the sampling and analysis of zinc and zinc alloys.

Part 5. Iron in ingot zinc and zinc alloys (photometric method).

BS 3650. Raw oil-extended styrene-butadiene rubbers (1700 series).

BS 3978. Water for laboratory use.

BS 4113. Methods of test for sulphur for general industrial use.



'BS 4634. Method for the determination of melting point and/or melting range

This standard also makes reference to the following international standards:

ISO 2393. Rubber test mixes—Preparation, mixing and vulcanization—Equipment and procedures

ISO 6528/1. Rubber—Determination of total sulphur content—Part 1: Oxygen combustion flask method'

British Standards are revised, when necessary, by the issue either of amendment slips or of revised editions. It is important that users of British Standards should ascertain that they are in possession of the latest amendments or editions.

The following BSI references relate to the work on this standard:
Committee reference RUC/25
Draft for comment D65/4441

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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:

British Association of Synthetic Rubber Manufacturers
British Rubber Manufacturers Association Ltd.

Institution of the Rubber Industry

Ministry of Technology

Natural Rubber Bureau

Natural Rubber Producers' Research Association

Rubber Growers' Association

*Rubber and Plastics Research Association of Gt. Britain

Society of Motor Manufacturers and Traders Ltd.

*Tyre Manufacturers Conference Ltd.

The 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:

Association of Fatty Acid Distillers

Chemical Industries Association

Ministry of Defence (Navy Dept.)

Research Association of British Paint, Colour & Varnish
Manufacturers

United Kingdom Carbon Black Distributors Association

Zinc Pigment Development Association

Individual company

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BRITISH STANDARD SPECIFICATION FOR COMPOUNDING INGREDIENTS FOR RUBBER TEST MIXES

FOREWORD

This British Standard has been prepared under the authority of the Rubber Industry Standards Committee.

For various purposes in rubber testing it is necessary to mix and vulcanize experimental batches of compounded rubber. Thus, some standard tests such as that for abrasion resistance (BS 903, 'Methods of testing vulcanized rubber', Part A9, 'Determination of abrasion resistance') require the rubber under test to be compared with a standard rubber; a similar procedure would be useful also in ozone-cracking tests if the standard rubber could be satisfactorily reproduced. Moreover, the evaluation of raw synthetic rubbers may include physical tests on a vulcanized mix (see for instance BS 3472, 'Raw styrene-butadiene rubbers (1500 series)' and BS 3650, 'Raw oil-extended styrene-butadiene rubbers (1700 series)').

Hitherto it has been found difficult to reproduce such experimental batches of rubber. This arises from three main causes:

- (1) Differences between equipment used in different laboratories.
- (2) Variations in procedure.
- (3) Variations in the compounding ingredients used.

Differences in equipment are not readily eliminated and even procedure may be difficult to standardize (for instance the details and conditions of roll mill mixing) but it should be possible to set up standards for compounding ingredients that will render their contribution to test variation insignificant.

The present standard has accordingly been prepared to define the characteristics of certain compounding ingredients commonly required for use in experimental rubber mixes.

SPECIFICATION

1. SCOPE



'This British Standard specifies requirements for compounding ingredients for use in making rubber test mixes but not for use in rubber manufacturing.'

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2. ZINC OXIDE

2.1 Description. The material shall consist of zinc oxide in the form of a dry, soft powder or in such a condition that it may be readily reduced thereto without any grinding action. It shall be readily dispersible in rubber.

2.2 Physical analysis and residue on sieve. When subjected to microscopic examination by the method described in BS 3406, Part 4*, the material shall appear as irregular nodular particles predominantly below $0.5 \mu\text{m}$ in size. The surface area measured by the method described in Appendix A shall be in the range $4.5 \text{ m}^2/\text{g}$ to $6.0 \text{ m}^2/\text{g}$.

When tested by a wet method described in BS 1796† the material shall meet the following requirements:

Retained on $125 \mu\text{m}$ BS test sieve‡,	0.01 % max.
Retained on $63 \mu\text{m}$ BS test sieve‡,	0.1 % max.

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

Lead	0.025 % max.	BS 1225§	} Part II, Section B, 'Method for high purity zinc'
Cadmium	50 p.p.m. max.	BS 1225§	
Iron	50 p.p.m. max.	Appendix R	
Copper	10 p.p.m. max.	Appendix B	
Manganese	50 p.p.m. max.	Appendix C	
Loss on heating	0.25 % max.	Appendix D	
Loss on ignition	0.75 % max.	Appendix E	
Water soluble material	0.2 % max.	Appendix F	
Material insoluble in acetic acid	0.1 % max.	Appendix G	

3. SULPHUR

3.1 Description. The material shall consist of finely ground rhombic sulphur. It shall be readily dispersible in rubber.

* BS 3406, 'Methods for the determination of particle size of powders'. Part 4, 'Optical microscope method'.

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

‡ BS 410, 'Test sieves'.

§ BS 1225 : 1945, 'Recommended methods for polarographic and spectrographic analysis of high purity zinc and zinc alloys for die casting'.

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

Retained on 125 μ m BS test sieve†,	0.01 % max.
Retained on 63 μ m BS test sieve,	10 % min.

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

Ash	0.03 % max.	Appendix E
Carbon	0.05 % max.	BS 4113‡
Acidity	0.01 % max.	BS 4113‡
Matter insoluble in CS ₂	0.1 % max.	Appendix M
Matter volatile at 105 °C	0.1 % max.	BS 4113‡
Copper	10 p.p.m. max.	Appendix B
Manganese	50 p.p.m. max.	Appendix C

4. STEARIC ACID

4.1 Description. The material shall be white in colour and in the form of small flake. It shall be readily dispersible in rubber.

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

Acid value	197 to 199	'BS 684 : Section 2.10 §	
Saponification value	198 to 200	BS 684 : Section 2.6	
Iodine value	1 max.	BS 684 : Section 2.13 ¶	
Titre (solidification point)	65 °C min.	BS 684 : Section 1.6 **	
Unsaponifiable matter	0.5 % max.	BS 684 : Section 2.7 ††	
Stearic acid content (C ₁₈)	95 % min.	Appendix N	
Ash	0.1 % max.	Appendix E	
Mineral acidity—equivalent weight of H ₂ SO ₄ /100 g of sample	0.01 % max.	BS 684 : Section 2.10 §	
		Section B.	
Copper	5 p.p.m. max.	Appendix B	
Manganese	50 p.p.m. max.	Appendix C	

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

† BS 410, 'Test sieves'.

‡ BS 4113, 'Methods of test for sulphur for general industrial use'.

§ BS 684, 'Methods of analysis of fats and fatty oils', Section 2.10, 'Determination of acidity, acid value and mineral acidity'.

|| BS 684 : Section 2.6, 'Determination of saponification value'.

¶ BS 684 : Section 2.13, 'Determination of iodine value'.

** BS 684 : Section 1.6, 'Determination of titre'.

†† BS 684 : Section 2.7, 'Determination of unsaponifiable matter'.

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5. DIBENZTHIAZYL DISULPHIDE (MBTS)

5.1 Description. The material shall be a white to cream coloured powder consisting essentially of dibenzthiazyl disulphide. It shall be readily dispersible in rubber.

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

Retained on 125 μm BS test sieve†, 0.03% max.

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

Melting point	170°C min. (melting range not more than 3 degC)	BS 4634	
Ash	0.25% max.	Appendix E	
Loss on heating	0.25% max.	Appendix D	
Mercaptobenzthiazole	1.0% max.	Appendix J	
Copper	20 p.p.m. max.	Appendix B	
Manganese	100 p.p.m. max.	Appendix C	

6. N-CYCLOHEXYL-2-BENZTHIAZYL SULPHENAMIDE (CBS)

6.1 Description. The material shall be a white to light buff coloured powder consisting essentially of *N*-cyclohexyl-2-benzthiazyl sulphenamide. It shall be readily dispersible in rubber.

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

Retained on 125 μm BS test sieve†, 0.03% max.

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

Melting point	100°C min. (melting range not more than 3 degC)	BS 4634	
Ash	0.25% max.	Appendix E	
Loss on heating	0.75% max.	Appendix D	
Matter insoluble in ether	0.5% max.	Appendix K	
Free amine	0.5% max.	Appendix L	
Copper	20 p.p.m. max.	Appendix B	
Manganese	100 p.p.m. max.	Appendix C	

7. N-TERTIARY-BUTYL-2-BENZTHIAZYL SULPHENAMIDE (TBBS)

7.1 Description. The material shall be a white to light buff coloured powder consisting essentially of *N*-tertiary-butyl-2-benzthiazyl sulphenamide. It shall be readily dispersible in rubber.

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

† BS 410, 'Test sieves'.

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

Retained on 125 μm BS test sieve†, 0.03% max.

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

Melting point	104°C min. (range not more than 3 degC)	BS 4634 [‡]	
Ash	0.25% max.	Appendix E	
Loss on heating	0.75% max.	Appendix D	
Free amine	0.5% max.	Appendix L	
Matter insoluble in ether	0.5% max.	Appendix K	
Copper	20 p.p.m. max.	Appendix B	
Manganese	100 p.p.m. max.	Appendix C	

8. TETRAMETHYLTHIURAM DISULPHIDE (TMTD)

8.1 Description. The material shall be a white to pale cream coloured powder consisting essentially of tetramethylthiuram disulphide. It shall be readily dispersible in rubber.

8.2 Sieve analysis. When tested by a wet method described in BS 1796* the material shall meet the following requirements.

Retained on 125 μm BS test sieve†, 0.03% max.

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

Melting point	145°C min. (range not more than 3 degC)	BS 4634 [‡]	
Ash	0.25% max.	Appendix E	
Loss on heating	0.25% max.	Appendix D	
Copper	20 p.p.m. max.	Appendix B	
Manganese	100 p.p.m. max.	Appendix C	
Water soluble material	0.25% max.	Appendix F	

9. ETHYLENETHIOUREA

 **WARNING.** Some evidence exists to indicate that ethylene thiourea is a possible health hazard, in particular to women of childbearing age. Full recommendations on the necessary precautions are available from the suppliers.

9.1 Description. The material shall be in the form of a dust-free polymer-based masterbatch subdivided into pellets of a suitable size range for easy weighing-out and incorporation into rubber mixes. The material will contain nominally 71.25% ethylene thiourea completely and uniformly dispersed in oil (3.75%) and saturated hydrocarbon polymer (25.00%), all percentages being by mass. The material shall be readily dispersible in rubber using the ISO 2393 standard mixing techniques.

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

Ash	0.3% max.	Appendix E
% Sulphur (total)	21.4% to 23.4%	Schöniger oxygen flask method (ISO 6528/1)

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

† BS 410, 'Test sieves'.

‡ BS 3406, 'Methods for the determination of particle size of powders'. Part 4, 'Optical microscope method'.

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

Melting point	195–205°C (melting range not more than 3 degC)	Appendix H
Ash	0.3 % max.	Appendix E
Light petroleum extract	5 ± 1 %	Appendix P

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.

		<i>Method</i>
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 ₂ O 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 m²/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.

* 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.

		<i>Method</i>
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:

$$\text{VGC} = \frac{d - 0.24 - 0.022 \log (V - 35.5)}{0.755}$$

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.

		<i>Method</i>
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

* 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 BS 903*, Part B15
Manganese	10 p.p.m. max.	

NOTE. 1 centistoke (cSt) = 10^{-6} m²/s.

13. CARBON BLACK

13.1 Description. Industry Reference Black (I.R.B.) of N330 Type made by the furnace process for the rubber industry as an ingredient for test mixes.

13.2 Properties and availability. Because of the difficulty of defining all the necessary properties to ensure adequate uniformity, this compounding ingredient for rubber test mixes is available as a standard blended batch whose uniformity has been carefully checked and controlled.

As each batch of I.R.B. is exhausted, it is replaced by a fresh batch of similarly uniform, but not necessarily identical, properties.

Each batch is numbered. In 1984 I.R.B. 5 was in use. It will be replaced by I.R.B. 6, 7, etc., as necessary.

The name of the supplier of the current I.R.B. (which is the one which should be used in current work) may be obtained from the Secretary of the Rubber Standards Committee, British Standards Institution, 3 York Street, Manchester M2 2AT.'

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

APPENDIX A

MEASUREMENT OF SURFACE AREA

A.1 Theoretical. The principle of the method is to determine the amount of nitrogen (or other suitable gas) required to form a monomolecular layer on the surface of the powder by adsorption at low temperature (e.g. -195.8°C , i.e., the boiling point of liquid nitrogen at atmospheric pressure).

The monolayer capacity (V_m) can sometimes be estimated by inspection of the isotherm obtained, but normally the equation of Brunauer, Emmett & Teller* is used.

$$\frac{P}{V_a(P_o - P)} = \frac{1}{V_m C} + \frac{(C - 1)}{V_m C} \times \frac{P}{P_o}$$

where V_a = amount of gas adsorbed (ml/g at N.T.P.)

V_m = amount of gas adsorbed to form a monolayer

P = pressure of adsorbate

P_o = saturation vapour pressure of adsorbate at the temperature of adsorption

C = a constant.

This equation can be applied to the so-called Type II isotherm, corresponding to monolayer followed by multilayer adsorption, to determine the monolayer capacity. From the equation it can be seen that if $P/[V_a(P_o - P)]$ is plotted against the relative pressure P/P_o , a straight line will result, and from the slope of the line and its intercept on the $P/[V_a(P_o - P)]$ axis the values for C and for V_m , the monolayer capacity, can be calculated. This equation has been found to fit experimental data extremely well in the range of pressures where P/P_o lies between 0.05 and 0.35 and thus forms an accurate method of determination of the monolayer capacity.

The area occupied by the nitrogen molecule in the adsorbed condition is generally assumed to be that derived from the density of liquid nitrogen; that is, each molecule of nitrogen is assumed to occupy the volume it would occupy in the liquid state†, with a correction made for the packing of the molecules. An area of 0.162 nm^2 per molecule is obtained in this way, from which the surface area of the powder may be calculated.

The technique described below is a static volumetric method, which has been found suitable for regular use with a high degree of accuracy. Alternative forms of apparatus may be used‡, including those based on adsorption from a stream

* S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, 1938, 60, 309.

† S. Brunauer and P. H. Emmett, *J. Am. Chem. Soc.*, 1935, 57, 1754.

‡ See A. S. Joy, *Vacuum*, 1953, 3, No. 3, 254; W. E. Burr & V. J. Anhorn, *Scientific and Industrial Glass Blowing and Laboratory Techniques*, 1949, 257.

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of inert carrier gas, the so called continuous flow methods*. In all cases, having determined the adsorption isotherm, the monolayer capacity should be obtained using the B.E.T. equation.

A.2 Apparatus. A static volumetric apparatus is used, consisting of a sample bulb, gas burette and manometer, together with nitrogen and helium reservoirs, connected to a normal high vacuum system consisting of rotary and diffusion pumps.

A suitable design of apparatus is shown in Fig. 1. In this form of apparatus the gas burette G and the mercury manometer M form the two arms of a constant volume of the dead space in the apparatus. The gas burette has three bulbs, each of about 10–11 ml capacity, and is provided with calibration marks. The connections shown within the rectangle in the diagram should be made with 2 mm bore capillary tubing, and kept as short as possible. Other portions of the apparatus should be made with wider bore glass tubing (7–8 mm) to obtain maximum pumping speeds, and the backing line should be about 20 mm bore. The sample bulb, gas burette and manometer may be duplicated to enable more than one determination to be carried out at the same time.

The sample bulb B shown in the diagram has a narrow tube connecting the bottom of the bulb to the main stem to aid the removal of gas from the powder during degassing by reducing the tendency of the powder to be blown up the main tube. Sample bulbs of various size are used, depending on the expected surface area of the powder. A size in common use has a capacity of about 10 ml.

The gas burette G is water jacketed, and the temperature of the tap water circulating is measured at intervals during each adsorption run; it is generally found to be constant on any one day to within a fraction of a degree, which is adequate for the purpose. The volume of the gas burette, to the various calibration marks, is determined by calibration with mercury when the apparatus is being set up. The gas burette is connected at the lower end to the wide bored mercury manometer and the mercury reservoir, by means of which the mercury levels may be adjusted. The top of the gas burette is connected through narrow bore capillary tubing and capillary taps to the sample bulb and the manifold leading to the vacuum system and the gas storage vessels.

In the construction of the apparatus it is essential to use only high grade vacuum taps, and these must be replaced when any sign of wear is shown. It is impossible to prevent traces of powders from being carried up into the vacuum lines, and it is, therefore, advisable to construct the apparatus so that all parts are easily accessible for cleaning and replacement. The main vacuum line, with plugs at each end for cleaning, is connected through solid carbon dioxide or liquid nitrogen traps to a mercury diffusion pump and a rotary pump.

* F. M. Nelsen and F. T. Eggertsen, *Anal. Chem.*, 1958, 30, No. 8, 1387.

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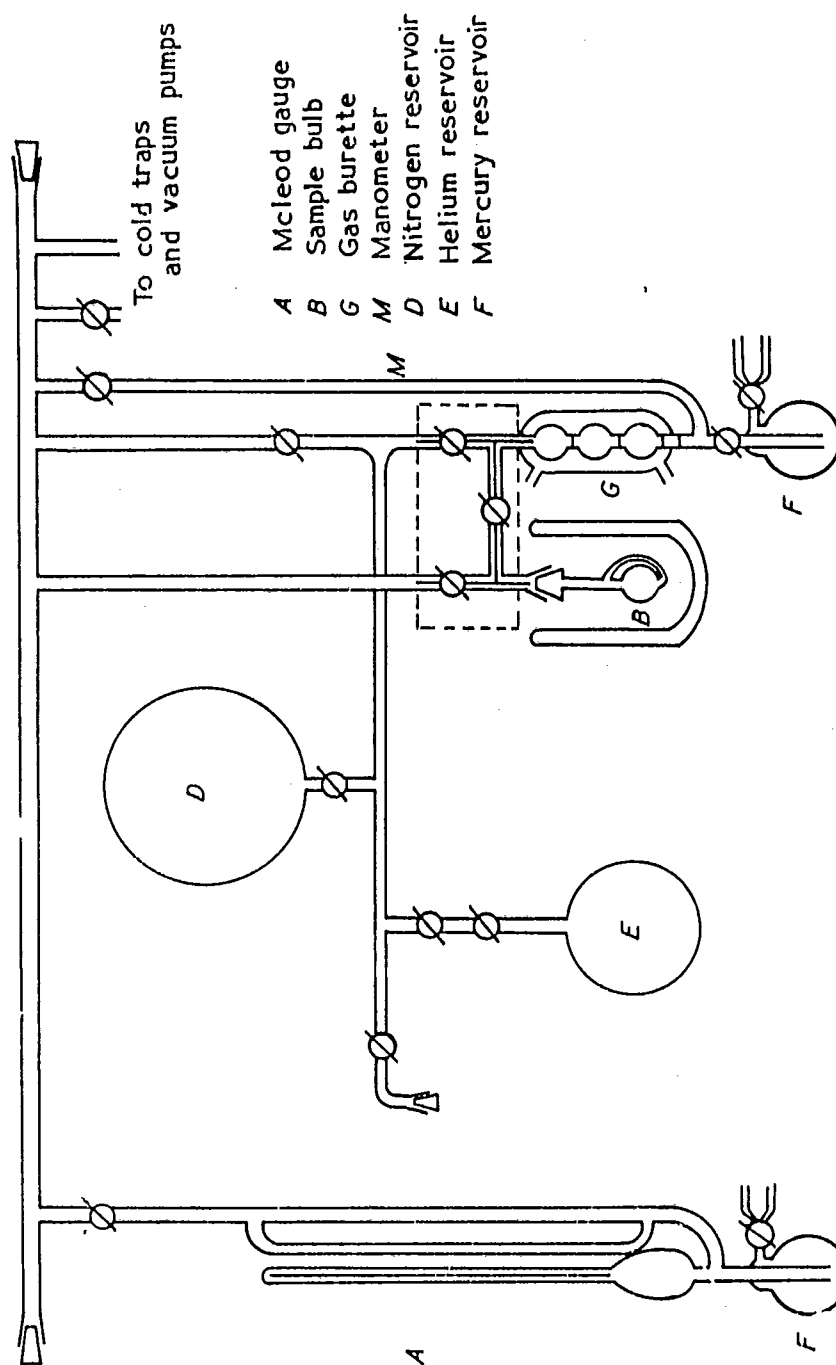


Fig. 1. Apparatus for determination of surface area

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During the adsorption runs, and also in the determination of the volume of the cooled space during the helium calibration, the level of liquid nitrogen in the Dewar vessel surrounding the sample bulb is kept constant as indicated by its just touching the end of a wire level gauge attached to the sample bulb manifold.

A.3 Experimental procedure. A sample of the powder having a surface area of the order of 50 m^2 is placed in the sample bulb, and a small piece of cotton or glass wool is placed in the stem to prevent the powder being carried out of the bulb during the degassing. It is customary to weigh the amount of powder used at the end of the determination; this allows for any loss of sample during degassing. The sample bulb is connected to the apparatus and evacuated whilst being heated, using a Dewar vessel of hot oil or a small electric furnace, and pumping out is continued until a vacuum of $10^{-4} - 10^{-5} \text{ mmHg}$ can be maintained in the system while pumping. The temperature and time of evacuation required are determined by the material being examined. For many powders about 1 hour at 130°C is sufficient.

It is now necessary to calibrate the dead space in the apparatus with helium, which is not adsorbed on the powder. The helium is introduced into the gas burette, which is levelled off to the selected calibration mark (depending on the expected surface area), and the gas pressure is recorded (P_b). The helium is then allowed to expand into the sample bulb (at temperature T_s), and after levelling off the burette the pressure is again recorded (P_s). Finally the sample bulb is immersed in liquid nitrogen to the standard depth indicated by the wire gauge, and after levelling off the burette the final pressure is recorded (P_t). The sample bulb is then allowed to warm up and the helium is pumped off, until a hard vacuum is again obtained.

The sample bulb is again cooled in liquid nitrogen, and nitrogen is introduced into the gas burette from the reservoir. After levelling off the burette and recording the pressure (P_A), the nitrogen is allowed into the sample bulb. When equilibrium is reached (generally in 10–20 minutes) the burette is again levelled off and the equilibrium pressure (P) is recorded. This cycle of introduction of nitrogen into the burette, measurement, adsorption on the sample, and final measurement of equilibrium pressure is repeated several times, each cycle providing a point on the adsorption isotherm. The time taken to attain equilibrium, and the number of points required, will depend on the surface area and nature of the powder. In selecting the size of the sample bulb, the volume of the gas burette (i.e. which calibration mark to use), and the amount of nitrogen to introduce at each step, it is necessary to use existing knowledge and experience of the particular type of material being examined. It is customary to have at least four points with equilibrium relative pressures (P/P_0) in the range 0.05–0.35.

When the adsorption run is completed, the sample is allowed to warm up to normal temperature. The sample bulb is then removed and weighed to determine the amount of sample which was used. This procedure is preferred to attempting to weigh the sample as it is put into the sample bulb, in view of the possibility of carry-over of powder during the evacuation. The sample at the end of the experiment is also dry and ready for weighing.

It is convenient to record the various measurements as they are made on a printed form, with space for the arithmetical operations involved in conversion of the various pressure and volume measurements to N.T.P.

A suitable form is shown below with typical results. The measurements made are given in A.4 and the details of the necessary calculations are shown in Table 1.

TABLE 1. SURFACE AREA OF POWDER BY
NITROGEN ADSORPTION

Sample: Zinc oxide

Weight of bulb and sample = 16.6714 g

Weight of bulb = 10.5188 g

Weight of sample = 6.1526 g

Calibration of free space with helium

Volume of burette v	P_b	P_s	P_1	P_0	T_s	T_1	γ	V_1
23.4189	159.2	94.2	49.6	760.0	283.5	77.3	16.1595	13.3414
$P_s - P_1 = 44.6$							$T_s = 10.0^\circ\text{C}$	
$T_s - T_1 = 206.2$							$V_b = 26.2370$	

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Adsorption of nitrogen

P_A	203.6	261.3	279.5	300.2	319.1	337.6
P	2.8	68.9	123.9	170.6	208.6	242.8
ΣP	203.6	462.1	672.7	849.0	997.5	1 126.5
V_t	6.050 7	13.733 0	19.991 7	25.231 1	29.644 3	33.478 0
V_B	0.093 2	2.294 0	4.125 2	5.680 1	6.945 3	8.084 0
V_c	0.173 7	4.273 5	7.684 8	10.581 3	12.938 2	15.059 5
$V_B + V_c$	0.266 9	6.567 5	11.810 0	16.261 4	19.883 5	23.143 5
V_a	5.783 8	7.165 5	8.181 7	8.969 7	9.760 8	10.334 5
$P/P_o = x$	0.003 7	0.090 7	0.163 0	0.224 5	0.274 5	0.319 4
$\frac{x}{1-x}$	0.003 7	0.099 7	0.194 7	0.289 5	0.378 4	0.469 2
$\frac{x}{V_a(1-x)}$	0.000 6	0.013 9	0.023 8	0.032 3	0.038 8	0.045 4

B.E.T. plot intercept = 0.001 4

B.E.T. plot slope = $\frac{0.008 2}{0.060} = 0.136 7$

Surface area = $\frac{4.38}{\text{wt. of sample}} \times \frac{1}{\text{slope} + \text{intercept}}$

= $\frac{4.38 \times 1}{6.152 6 \times 0.138 1}$

= 5.15 m²/g.

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A.4 Measurements made

NOTE. Pressures are in mmHg and temperatures in degrees Kelvin.

- P_b Initial pressure of helium in gas burette
 P_s Pressure of helium in gas burette and bulb at temperature T_s
 P_1 Pressure of helium in gas burette and bulb at temperature T_1
 T_s Water jacket temperature
 T_1 Liquid nitrogen temperature*
 P_o Saturated vapour pressure of nitrogen at T_1 *
 P_A Initial pressure of nitrogen in burette
 P Equilibrium pressure of nitrogen in burette and bulb.
 v Volume of burette (determined when the apparatus is being set up).

A.5 Values calculated

- V_1 Volume of cooled space
 y Volume of free space
 V_b Volume of non-cooled space
- } From helium calibration
- ΣP Sum of the added pressures (P_A) minus the sum of the residual pressures (P)
 V_t Volume of nitrogen in system (N.T.P.)
 V_B Volume of nitrogen in non-cooled space (V_b) (N.T.P.)
 V_c Volume of gaseous nitrogen in cooled space (N.T.P.)
 V_a Volume of adsorbed nitrogen (N.T.P.)
 P/P_o Relative equilibrium pressure = x

$$\frac{P}{P_o - P} = \frac{x}{1 - x}$$

$$\frac{P}{V_a(P_o - P)} = \frac{x}{V_a(1 - x)}$$

* Standard values may be used, or the temperature of the liquid nitrogen may be determined.

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A.6 Helium calibration of dead space

y = volume of free space, i.e., volume of space in sample bulb not occupied by powder,

$$= \frac{v(P_b - P_s)}{P_s}$$

V_1 = volume of cooled space, i.e., volume of space in sample bulb not occupied by powder and which is immersed in liquid nitrogen,

$$= \frac{(v + y)T_1}{P_1} \times \frac{P_s - P_1}{T_s - T_1}$$

V_b = volume of non-cooled space, i.e., volume of space in burette and sample bulb above level of liquid nitrogen,

$$= v + y - V_1$$

A.7 Calculation of nitrogen adsorbed (V_a). For each set of readings of the nitrogen pressures calculate ΣP , the net addition of nitrogen to the system, thus:

$$\Sigma P(1) = P_A(1) \quad \text{(1st point)}$$

$$\Sigma P(2) = \Sigma P(1) + P_A(2) - P(1) \quad \text{(2nd point)}$$

$$\Sigma P(3) = \Sigma P(2) + P_A(3) - P(2) \quad \text{(3rd point)}$$

Calculate

$$V_t = \text{total volume of nitrogen in system (N.T.P.)}$$

$$= v \times \Sigma P \times \text{N.T.P. correction.}$$

$$V_B = \text{volume of nitrogen in non-cooled space (N.T.P.)}$$

$$= V_b \times P \times \text{N.T.P. correction.}$$

$$V_c = \text{volume of gaseous nitrogen in cooled space (N.T.P.)}$$

$$= V_1 \times P \times 0.004\,649 \quad \text{(This is the N.T.P. correction for liquid nitrogen temperature)}$$

$$V_a = \text{volume of adsorbed nitrogen (N.T.P.)}$$

$$= \text{total volume of nitrogen added to system} - (\text{volume of nitrogen in non-cooled space} + \text{volume of nitrogen in cooled space})$$

$$\therefore V_t - (V_B + V_c)$$

Calculate

$$\frac{P}{V_a(P_o - P)} = \frac{x}{V_a(1 - x)}$$

Plot $\frac{P}{V_a(P_o - P)}$ against $\frac{P}{P_o}$

Determine slope and intercept

Monolayer capacity $V_m = \frac{1}{\text{slope} + \text{intercept}}$

Surface area (m^2/g) = $\frac{4.38}{\text{wt. of sample, g}} \times V_m$

[NOTE. $4.38 = \frac{6.02 \times 10^{23} \times 0.162 \times 10^{-18}}{22.414}$]

When plotting $\frac{P}{V_a(P_o - P)}$ against $\frac{P}{P_o}$, it is advisable to use large scale graph paper. Four points should lie *exactly* on a straight line, between the relative pressures of 0.05 and 0.35. If the points are not exactly on a straight line the results should be discarded, and a fresh determination carried out, since drawing the 'best' line through a number of points leads to ambiguities. It has been found that with careful attention to detail a reproducibility of within 1-2% can be obtained in the measured surface area.

APPENDIX B

DETERMINATION OF COPPER

B.1 Reagents. All reagents shall be of a recognized analytical reagent quality. Demineralized water shall be used whenever water is specified.

- (1) *Hydrochloric/nitric acid mixture.* 2 volumes of hydrochloric acid ($d = 1.18$), 1 volume of nitric acid ($d = 1.42$), plus 3 volumes of water.
- (2) *Citric acid solution.* Dissolve 50 g of citric acid in 100 ml of water.
- (3) *Ammonia.* Aqueous solution, $d = 0.880$.
- (4) *Litmus paper.*

B.2 Procedure

B.2.1. Zinc oxide. Weigh to the nearest 0.01 g, about 5 g of the sample and place in a 250 ml conical flask. Add first 25 ml of water and then the hydrochloric/nitric acid mixture until all the sample dissolves and then 2-3 ml in excess. Add