METHODS OF TESTING VULCANIZED RUBBER

PART A23. DETERMINATION OF RESISTANCE TO OZONE CRACKING UNDER STATIC CONDITIONS

B.S. 903 : Part A23 : 1963

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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.

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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 B.S.I. references relate to the work on this standard:
Committee references RUC/10 and RUC/10/4
Draft for comment D62/1711

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

*Federation of British Rubber and Allied Manufacturers
*Institution of the Rubber Industry
*Ministry of Aviation
Natural Rubber Bureau
*Natural Rubber Producers' Research Association
*Rubber and Plastics Research Association of Great Britain
Rubber Growers' Association
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BRITISH STANDARD

METHODS OF TESTING VULCANIZED RUBBER

Part A23

Determination of Resistance to Ozone Cracking under Static Conditions

FOREWORD

This British Standard has been published under the authority of the Rubber Industry Standards Committee. In deciding to issue a revision of the 1950 edition of B.S. 903 it has been considered desirable to publish it in separate parts, and the present part gives a hitherto unpublished determination.

The group of parts in which the prefix letter 'A' is used covers methods of testing the physical properties of rubber.

METHODS OF DETERMINATION

SECTION 1. SUMMARY AND EXPLANATORY NOTE

This method is intended for use in estimating the resistance of vulcanized rubbers to cracking when exposed, under static tension, to air containing a definite, low, concentration of ozone and at a definite humidity and temperature, but in circumstances where the effects of light are completely excluded. The development of cracks is influenced by the nature of the surface of the rubber and this must be borne in mind especially in using laboratory tests to predict service performance. The cracking may also be influenced by surface contamination, e.g. finger marks.

Attention is drawn to the highly toxic nature of ozone.

SECTION 2. TEST PIECE

The standard test pieces shall be strips of substantially uniform cross-section and thickness, not less than 1 cm wide, of such length that the exposed surface of the stretched test piece is not less than 4 cm long.

The cracking shall not be assessed on surfaces that have been cut or buffed. Comparisons of different materials are only valid if made on surfaces of similar finish produced by the same method, e.g. moulding.

The edges and the ends adjacent to the clamps shall be coated with an ozone-resistant material, e.g. collodion, chloro-sulphonated polyethylene.

NOTE. Silicone grease is not suitable.

SECTION 3. APPARATUS

3.1. *Test chamber.* A closed dark test chamber, thermostatically controlled to ± 1 degC of the working temperature, lined with, or constructed of, a material (e.g. glass) which does not readily decompose ozone, and of dimensions such that the ratio of exposed surface area of the test pieces to the effective cross-sectional area of the chamber (nominal to the gas flow) does not exceed 0·0033 V, where V is the velocity in cm/min of flow of ozonized gas in the chamber as defined in Clause 3.6.

3.2. *Ozone generator.* This is either (a) an ultra-violet lamp supplied with air or oxygen to produce ozonized air, if necessary by dilution, or (b) an electrical discharge tube supplied with oxygen to produce ozonized oxygen; the use of oxygen instead of air in this case is necessary to avoid formation of oxides of nitrogen, which may affect the degree of cracking and interfere with the estimation of ozone concentration. Source (a) may not be suitable for producing the high ozone concentration C specified in Section 4.

3.3. *Ozone concentration control.* Means for adjusting the concentration of ozone in the chamber; this may be automatic. When an ultra-violet light source is used control may be obtained by adjusting the voltage applied to the tube, or by shielding part of the tube exposed to the gas flow. When an electrical discharge tube is used a two-stage dilution of the ozonized oxygen is generally necessary, and control of the concentration is then obtained by adjustment of the metering device used for the diluting air. The adjustment is such that it will maintain the concentration within the tolerance specified in Section 4.

3.4. *Purification and humidity control of air.* The air supplied to an ozone generator of Type (a) or that used for dilution with Type (b) shall first be purified by passing over activated charcoal and, unless otherwise specified, shall have a relative humidity corresponding to a value between 50 and 80 per cent at 20°C.

3.5. *Means for determining the ozone concentration.* A means of sampling the ozonized gas from near the centre of the length of the test pieces in the chamber.

Apparatus for determining the ozone concentration in the chamber; an apparatus and procedure which have been shown to have adequate accuracy and sensitivity, are described in the Appendix*.

* Other suitable methods are those described by A. W. Brewer and J. R. Milford (*Proc. Roy. Soc. Sci. A*, 1960, **256**, No. 1287, 470) and by A. G. Veith (ASTM Special Tech. Publ. No. 229, 1958, 113).

3.6. *Flow control.* Means of adjusting the average velocity of flow of ozonized gas in the test chamber to a value between 75 and 185 cm/min calculated from the measured gas flow rate in the chamber divided by the effective cross-sectional area of the chamber normal to the gas flow.

In tests intended to be comparable the velocity shall not vary by more than ± 10 per cent.

A diffusing screen shall be used to assist thorough mixing of the incoming gas with that in the chamber.

3.7. *Test piece carrier. a.* Clamps for holding the test pieces at the required elongation, in such a manner that the length of the test piece shall be substantially parallel to the ozonized gas flow. These shall be made of a material inert to ozone, e.g. steel, polymethylmethacrylate.

b. An arrangement whereby test pieces and clamps shall move at a speed between 125 and 150 cm/min in a plane normal to the ozonized gas flow, and shall each follow consecutively the same path in such a manner that the same position within the chamber shall only be visited by the same test piece every 8–12 minutes, and that the area swept by the test piece (shown shaded in Fig. 1) is at least 40 per cent of the available cross-sectional area of the chamber.

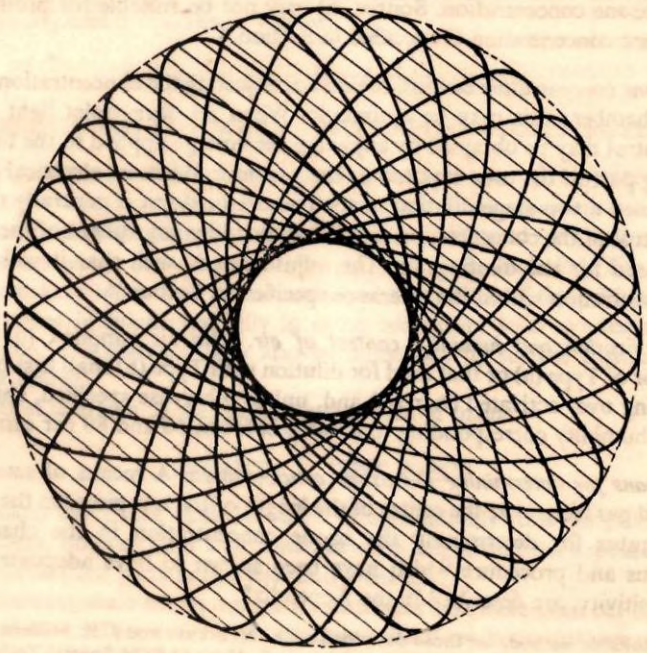

Fig. 1. Path of test piece, and swept area (shaded)

SECTION 4. PROCEDURE

The apparatus shall be adjusted to the specified rate of flow of ozonized gas through the test chamber, and the ozone concentration and temperature of the ozonized gas in the chamber shall be maintained at one of the following conditions:

A. 25 ± 5 parts per 100 million at 30 ± 1°C
B. 50 ± 5 parts per 100 million at 50 ± 1°C
C. 15 000 ± 1000 parts per 100 million at 30 ± 1°C

or such other conditions as may be appropriate.

Condition A is suitable for rubbers of low ozone resistance, e.g. natural rubber, styrene-butadiene copolymers; condition B is suitable for rubbers of high ozone resistance, e.g. butyl, neoprene; condition C is suitable for rubbers subject to corona discharges.

Test pieces shall be tested at at least four of the following elongations*:

10, 20, 30, 50, 75, 100, 125, 150 per cent

at least two test pieces being stretched between the clamps for each elongation. The stretched test pieces shall be conditioned for 48 hours in a substantially ozone-free atmosphere in the dark at a temperature of 20 ± 2°C and shall then be placed in the test chamber.

After exposure, the test pieces complete with clamps shall be removed from the chamber and examined with a lens of between × 5 and × 10 magnification. Observations shall be made at intervals† sufficiently frequent for the earliest appearance of cracking to be detected. The exposure periods between observations shall be continuous. The nature of the cracking shall be recorded.

SECTION 5. EXPRESSION OF RESULTS

The report shall include:

a. Temperature of test.
b. Ozone concentration.
c. Total times between which the first signs of cracking appeared.
d. Nature of cracking, e.g. single crack, many fine cracks.
e. Elongation of test piece.
f. Nature of test piece surface, e.g. moulded.

* It is necessary to use several elongations because rubbers differ in respect of the dependence of cracking on elongation. For rubbers of unknown ozone resistance, select 10, 30, 75, 150 per cent; when the elongation in use is approximately known, select a range around this value.
† It is suggested that total times be selected from the following series 2, 4, 8, 24, 48, 72, 96 hours, etc.

APPENDIX

DETERMINATION OF OZONE

The determination of ozone is based on the reaction of ozone with a solution of potassium iodide to release iodine, followed by the reaction of this iodine with sodium thiosulphate also present. Subsequently, the excess of sodium thiosulphate is determined by acidification of the solution and titration against standard potassium iodate solution amperometrically.

A1. Reagents. All reagents used shall be of recognized analytical reagent quality and distilled water or water of at least equal purity shall be used wherever water is specified.

Buffer solution to give pH 6·8 *at* 20°C. 9·4654 g disodium hydrogen orthophosphate and 9·0729 g potassium dihydrogen orthophosphate dissolved in water and the volume made up to 2 litres.

Sodium thiosulphate, approximately 0·001N*. 0·25 g $Na_2S_2O_3 . 5H_2O$ and 0·1 g sodium carbonate dissolved in water and the volume made up to 1 litre.

Potassium iodate, about 0·0025N*. 0·1N solution prepared by dissolving 0·8918 g KIO_3 in 250 ml of water and then diluting 25 ml of this solution to 1 litre.

Potassium iodide.

Dilute sulphuric acid. 28 ml of concentrated sulphuric acid ($d = 1·84$) added to 170 ml of water.

A2. Titration apparatus.

5 ml burette graduated in 0·01 ml divisions.
Calomel electrode.
Platinum wire electrode, bright, 28 s.w.g. about 1 in exposed length.
Galvanometer—*sensitivity* 40 mm/μA.
Stirrer driven by an electric motor.

A3. Ozone absorption apparatus. This consists of two glass vessels in series as shown in Fig. 2. By this duplication, corrections for the amount of free iodine in the potassium iodide and for the amount of liquid which hangs up in the apparatus and cannot be run out are eliminated. Experiments have shown that all the ozone is absorbed in the first flask through which the gas stream passes, and the solution in the second flask can therefore be used as a blank for comparison with the solution from the first flask. Samples of ozonized air are taken from the test cabinet at the level of the mid-point of the test pieces (to allow for any change in ozone concentration between top and bottom), pass along a pipe-

* For ozone concentrations *A* and *B*. For higher concentrations it is advisable to use more concentrated reagents.

line consisting of sections of glass tubing butted together with sleeves of polythene* tubing over the joints, through an accurate flowmeter, and then into the actual absorption apparatus. The pipeline should be as short as possible, and before using it, a stream of air with relatively high ozone concentration should be drawn through it for a period sufficient to destroy any reactivity of the glass and polythene surfaces towards ozone, the pipeline being finally flushed through with purified air. The gas stream is drawn through the absorption apparatus by a rotary pump. The usual rate of sampling is about 3 litres/min. Incorporated in the pipeline is a tap so that air can be drawn through the absorption apparatus either from the ozone test cabinet or from the atmosphere.

A4. Procedure. Before starting a determination of ozone concentration the absorption apparatus should be rinsed out with water as follows:

Taps C and F are closed, and taps A, B, D and E are opened. About 30 ml of water are added to each flask through taps A and D, and taps A, B, D and E are closed. The tap in the pipeline is then turned so that air will be drawn from the atmosphere and not from the test cabinet. The pump is switched on so that air is drawn through the absorption apparatus for about one minute, during which time a fine spray should appear in each flask. The pump is switched off and taps A and D opened, followed by B, E, C and F. The water is allowed to drain out for one minute and then C and F are closed.

To determine ozone concentration, firstly 5 ml of 0·001N sodium thiosulphate solution are added to each flask via taps A and D. Between 55 and 60 ml of the buffer solution are then placed in a small beaker and about 5 g of potassium iodide added and stirred until it is dissolved. 25 ml of this solution are then added by pipette to each flask via taps A and D. Taps A, B, D and E are then closed. The tap in the pipeline is then turned so that air may be drawn from the ozone test cabinet. The pump is switched on and the time noted. The pump is allowed to run for 15 minutes, and during this time the barometric pressure, the air temperature at the flowmeter and also the rate of flow registered by the flowmeter are recorded. After 15 minutes the pump is switched off and the taps opened in the order A, D, B and E. A titration beaker encased in dark paper is placed under each flask and taps C and F are opened. The flasks are allowed to drain for one minute and then these two taps are closed. 25 ml of water are then added to each flask via taps A and D and then those taps, together with B and E, are closed. The tap in the pipeline is turned so that air may be drawn from the atmosphere and then the pump is switched on for one minute. After this, the taps are opened in the order A, D, B, E, C and F, and the flasks allowed to drain into the titration beakers for one minute.

The solutions in the two beakers are then acidified and titrated against standard potassium iodate solution. The end point indicator consists of a platinum wire electrode coupled to one terminal of a galvanometer and a calomel

* The terms ' polythene ' and ' polyethylene ' are synonymous.

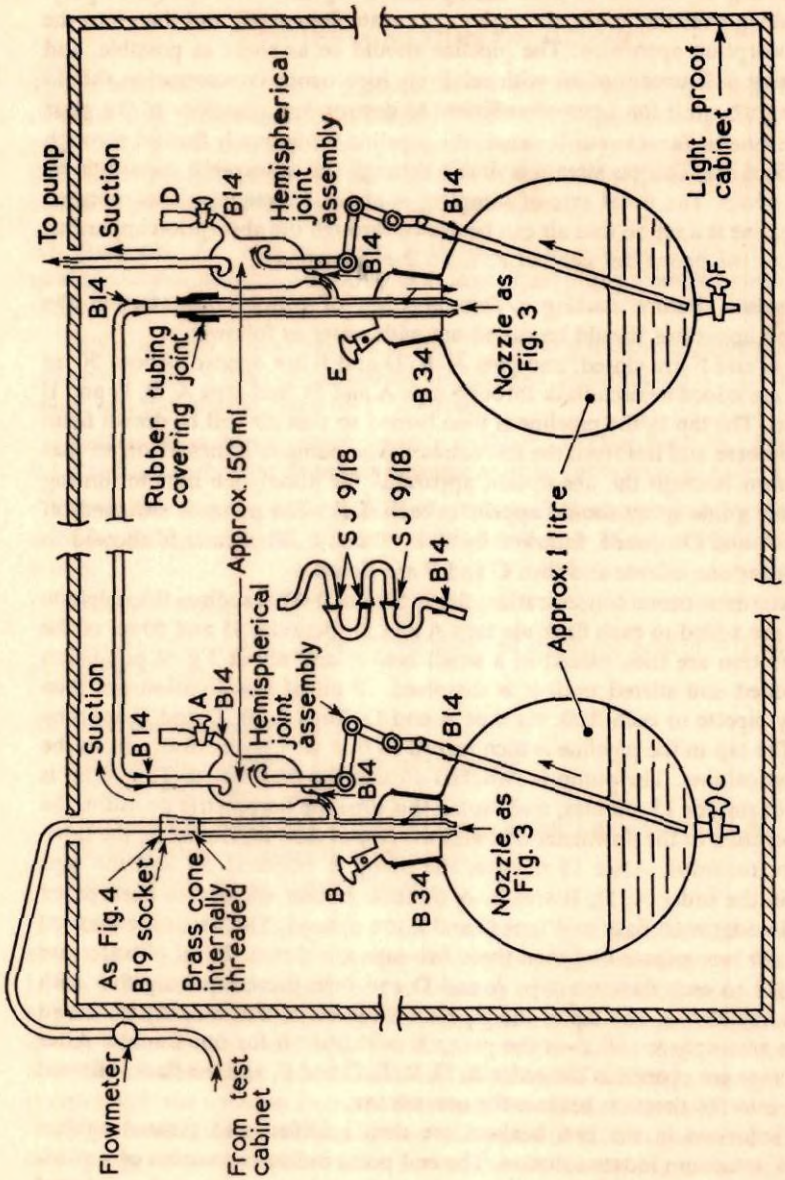

Fig. 2. Ozone absorbing apparatus

NOTE. The liquid circulates by being drawn up by suction through the tube that reaches near the bottom of the flask, as shown in the figure.

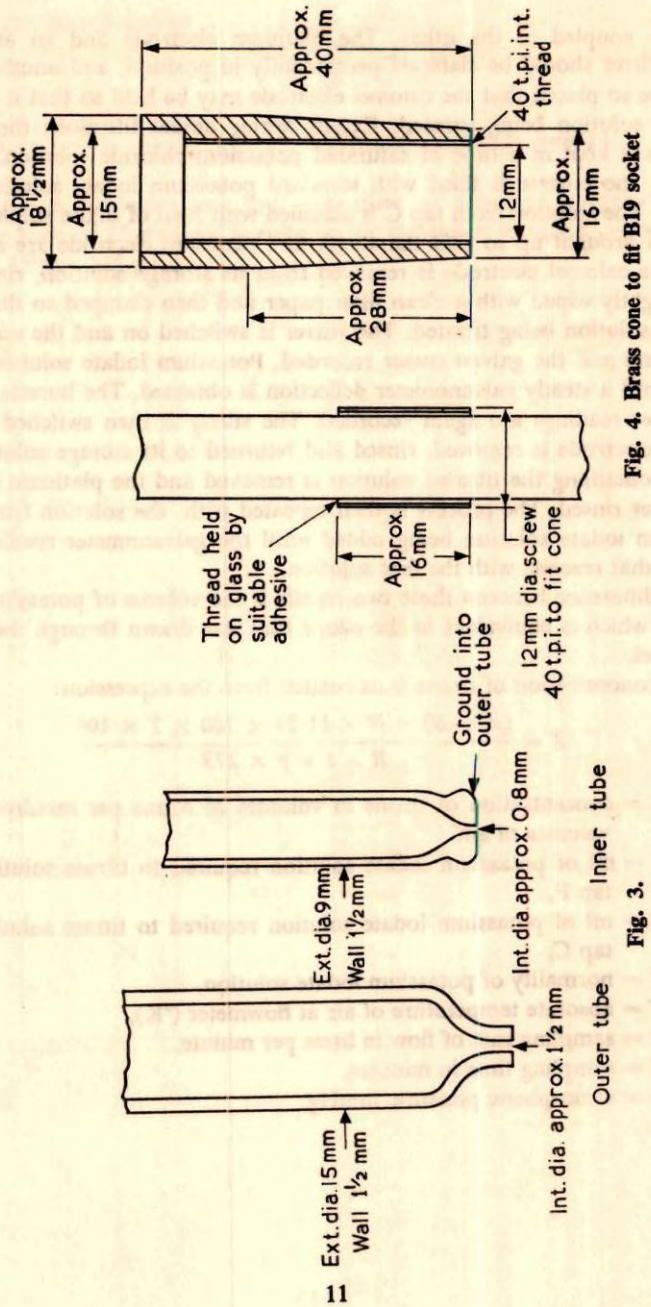

Fig. 4. Brass cone to fit B19 socket

Fig. 3.

electrode coupled to the other. The platinum electrode and an electrically driven stirrer should be clamped permanently in position, and another clamp should be so placed that the calomel electrode may be held so that it also dips into the solution being titrated. Except during actual titrations the calomel electrode is kept in a tube of saturated potassium chloride solution. For the titration, the burette is filled with standard potassium iodate solution about 0·0025N. The solution from tap C is acidified with 5 ml of dilute sulphuric acid and then brought up so that the stirrer and platinum electrode are immersed in it. The calomel electrode is removed from its storage solution, rinsed with water, lightly wiped with a clean filter paper and then clamped so that it dips into the solution being titrated. The stirrer is switched on and the readings of the burette and the galvanometer recorded. Potassium iodate solution is then added until a steady galvanometer deflection is obtained. The burette and galvanometer readings are again recorded. The stirrer is then switched off. The calomel electrode is removed, rinsed and returned to its storage solution. The beaker containing the titrated solution is removed and the platinum electrode and stirrer rinsed. The process is then repeated with the solution from tap F, potassium iodate solution being added until the galvanometer reading is the same as that reached with the first solution.

The difference between these two results is the volume of potassium iodate solution which is equivalent to the ozone that was drawn through the absorption vessel.

The concentration of ozone is calculated from the expression:

$$Z = \frac{(A - B) \times N \times 11{\cdot}21 \times 760 \times T \times 10^5}{R \times t \times p \times 273}$$

where Z = concentration of ozone in volumes of ozone per hundred million volumes of air.

A = ml of potassium iodate solution required to titrate solution from tap F,

B = ml of potassium iodate solution required to titrate solution from tap C,

N = normality of potassium iodate solution,

T = absolute temperature of air at flowmeter (°K),

R = sampling rate of flow in litres per minute,

t = sampling time in minutes,

p = atmospheric pressure, mmHg.

This can be reduced to

$$Z = \frac{(A - B) \times T \times S}{R \times p}$$

where $S = \dfrac{N \times 11{\cdot}21 \times 760 \times 10^6}{t \times 273}$ if N and t are kept constant.

Using the concentrations and quantities of solutions suggested here a sampling time of 15 minutes is suitable for the range of ozone concentrations between 15 and 125 p.p.h.m.

BRITISH STANDARDS INSTITUTION

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