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भारतीय मानक मसौदा

रबर उद्योग के लिए अवक्षेपित सिलिका — विशिष्टि

(IS12076 का पहला पुनरीक्षण)

*Draft Indian Standard*

**PRECIPITATED SILICA FOR RUBBER INDUSTRY — SPECIFICATION**

*(First Revision of IS 12076)*

(ICS No.83.040.20)

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Rubber and Rubber Products Sectional  
Committee, PCD 13

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**FOREWORD**

*(Formal clauses will be added later)*

This standard was first published in 1986.

The first revision has been brought out to bring the standard in the latest style and format of Indian standard and to update the cross-referred standards in the standard and incorporate previous amendments.

Precipitated silica is an important reinforcing filler for the rubber industry. It is essential that it should be of proper quality so that through it no unwarranted impurities are added to the vulcanizate.

Besides specifying chemical requirements, this standard includes a recommended recipe and schedule for compounding for evaluation of precipitated silica (Annex J). Suitable values for physical properties would be included in Annex J later on the basis of results obtained by inter laboratory investigation. For the time being requirements for physical properties may be agreed to between the purchaser and the supplier.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off

in accordance with IS 2: 2022 ‘Rules for rounding off numerical values (*second revision*)’. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

## 1 SCOPE

This draft standard prescribes the requirements, and the methods of sampling and test for precipitated silica used for rubber industry.

## 2 REFERENCE

The standards given below contain provisions which, through reference in this text, constitute provision of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent edition of these standards:

<i>IS No.</i>	<i>Title</i>
IS 918 :1985	Calcium carbonate, precipitated for Cosmetic Industry ( <i>second revision</i> )
IS 1070 :2023	Reagent grade water — Specification ( <i>fourth revision</i> )
IS 3400 (Part 1) : 2021/ ISO 37 : 2017	Methods of test for vulcanized rubber Part 1 Tensile stress-strain properties ( <i>fourth revision</i> )
IS 7086 ( Part 1) :1973	Method of sampling and test for rubber compounding ingredients, Part 1

## 2 REQUIREMENTS

**2.1 Description** — The material shall be fine, white powder or granules, free of lumps, consisting essentially of silicon dioxide (amorphous hydrated).

**2.2** The material shall also comply with the requirements given in Table 1, when tested according to the methods prescribed in Annex A. Reference to the relevant clauses of Annex A and IS 7086 (Part 1) is given in col (4) and col (5) of Table 1.

**Table 1 Requirements for Precipitated Silica for Rubber Industry**  
(*Clauses 2.2 and 4.1*)

SL No.	Characteristics	Requirement	Method of test ref to	
			Annex	Cl No. / IS No.
(1)	(2)	(3)	(4)	(5)
i)	Silica (as SiO <sub>2</sub> ) on dried sample percent by mass, <i>Min</i>	95	A-1	—

ii)	Residue on 53- micron IS sieve percent by mass, <i>Max</i>	0.5	—	3 of IS 7086(Part 1) : 1973
iii)	pH of slurry	6.0 to 7.0	A-2	—
iv)	Moisture percent by mass	4.0 to 6.0	A-3	—
v)	Loss on ignition on dried sample percent by mass, <i>Max</i>	7.0	A-4	—
vi)	Total copper, ppm, <i>Max</i>	10	A-5	—
vii)	Total manganese, ppm, <i>Max</i>	50	A-6	—
viii)	Total iron, ppm, <i>Max</i>	1500	A-7	—
ix)	Relative density 27°/27° C	1.90 to 2.00	—	4 of IS 7086: (Part 1) : 1973
x)	Bulk density, g/l	200 to 400	—	A-4 of IS 918 : 1985
xi)	BET Surface area m <sup>2</sup> /g	100 to 300	A-8	—

### 3. PACKING AND MARKING

**3.1 Packing** — The material shall be packed in polyethylene lined hessian bags laminated with bitumen or in suitable containers as agreed to between the purchaser and the supplier. The containers shall be securely closed.

**3.2 Marking** — Each container shall be marked legibly and indelibly with the following information:

- a) Name of the material;
- b) Name of the manufacturer and his recognized trade-mark, if any;
- c) Net mass in kg of the material; and
- d) Lot number to enable the batch of manufacture to be traced back from records.

#### 3.2.1 BIS Certification Marking

The product(s) conforming to the requirements of this standard may be certified as per the conformity assessment schemes under the provisions of the *Bureau of Indian Standards Act, 2016* and the rules and regulations framed thereunder, and the products may be marked with the Standard Mark.

### 4. METHOD OF TEST

**4.1** The material shall be tested according to the test methods as given in 2.1, and Table 1. Reference to the relevant clauses is given in col (4) and col (5) of Table 1.

**4.2 Quality of Reagents** — Unless specified otherwise, pure chemicals and distilled water (*see* IS 1070) shall be employed in tests.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

## **5. SAMPLING AND CRITERIA FOR CONFORMITY**

**5.1 Sampling** — For the purpose of ascertaining the conformity of precipitated silica in a consignment to this specification, sampling as prescribed in 15 of IS 7086 (Part 1) shall be followed.

**5.2 Number of Tests** — Tests for all characteristics shall be conducted on a composite sample.

**5.3 Criteria for Conformity** — The lot shall be considered as conforming to the specification if the composite sample satisfies each one of the requirements.

## **ANNEX A**

[*Clause 2.2 and Table 1, Sl no. (i)*]

### **DETERMINATION OF SILICON DIOXIDE**

#### **A-1 REAGENTS**

**A-1.1 Concentrated Hydrochloric Acid** — Density 1.18 g/ml.

**A-1.1 Hydrofluoric Acid** — 40 percent.

**A-1.1 Concentrated Sulphuric Acid** — Density 1.84 g/ml.

#### **A-2 PROCEDURE**

The sample is first dried to constant mass at  $(105 \pm 2)^{\circ}\text{C}$ . Weigh about 0.5 g, nearest to 0.001 g ( $M$ ), in a porcelain dish and carefully moisten it with distilled water. Add slowly 25 ml concentrated hydrochloric acid and 10 ml distilled water and evaporate to dryness. This treatment is repeated twice, each time with an addition of 15 ml concentrated hydrochloric acid and some distilled water. The entire dried contents of the dish are then transferred with 15 ml concentrated hydrochloric acid and about 150 ml distilled water into a beaker, and heated with continuous stirring, but not up to boiling. The left-over silica is filtered through an ashless filter paper and washed repeatedly with hot water until neutral. The filtrate and the washings are collected and, if necessary, used for further analysis. The filter paper with the silica is carefully ashed in a platinum crucible and the residue is kept for 20 minutes at about  $900^{\circ}\text{C}$ . Cool and weigh to nearest 0.001 g ( $M_1$ ). To the contents of the crucible, add a little distilled water, 5 drops of concentrated sulphuric acid, and 15 ml of hydrofluoric acid. Under careful heating, and slow rise of temperature, the contents of the crucible are dried. This step is repeated two more times. The residue is then heated to red-heat for 5 minutes at  $1000^{\circ}\text{C}$ , and after cooling to room temperature in a desiccator, weighed accurately to 0.001 g ( $M_2$ ).

### **A-3 CALCULATION**

The content of SiO<sub>2</sub> in percentage is

$$\text{percentage SiO}_2 = \frac{M_1 - M_2}{M} \times 100$$

where

$M_1$  = mass in g before the treatment with hydrofluoric acid,

$M_2$  = mass in g after treatment with hydrofluoric acid, and

$M$  = mass in g of sample.

### **ANNEX B**

[Table1, Sl no. (iii)]

#### **DETERMINATION OF pH**

### **B-1 PROCEDURE**

Weigh about 5 g of the material and transfer it to a 500-ml beaker. Add 100 ml of freshly boiled and cooled distilled water. Allow to stand for 30 minutes with occasional stirring. Filter, reject the first 50 ml of the filtrate and collect the remaining filtrate in a breaker. Determine the pH of the solution by means of a suitable pH meter using glass electrodes.

### **ANNEX C**

[Table1, Sl no. (iv)]

#### **DETERMINATION OF MOISTURE**

### **C-1PROCEDURE**

**C-1.1** Weigh accurately about 10 g of the material and heat in a squat weighing bottle at 105°C for 2 hours. Cool and weigh till a constant mass is obtained.

**C-1.2** Preserve the sample in a desiccator for subsequent tests.

### **C-2 CALCULATION**

$$\text{Moisture, percent by mass} = \frac{100 \times M_2}{M_1}$$

where

$M_2$  = loss in mass in g, and

$M_1$  = mass in g, of the material taken for the test.

## **ANNEX D**

[Table 1, Sl no. (v)]

### **DETERMINATION OF LOSS ON IGNITION**

#### **D-1 PROCEDURE**

Weigh accurately about 1 g of the material as dried in a silica or platinum crucible (*see* C-1.2). Ignite at 900°C for 2 hours. Cool and weigh till constant mass is obtained.

#### **D-2 CALCULATION**

Loss on ignition, percent by mass =  $\frac{100 \times M_2}{M_1}$

where

$M_2$  = loss in mass in g, and

$M_1$  = mass in g of the material taken for the test.

## **ANNEX E**

[Table 1, Sl no. (vi)]

### **DETERMINATION OF COPPER**

#### **E-1 PROCEDURE**

Two methods have been prescribed for determination of copper. For routine work, Method I, using calorimeter given in **E-1.1** may be followed. For more accurate work, Method II, using atomic absorption spectrometer given in **E-1.2** may be followed.

##### **E-1.1 Calorimetric Method (Method I)**

**E-1.1.1 Principle** — Copper is determined calorimetrically using sodium diethyldithiocarbamate by visual comparison.

##### **E-1.1.2 Apparatus**

**E-1.1.2.1 Nessler tubes** — 100-ml capacity.

##### **E-1.1.3 Reagents**

**E-1.1.3.1 Concentrated ammonium hydroxide** — 18 N (*relative density* 0.90).

**E-1.1.3.2 Ammonium citrate solution** — Dissolve 100 g of citric acid in 100 ml of ammonium hydroxide and make up to 200 ml with water.

**E-1.1.3.3** *Gum arabic solution* — 5 percent (m/v).

**E-1.1.3.4** *Sodium diethyl dithiocarbamate solution* — Dissolve 1.0 g of sodium diethyl dithiocarbamate in 1 000 ml of copper-free water. Keep in an amber- coloured bottle and protect from strong light.

**E-1.1.3.5** *Standard copper solution* — Dissolve 0.313 9 g of copper sulphate crystals ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in copper-free water and make up the volume to 1 000 ml with copper free water. Take 100 ml of this solution and further dilute to 1 000 ml with copper-free water. One millilitre of the solution is equivalent to 0.01 mg of copper oxide as CuO (0.01 mg/ml) is equivalent to 10 ppm.

#### **E-1.1.4 Procedure**

**E-1.1.4.1** *Prepared sample solution* — Weigh accurately 2.0 g of the dry sample and mix with 8 g of anhydrous sodium carbonate and fuse in a platinum crucible until the melt is clear. Leach out the melted mass with water into a porcelain dish, and then put the crucible in the same dish. Add about 20 ml of water and heat on a water bath until the product is disintegrated. Remove the crucible after washing in the dish. Evaporate the contents of the dish to dryness. Add a mixture of 12 ml of concentrated sulphuric acid and 2 ml of concentrated nitric acid. Evaporate till fumes of sulphur trioxide appear. Dilute to exactly 500 ml and filter through a filter paper to remove silica. Use this prepared sample solution for the test.

**E-1.1.4.2** Pipette 25 ml of the prepared sample solution into a small conical flask or beaker. Drop into it a small piece of litmus paper and make the solution just alkaline with ammonium hydroxide. Add 2.5 ml of ammonium hydroxide in excess and heat to boiling. Allow to stand on a waterbath for one hour to ensure complete precipitation of aluminium hydroxide and then filter through filter paper Whatman No. 1 or equivalent, into a Nessler tube, washing the filter paper with two or three small portions of hot water. To the solution in the Nessler tube, add 5 ml of ammonium citrate, 5 ml of gum arabic solution, 10 ml of ammonium hydroxide solution and 10 ml of sodium diethyldithio carbamate solution in the order mentioned. Dilute to 100 ml mark and mix well. To the other Nessler tube containing an equal aliquot of blank solution, carry through the entire analysis in the same manner as the prepared sample solution, add equal amounts of the same reagents, dilute to about 90 ml and mix. Add to this solution, standard copper solution from a 10 ml burette until its colour matches that of the material under test after diluting to the same volume. Mix well after each addition of standard copper solution.

**E-1.1.4.3** If the colour produced with the prepared sample solution is too deep for comparison, a smaller aliquot of the prepared sample solution from the acid digestion should be used.

#### **E-1.1.5 Calculation**

Copper (as CuO), percent by mass =  $\frac{0.02 V}{M}$

where

V = volume in ml of standard copper solution used for the blank, and

$M$  = mass in g of the dry material taken for the test.

## **E-1.2 Atomic Absorption Spectrometric Method\* (Method II)**

**E-1.2.1 Principle** — A test portion is digested with hydrofluoric acid and sulphuric acid, and silicon is volatilized as silicon tetrafluoride.

Any metals in the digested test portion are dissolved in hydrochloric acid, then the solution is diluted and aspirated into the flame of an atomic absorption spectrometer set at a wavelength of 324.7 nm.

The method is applicable for the determination of copper contents up to 125 mg/kg, and there is provision for extending the range to 1250 mg/kg.

**E-1.2.2 Reagents and Materials** — All reagents shall be of recognized analytical grade. The water used shall be distilled water or water of equivalent purity.

**WARNING** — All recognized health and safety precautions shall be taken when performing this method of analysis.

**E-1.2.2.1 Acetylene** — compressed gas supply.

**E-1.2.2.2 Air** — compressed gas supply.

**E-1.2.2.3 Hydrochloric acid** — 10 percent ( $m/m$ ) solution.

Dilute 35 percent ( $m/m$ ) hydrochloric acid solution (20 ml) ( $\rho = 1.18$  g/ml) with water (50 ml).

**E-1.2.2.4 Hydrofluoric acid** — 40 percent ( $m/m$ ) solution ( $\rho = 1.13$  g/ml).

**E-1.2.2.5 Sulphuric acid** — 98 percent ( $m/m$ ) solution ( $\rho = 1.84$  g/ml).

**E-1.2.2.6 Copper** — standard solution corresponding to 1 g of Cu per litre.

Dissolve  $(1.000 \pm 0.001)$  g of high purity copper turnings in a mixture of 10 ml of water and 5 ml of nitric acid ( $\rho = 1.42$  g/ml) in a 100 ml beaker. Boil under a fume hood to expel oxides of nitrogen. Cool, transfer to a 1 litre volumetric flask, make up to the mark with water and mix.

1 ml of this standard solution contains 1 000  $\mu\text{g}$  of copper.

**E-1.2.2.7 Copper** — standard solution corresponding to 50 mg of Cu per litre.

Pipette 50.0 ml of the standard copper solution (**E-1.2.2.6**) into a 1 litre volumetric flask, add 5 ml of nitric acid ( $\rho = 1.42$  g/ml), make up to the mark with water and mix.

1 ml of this standard solution contains 50  $\mu\text{g}$  of copper.

**E-1.2.2.8 Copper** — standard solution corresponding to 10 mg of Cu per litre.

Pipette 50.0 ml of the standard copper solution (**E-1.2.2.7**) into a 250 ml volumetric flask, add 1 ml of nitric acid ( $\rho = 1.42$  g/ml), make up to the mark with water and mix.



1 ml of this standard solution contains 10 µg of copper.

NOTE — Commercially available standard copper solutions may be used, if preferred, instead of **E-1.2.2.6**, **E-1.2.2.7** and **E-1.2.2.8**.

**E-1.2.3 Apparatus** — Usual laboratory equipment.

**E-1.2.3.1 Platinum dish** — of capacity approximately 35 ml.

**E-1.2.3.2 Atomic absorption spectrometer** — fitted with an air-acetylene burner.

**E-1.2.3.3 Analytical balance** — capable of weighing to 0.001 g.

**E-1.2.4 Procedure**

**E-1.2.4.1 Test portion** — Weigh, to the nearest 0.001 g, approximately 2 g of sample into the platinum dish (**E-1.2.3.1**).

**E-1.2.4.2 Blank test** — Carry out a blank test simultaneously with the determination, using the same reagents and same procedures, but omitting the test portion.

**E-1.2.4.3 Preparation of the calibration graph**

a) *Preparation of standard calibration solutions* — Into a series of six 50 ml volumetric flasks, transfer the volumes of the standard copper solution (**E-1.2.2.8**) indicated in Table 2, dilute to the mark with water and mix.

**TABLE 2 STANDARD CALIBRATION SOLUTIONS FOR DETERMINATION OF COPPER**

Volume of Standard Copper Solution (E-1.2.2.8) ml (1)	Corresponding Copper Content µg/ml (2)
0.5	0.1
2.5	0.5
5.0	1.0
10.0	2.0
15.0	3.0
25.0	5.0

b) *Spectrometric measurements* — Aspirate each of the standard calibration solutions, in turn, into the flame of the atomic absorption spectrometer (**E-1.2.3.2**) and record their absorbances at a wavelength of 324.7 nm, following the instructions of the instrument manufacturer.

Aspirate water into the flame after each measurement.

c) *Plotting the graph* — Plot a graph having, for example, the copper contents, in micrograms per cubic centimetre, as abscissae and the corresponding values of absorbance as ordinates.

#### **E-1.2.4.4 Determination**

a) *Preparation of the test solution* — Add 10 ml of the hydrofluoric acid solution (E-1.2.2.3) and 0.5 ml of sulphuric acid solution (E-1.2.2.5) to the test portion (E-1.2.4.1) in the dish (E-1.2.3.1).

Place the dish and contents on a heated sand tray and evaporate under a fume hood until the evolution of dense white fumes ceases.

Dissolve any residue in 5 ml of hydrochloric acid solution (E-1.2.2.3) and transfer to a 10 ml volumetric flask. Make up to the mark with water, and transfer the solution to a dry polyethylene bottle.

b) *Spectrometric measurements* — Aspirate the test solution [E-1.2.4.3 (a)] and the blank test solution (E-1.2.4.2) into the flame of the atomic absorption spectrometer and measure their absorbances at 324.7 nm, following the instructions of the instrument manufacturer. Repeat this procedure and record the mean values of absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

If the absorbance of the test solution is greater than that of the standard calibration solution having the highest copper content, dilute 5 ml of the test solution to 50 ml with water, repeat the measurement and take the dilution into account in the expression of results.

**E-1.2.5 Expression of Results** — By reference to the calibration graph, determine the copper contents corresponding to the absorbances of the test solution and the blank test solution.

The total copper content of the sample, expressed in milligrams per kilogram, is given by the formula.

$$\frac{10(M_1 - M_2)}{m}$$

where

$M_1$  = is the copper content, in micrograms per ml of the test solution;

$M_2$  = is the copper content, in micrograms per ml of the blank test solution; and

$m$  = is the mass, in grams, of the test portion.

If the test solution was diluted as described in E-1.2.2.4 (b), multiply the formula by 10.

Express the result to the nearest 0.1 mg/kg.

**E-1.2.6 Test Report** — The test report shall include the following information:

a) All details required for complete identification of the sample,

- b) Test conditions,
- c) Result obtained for each sample, and
- d) Any deviations from the procedure specified which might have affected the results.

## **ANNEX F**

[Table 1, Sl no. (vii)]

### **DETERMINATION OF MANGANESE**

**F-1 Outline of the Method** — Manganese is determined by comparing the colour produced by oxidation with periodate against the colour of standard potassium permanganate solution.

#### **F-2 Apparatus**

**F-2.1 Nessler Tubes** — 50ml capacity.

#### **F-3 Reagents**

**F-3.1 Phosphoric Acid** – 85 percent (v/v).

**F-3.2 Standard Potassium Permanganate Solution** — Prepare a dilute solution of potassium permanganate by diluting to 50 ml in a volumetric flask a quantity of freshly standardized solution in accordance with the following formula:

$$V = \frac{0.3524}{M}$$

where

$V$  = volume in ml of the standard potassium permanganate solution to be made up to a volume of 50 ml, and

$M$  = normality of the standard potassium permanganate solution.

One millilitre of this solution is equivalent to 0.1 mg of manganese oxide (as MnO). The solution shall be freshly prepared.

**F-3.3 Potassium Periodate** — solid.

#### **F-4 PROCEDURE**

Transfer 125 ml of the prepared sample solution to a 250 ml beaker and evaporate to 75 ml. Add 10 ml of phosphoric acid, sprinkle 0.5 g of potassium periodate into the solution and bring it to boil. Cool slightly, sprinkle again 0.1 g of potassium periodate and boil. When the colour appears to have developed to the maximum, place the beaker on a steam bath and keep for 15 minutes. If there is any doubt about the completeness of reaction, add more potassium periodate. After the sample has stood on the steam bath for 15 minutes, remove the beaker and cool. Place an equal aliquot of a blank solution carried through the entire analysis in the same manner as the prepared sample solution in the other Nessler tube and dilute almost to the mark. To this solution add

standard potassium permanganate solution from a 10 ml burette until the colour matches that of the material under test when diluted to the same volume.

## **F-5 CALCULATION**

$$\text{Manganese (as MnO), percent by mass} = \frac{0.04 V}{M}$$

where

$V$  = volume in ml, of standard potassium permanganate solution used for the blank, and

$M$  = mass in g, of the dry sample taken for the test.

## **ANNEX G**

[Table 1, Sl no. (viii)]

### **DETERMINATION OF IRON**

#### **G-1 PRINCIPLE**

The principle is the same as for the determination of total copper content (*see* E-1.2) except that the absorbance of the test solution is measured at a wavelength of 248.3 nm and is compared with the absorbances of standard calibration iron solutions.

The method is applicable for the determination of iron contents up to 125 mg/kg and there is provision for extending the range to 2 500 mg/kg.

**G-2 Reagents and Materials** — All reagents shall be of recognized analytical grade. The water used shall be distilled water or water of equivalent purity.

**WARNING** — All recognized health and safety precautions shall be taken when performing this method of analysis.

**G-2.1 Acetylene** — compressed gas supply.

**G-2.2 Air** — compressed gas supply.

**G-2.3 Hydrochloric Acid Solution** — 10 percent (m/m) solution.

Dilute 35 percent (m/m) hydrochloric acid solution (20 ml) ( $\rho = 1.18$  g/ml) with water (50 ml).

**G-2.4 Hydrofluoric Acid Solution** - 40 percent (m/m) solution ( $\rho = 1.13$  g/ml).

**G-2.5 Sulphuric Acid Solution** - 98 percent (m/m) solution ( $\rho = 1.84$  g/ml).

**G-2.6 Iron** - standard solution corresponding to 1 g of Fe per litre.

Dissolve  $(1.000 \pm 0.001)$  g of high purity iron in a mixture of 10 ml of water and 5 ml of nitric acid ( $\rho = 1.42$  g/ml) in a 100 ml beaker. Boil under a fume hood to expel oxides of nitrogen. Cool transfer to a one litre volumetric flask, make up to the mark with water and mix.

1 ml of this standard solution contains 1 000  $\mu\text{g}$  of iron.

**G-2.7 Iron** — standard solution corresponding to 50 mg of Fe per litre.

Pipette 50.0 ml of the standard iron solution (**G-2.6**) into all of nitric acid ( $\rho = 1.42$  g/ml), dilute to the mark with water and mix.

1 ml of this standard solution contains 50  $\mu\text{g}$  of iron.

**G-2.8 Iron** — standard solution corresponding to 10 mg of Fe per litre.

Pipette 50.0 ml of the standard iron solution (**G-2.7**) into a 250 ml volumetric flask, add 1 ml of nitric acid ( $\rho = 1.42$  g/ml), make up to the mark with water and mix.

1 ml of this standard solution contains 10  $\mu\text{g}$  of iron.

NOTE - Commercially available standard iron solutions may be used, if preferred, instead of **G-2.6**, **G-2.7** and **G-2.8**.

**G-3 Apparatus** - As specified in **E-1.2.3**

#### **G-4 Procedure**

**G-4.1 Test Portion** — Weigh, to the nearest 0.001 g, approximately 2 g of sample into the platinum dish (E-1.2.3.1).

**G-4.2 Blank Test** — Carry out a blank test simultaneously with the determination. Using the same reagents and the same procedures, but omitting the test portion.

#### **G-4.3 Preparation of the Calibration Graph**

**G-4.3.1 Preparation of standard calibration solutions** - Into a series of six 50 ml volumetric flasks, transfer the volumes of the standard iron solution ( G-2.8 ) indicated in Table 3, dilute to the mark with water and mix.

**G-4.3.2 Spectrometric measurements** - Aspirate each of the standard calibration solutions, in turn, into the flame of the atomic absorption spectrometer and record their absorbances at a wavelength of 248.3 nm, following the instructions of the instrument manufacturer.

Aspirate water into the flame after each measurement.

**Table 3 Standard Calibration Solutions for Determination of Iron**  
(Clause G-4.3.1)

volume of standard iron solution (G-2.8) ml (1)	corresponding iron content $\mu\text{g/ml}$ (2)
0.5	0.1
2.5	0.5
5.0	1.0
10.0	2.0

15.0	3.0
25.0	5.0

**G-4.3.3 Plotting the graph** - Plot a graph having, for example, the iron contents, in micrograms per cubic centimetre, as abscissae and the corresponding values of absorbance as ordinates.

#### **G-4.4 Determination**

**G-4.4.1 Preparation of the test solution** - Add 10 ml of the hydrofluoric acid solution (E-1.2.2.4) and 0.5 ml of sulphuric acid solution ( E-1.2.2.5 ) to the test portion ( E-1.2.4.1 ) in the dish (A-5.2.3.1 ).

Place the dish and contents on a heated sand tray and evaporate under a fume hood until the evolution of dense white fumes ceases.

Dissolve any residue in 5 ml of the hydrochloric acid solution (E-1.2.2.3) and transfer to a 10 ml volumetric flask. Make up to the mark with water, and transfer the solution to a dry polyethylene bottle.

**G-4.4.2 Spectrometric measurements** — Aspirate the test solution (G-4.4.1) and the blank test solution (G-4.2) into the flame of the atomic absorption spectrometer and measure their absorbances at 248.3nm, following the instructions of the instrument manufacturer. Repeat this procedure and record the mean values of absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

If the absorbance of the test solution is greater than that of the standard calibration solution having the highest iron content, dilute 5 ml of the test solution to 100 ml with water, repeat the measurement and take the dilution into account in the expression of results.

**G-5 Expression of Results** - By reference to the calibration graph, determine the iron contents corresponding to the absorbances of the test solution and the blank test solution.

The total iron content of the sample, expressed in milligrams per kilogram, is given by the formula:

$$\frac{10(M_1 - M_2)}{m}$$

where

$M_1$  = iron content, in micrograms per ml, of the test solution;

$M_2$  = iron content, in micrograms per ml, of the blank test solution; and

$M$  = mass, in grams, of the test portion.

If the test solution was diluted as described in A-4.4.2, multiply the formula by 20.

Express the result to the nearest 0.1 mg/kg.

**G-6 Test Report** — The test report shall include the following information:

- a) All details required for complete identification of the sample,
- b) Test conditions,
- c) Result obtained for each sample, and
- d) Any deviations from the procedure specified which might have affected the results.

## **ANNEX H**

[Table 1, Sl no. (xi)]

### **DETERMINATION OF SPECIFIC SURFACE AREA – METHOD USING AN AREAMETER APPARATUS**

**H-1 Principle** — Two flasks of equal volume — one containing the test portion, the other empty — are filled with nitrogen under atmospheric pressure at room temperature. Both flasks are then cooled by immersion in liquid nitrogen.

At this temperature, the test portion adsorbs nitrogen, whereby a pressure difference is created between the flask containing the test portion and the reference flask.

The pressure difference is measured by means of a differential pressure. The specific surface area is calculated from the measured pressure difference, the feed pressure and the mass of the test portion.

### **H-2 Materials**

**H-2.1 Nitrogen** — In a cylinder or other source of pre-purified nitrogen of recognized analytical quality.

### **H-2.2 Liquid Nitrogen**

### **H-3 Apparatus**

**H-3.1 Absorption Apparatus** (see Fig. 1) — Comprising a reference flask (7) and a sample flask (8) mounted with gas tight connections.

These connections are provided with one valve each (1 and 2) by means of which the flasks may be connected with the atmosphere. The gas to be adsorbed is fed into each flask through the connection pieces.

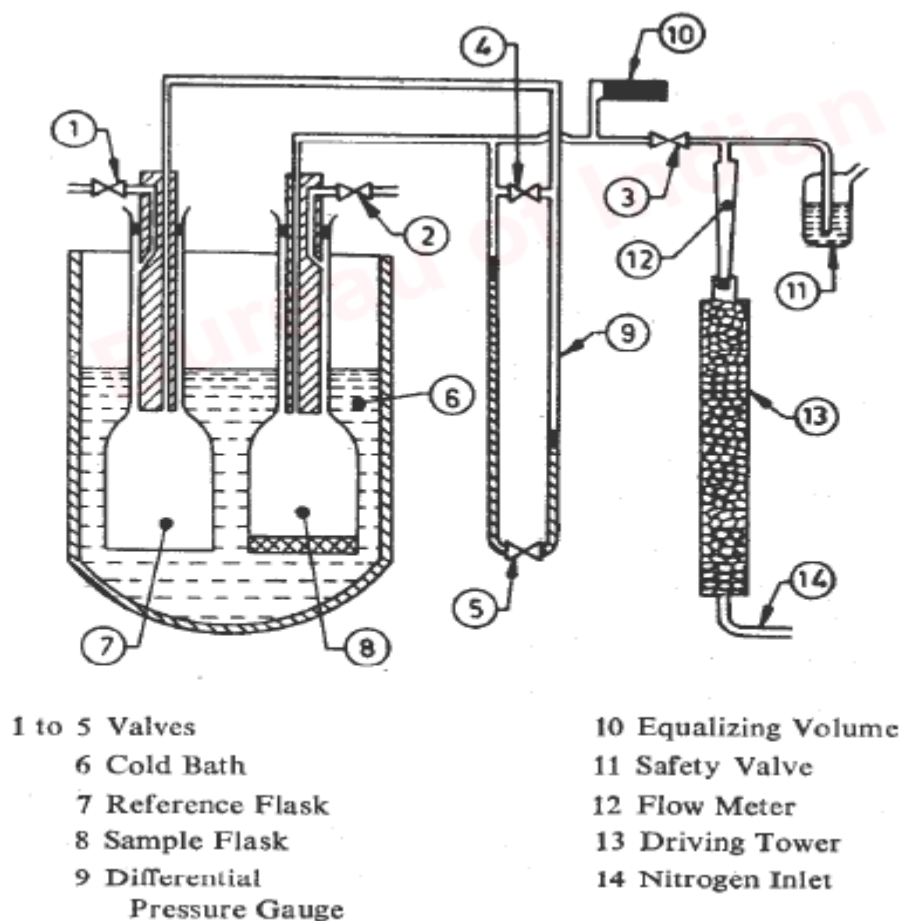


FIG .1 AREAMETER ADSORPTION APPARATUS

**H-3.1.1** The flasks are made of glass which is resistant to sudden changes of temperature and have a volume of approximately 100 ml. The volume difference between the two flask necks shall not exceed 0.1 percent.

The flask necks are made of calibrated precision glass tubes with an inside diameter of  $(5 \pm 0.02)$  mm. This ensures that several flasks may be used as sample or reference flasks without needing to adjust the equalizing volume for every combination.

**H-3.1.2** A U-tube is mounted between the two flasks, and the legs of the pressure gauge are connected by capillary tubes to the two adsorption flasks. By means of valve 4, the two adsorption vessels can be either separated from one another or connected to one another via their capillary tubes. Using valve 5, both liquid legs of the differential pressure gauge can be separated or joined together. The measuring fluid is dibutylphthalate.

The legs of the differential pressure gauge are made of calibrated precision glass tubing with an inside diameter of  $(5 \pm 0.02)$  mm. Therefore, any change in volume during the gas adsorption may be sufficiently accurately calculated. The feed capillary to the sample flask, owing to its short



length, is considered as an equalizing volume which is adjusted during the preparation of the equipment (*see* H-7).

The gas is allowed into the equipment through valve 3. If valves 1, 2 and 4 are open, the gas flows through both flasks. If valves 1 and 4 are closed, the reference flask is shut off and only the sample flask is rinsed with the gas.

During measurement, only part of the volume enclosed by valves 1, 2 and 3 is cooled to the measuring temperature by the liquid nitrogen. The remaining volume, at room temperature, may be only 10 percent of the total volume. The connections to the adsorption flasks are, therefore, capillaries which almost completely fill the necks of the flasks. In this manner, the volume of gas at room temperature is kept to a minimum.

NOTE — procedures for commissioning new equipment and for control purpose are given in H-7

**H-3.1.3 *Regulating Thermostat*** — Permitting maintenance of the adsorption flasks (with the test portions) at a constant temperature, and either rinsing with dry nitrogen or evacuation.

**H-3.1.4 *Analytical Balance*** — accurate to 0.1 mg.

**H-3.1.5 *Drying Oven*** — capable of being controlled at  $(105 \pm 2) ^\circ\text{C}$ .

**H-3.1.6 *Cold Bath*** — containing the liquid nitrogen (H-2.2)

## **H-4 Preparation of the Sample**

**H-4.1** The maximum indication (400 mm) on the differential pressure gauge corresponds to a surface area of approximately  $50 \text{ m}^2$ . The mass of the test portion must, therefore, be adjusted so that  $\Delta h$  on the differential pressure gauge is as great as possible and at least 50 mm. If the approximate specific surface area is not known, preliminary tests with various masses of test portion shall be performed to establish the most suitable mass of test portion.

NOTE - As a guide, Table 4 gives masses of test portion according to specific surface area.

**Table 4 Mass of Test Portion According to Specific Surface Area**

Specific surface area $\text{m}^2/\text{g}$ (1)	Mass of test portion g (2)
20	0.6 to 0.8
30	0.4 to 0.6
40	0.3 to 0.5
80	0.2 to 0.3
120	0.15 to 0.2
140	0.1 to 0.15
>200	<0.1

**H-4.2** Dry the sample for 2 h in the drying oven (H-3.1.6) controlled at  $(105 \pm 2)^{\circ}\text{C}$ . Transfer a suitable amount of sample to the previously tared sample flask by means of a funnel, introducing the test portion into the flask in such a manner that no material adheres to the walls of the neck.

Determine the mass of sample by difference, carrying out the both weighings to the nearest 0.1 mg.

**H-4.3** Before the determination, remove as much as possible of the matter that has already been adsorbed from the surface of the test portion. Carry out desorption by rinsing in a flow of nitrogen. This desorption shall be carried out in a thermoregulator at  $150^{\circ}\text{C}$  to  $160^{\circ}\text{C}$  (preferably  $155^{\circ}\text{C}$  to  $160^{\circ}\text{C}$ ), the desorption time being  $(65 \pm 5)$  min. The nitrogen flow in the sample flask shall be adjusted to 75 ml/min.

**H-4.4** After desorption, cool the test portion to room temperature under a flow of nitrogen, and stopper and store the flasks until required for the determination.

## **H-5 PROCEDURE**

**H-5.1** Connect the sample flask containing the prepared test portion to the nitrogen source and open valves 2 and 3.

**H-5.2** Open valves 4, 1 and 5, and place the flasks in a water bath controlled at  $(27 \pm 2)^{\circ}\text{C}$ .

**H-5.3** After 10 min to 15 min, determine the pressure difference in the flasks by closing valves 1, 2, 3 and 4. If a pressure difference exists, reopen the valves in the order 4, 3, 2 and 1, and continue rinsing with nitrogen. Close valves 1, 2, 3 and 4 when the pressure is equal.

**H-5.4** When pressure equilibrium is attained, close valve 5 and stop the nitrogen flow by closing the valves.

**H-5.5** Wipe off the water drops and immerse the flasks in the liquid nitrogen bath (H-3.1.5) to the lower mark on the neck and, after 1 min, open valve 5 very slowly.

**H-5.6** After the resulting pressure differential has stabilized, read the difference in liquid heights of the U-tube arms to the nearest 0.5 mm.

**H-5.7** Close valve 5 and open valve 4. Replace the cold bath with a water bath controlled at approximately  $40^{\circ}\text{C}$ . After a few minutes, start the nitrogen flow and open valves 3, 2, 1 and 5 in that order.

**H-5.8** As soon as the connections have reached room temperature, close valves 1, 4 and 5 and disconnect the sample flask.

## **H-6 EXPRESSION OF RESULTS**

**H-6.1 Method of Calculation** — Calculate the specific surface area  $S_m$  in square metres per gram, from the formula:

$$S_m = 1.187 \times 10^{-7} \left[ \frac{(1.044 \times 10^5) - p}{m} \right] \times [\{13.6458 + (6.65 \times 10^{-5} p)\} \Delta h + \frac{1}{P\rho} \left( \frac{P}{77.6} - \frac{P_B}{295} \right)]$$

where

$P$  = equilibrium pressure, in pascals ;

$$p = \frac{105.55pa}{393.11 + (0.0049\Delta h)} - 10.2 \Delta h;$$

$m$  = mass, in g, of the test portion;

$\Delta h$  = difference in liquid heights, in ml, in the U-tube arms;

$P_B$  = atmospheric pressure, in pascals; and

$\rho$  = density, in grams per ml of the test sample (assumed to be equal to 2.0 g/ml).

NOTE — For specific surface areas greater than 1 m<sup>2</sup>/g, the term

$$\frac{1}{P\rho} \left( \frac{P}{77.6} - \frac{Pa}{295} \right) \text{ may be ignored.}$$

Express the result to the nearest 1 m<sup>2</sup>/g.

**H-6.2 Calculation Using a Nomogram** — The calculation may be simplified by the use of a nomogram (*see* Fig. 2).

Draw a straight line connecting the measured value of  $\Delta h$  on the vertical  $\Delta h$  scale with the measured value  $P_B$ , on the vertical  $P_B$  scale. Record the value at the point of intersection of the line and scale  $A$ .

Draw a straight line connecting the measured value of  $\Delta h$  on the vertical  $\Delta h$  scale with the measured value of  $P_B$  on the inclined reduced  $P_B$  scale. Record the value at the point of intersection of the line and scale  $B$ .

The specific surface area, in square metres per gram, is given by the formula:

$$S_m = \frac{A\Delta h}{m} + \frac{B}{\rho P}$$

where

$A$  and  $B$  are values derived from the nomogram as described above; and  
 $\Delta h$ ,  $m$ ,  $\rho$  and  $p$  have the same meanings as in A-8.6.1.

Express the result to the nearest 1 m<sup>2</sup>/g.

## **H-7 Notes on Procedure — Preparation of the Areameter**

**H-7.1 General** — When commissioning new equipment or for control purposes, carry out tests to check whether the equalizing volume (*see* 10 in Fig. 1) is correctly adjusted and whether the apparatus is leakproof.

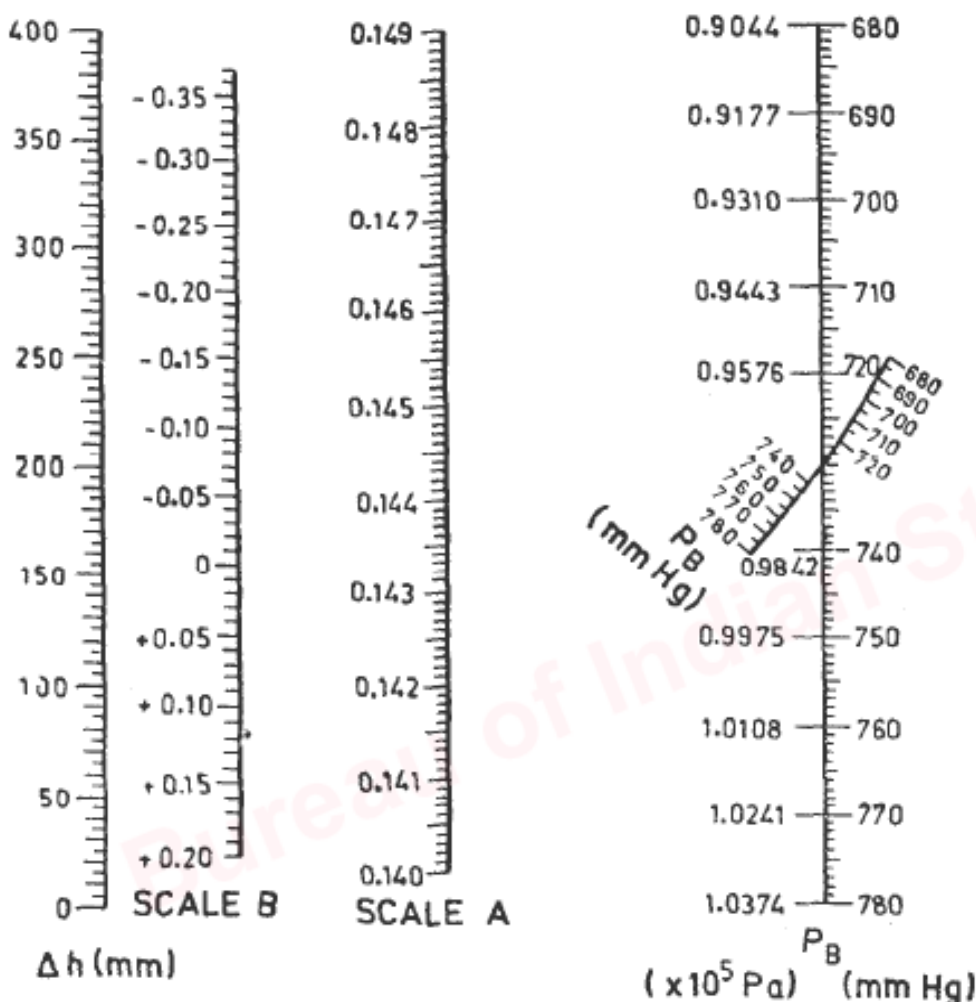


FIG. 2 NOMOGRAM

**H-7.2 Test for Volume Equalization** — The volume equalization balance pre-supposes the tightness of valve 4 (see H-7.3).

Connect the empty adsorption flasks to the apparatus, aligning the upper marks on the flask neck with the lower gasket. Then open all valves and rinse the apparatus with nitrogen. The flow rate should be  $(2.8 \pm 0.15)$  ml/s.

While rinsing, immerse the flasks in a water bath at  $(27 \pm 2)^\circ\text{C}$  to the lower mark on the flask neck so that both flasks may attain the same temperature. As soon as equality of temperature is expected (after at least 10 min), seal the apparatus from the atmosphere and separate the flasks from each other by closing valves 1,2,3 and 4 in that order. Closing valve 4 may cause a minor pressure differential. If this pressure differential changes within the next 2 min, complete temperature balance has not been achieved within the adsorption flasks. In this case, reopen valves 4, 3, 2 and 1 in that order and again rinse the apparatus with nitrogen. Repeat the test after a few minutes. When temperature balance is achieved, again close valve 5. Removed the water bath, wipe off the

adhering water drops and immerse the flasks to the lower marks on the flask in a cold bath of boiling nitrogen.

As soon as the flasks have assumed the temperature of the boiling nitrogen (for empty flasks, after approximately 1 min), open valve 5 very slowly. If the volumes of the sample flask and the reference flask are correctly balanced, no pressure difference will be present. In this case, again close valve 5 and reopen valve 4. Then remove the cold bath and replace by a water bath at approximately 40 °C to thaw the flasks. Remove the warm water bath as soon as the flasks have reached approximately room temperature. After a few minutes reopen valves 3, 2 and 1 in that order and rinse the apparatus with nitrogen.

Cooling and heating of the flasks may result in greater pressure differentials for a short time. This could cause the dibutylphthalate in the U-tube to enter other parts of the apparatus; valve 5 must, therefore, be open during the indicated stages.

If a pressure differential should arise during the preparation of the apparatus, change the equalizing volume (*see* 10 in Fig. 1) at room temperature in such a way that the volumes on both sides of the differential pressure gauge are equal. For control of the volume balance, repeat the above test.

**H-7.3 Leak Test** — If balancing the volumes at the temperature of boiling nitrogen shows continuously increasing or very considerable pressure differentials (greater than 400 mm) after valve 5 has slowly been opened, this is evidence of leaks from the apparatus of the atmosphere (that is, valves 1, 2 and 3 ).

The tightness of valve 4 cannot be checked by pressure differential and must be tested separately. To do this, immerse the flasks in the cold bath, close valves 2, 3 and 4 and open valves 1 and 5. By means of valve 1, produce a pressure differential giving a difference in liquid heights of 300 mm and again close valve 1.

The difference in height should not change by more than 1 mm within 10 min.

**H-7.4 Operational Test** — Check the correct operation of the apparatus initially, and periodically during use, by measurement of a silica of known specific surface area. The specific surface area of the reference material should have been measured using the same method.

**H-7.5 Maintenance** — Replace the dibutylphthalate in the U-tube, if it becomes polluted, or at least once a year. Also replace exhausted silica gel in the drying tower.

**H-8 Test Report** — The test report shall include the following information:

- a) All details required for complete identification of the sample,
- b) Test conditions,
- c) Mass of test portion used, and
- d) Results obtained.

## **ANNEX J**

*(Foreword)*

### **TEST RECIPE AND SCHEDULE FOR COMPOUNDING FOR EVALUATION OF PRECIPITATED SILICA**

#### **J-1 TEST RECIPE**

**J-1.1** The standard test recipe for testing precipitated silica is given below:

<i>Material</i>	<i>Parts by Mass</i>
SBR 1502	100
Silica	40
Zinc oxide	3
Stearic acid	1.5
TMTD	2
TBBS/ CBS	2
Sulphur	0.4

#### **J-2. COMPOUNDING AND VULCANIZATION**

**J-2.1 Mill Mixing Procedure** — The standard laboratory mill batch mass, in grams, shall be based on four times the test recipe mass. The surface temperature of the rolls shall commence at  $(30 \pm 5)^{\circ}\text{C}$  with proper cooling. The mass of the mixed batch shall not differ from the total mass of materials by more than 1.0 percent.

**J-2.1.1** Band the rubber with the mill opening set at 1.1 mm and make 3/4 cuts every 30 s from alternate sides (time 2.0 min.)

**J-2.1.2** Add the sulphur slowly and evenly across the rubber. When the sulphur has been incorporated, make one 3/4 cut from each side (time 2.0 min.)

**J-2.1.3** Add the zinc oxide and approximately 10 percent of the silica. No cuts shall be made at this stage (time 4 min.)

**J-2.1.4** Add the stearic acid and a further 10 percent of the silica, again without cutting the batch (time 4 min.)

**J-2.1.5** Add the rest of the silica slowly. Adjust the mill opening so that the rolling bank has a diameter of approximately 15 mm. Do not cut during incorporation of the silica. Add the material from the pan and when all the silica is incorporated, cut once from each side (time 10 min.)

**J-2.1.6** Add the accelerator and make three 3/4 cuts from each side (time 4 min.)

**J-2.1.7** Cut the batch from the mill, set the mill opening to 0.8 mm and pass the rolled batch endwise through the rolls three times (time 2 min.)

**J-2.1.8** Allow the compound to run for 5 min on the mill with a suitable mill opening so that the rolling bank has a diameter of approximately 15 mm (time 5 min.)

**J-2.1.9** Sheet the batch to approximately 5 mm and check the mass of the batch (total time 33 min.)

**J-2.1.10** Condition the batch for 18 h to 24 h.

**J-2.1.11** Remilling shall be performed in accordance with the following procedure.

With the surface temperature of the rolls maintained at  $(30 \pm 5)^{\circ}\text{C}$  set the mill opening to 0.2 mm and pass the batch once (without banding) through the rolls.

Set the mill opening to approximately 3 mm. Band the mix and allow it to work with a good rolling bank for 5 min without cutting.

Open the mill to give a minimum mix thickness of 6 mm and pass the mix through the mill four times, folding it back on itself each time.

Take samples for the determination of vulcanization characteristics.

Sheet the mix from the mill at such a setting as to obtain a finished thickness of approximately 2.2 mm for the preparation of the dumb-bell specimens (or another appropriate thickness for the preparation of the ring specimens).

Allow to stand for 2 h before vulcanizing.

## **J-2.2 Vulcanization**

**J-2.2.1** Vulcanize the test slabs at  $145^{\circ}\text{C}$  or alternatively at  $150^{\circ}\text{C}$  to optimum cure. Condition the vulcanized test slabs for 16 h to 72 h.

## **J-2.3 Physical Properties of Vulcanizates**

**J-2.3.1** Vulcanizates shall meet the following requirements when tested as per methods prescribed in IS 3400 (Part 1).

a) Tensile strength, MPa, Min	20
b) Elongation at break, percent, Min	650
c) Modulus at 300 percent, MPa	$4 \pm 1.25$