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Methods of testing vulcanized rubber

Part A43. Determination of resistance to ozone cracking (static strain test)

[ISO title : Rubber, vulcanized — Resistance to ozone cracking — Part 1 : Static strain test]

Méthodes d'essais des élastomères vulcanisés
Partie A43. Détermination de la résistance au craquelage par l'ozone
(essai sous allongement statique)

Prüfverfahren für vulkanisierte Elastomere
Teil A43. Bestimmung der Ozonrißfestigkeit (statischer Belastungsversuch)

British Standards Institution

Contents

National foreword

This British Standard has been prepared under the direction of the Rubber Standards Committee. It is identical with ISO 1431/1-1980 'Rubber, vulcanized – Resistance to ozone cracking – Part 1 : Static strain test' published by the International Organization for Standardization (ISO).

This Part of BS 903 replaces BS 903 : Part A23 : 1963 which has been withdrawn. The major changes in this revision, compared with the 1963 edition of Part A23, are as follows.

(a) An ozone concentration of 200 ± 20 parts per hundred million by volume (pphm) has been included as one of the alternative test conditions (see **8.1**) but the ozone concentration of 15 000 ± 1000 pphm has been omitted.

(b) The preferred test temperature is now 40 ± 2 °C but other temperatures may be used (see **8.2**); previously, 30 ± 1 °C and 50 ± 1 °C were specified for ozone concentrations of 25 pphm and 50 pphm, respectively.

(c) Three alternative evaluation procedures are now described (see **9.2**, **9.3** and **9.4**).

(d) The appendix describing a method for determination of ozone concentration has been omitted (see 'Additional information').

Warning note on toxicity

Attention is drawn to the highly toxic nature of ozone. Guidance Note EH15/78, published by the Health and Safety Executive in 1978, gives threshold limit values (TLV) for chemical substances in the workroom environment. The recommended TLV for ozone is 0.1 ppm (parts ozone per million parts air by volume), i.e. 0.1 ppm is the maximum average concentration that workers may safely be exposed to during a normal working week. However, it is essential that efforts be made to minimize exposure at all times, and 0.1 ppm should be regarded as an absolute maximum concentration and the maximum average concentration should be appreciably lower.

NOTE. *For the purposes of this warning note only, the TLV for ozone has been expressed in ppm in accordance with the convention in quoting TLV's. Units of pphm are used elsewhere in this standard since this is normal practice in the rubber industry.*

Terminology and conventions. The text of the international standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is especially drawn to the following.

The comma has been used throughout as a decimal marker. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

Wherever the words 'International Standard' appear, referring to this standard, they should be read as 'British Standard'.

Cross-references

International standard	Corresponding British Standard
ISO 471-1977	BS 903 Methods of testing vulcanized rubber Part A35 : 1978 Standard temperatures, humidities and times for the conditioning and testing of test pieces (Identical)
ISO 4661-1977	BS 903 : Part A36 : 1978 Preparation of test pieces (Identical)

Additional information. It is intended that the international standards for the dynamic strain test for determining resistance to ozone cracking (ISO 1431/2, as referred to in clause **1**) and for the reference method for estimating the ozone concentration (ISO 1431/3, as referred to in clause **1** and in **5.4**), at present in course of preparation, will be implemented as British Standards as BS 903 : Part A44 and BS 903 : Part A45, respectively. Until the reference method for estimating the ozone concentration is published, any suitable titrimetric or instrumental method may be used, although it will not be possible to calibrate such methods against the reference method. It is emphasized that details of the method of estimation of ozone concentration should be included in the test report (see clause **11**, item c) 1)).

In UK practice, the standard laboratory temperature of 23 ± 2 °C is normally chosen (see **7.1** and **7.2**).

British Standard

Methods of testing vulcanized rubber

Part A43. Determination of resistance to ozone cracking (static strain test)

1 Scope and field of application

This International Standard is intended for use in estimating the resistance of vulcanized rubbers to cracking when exposed, under static tensile strain, to air containing a definite concentration of ozone and at a definite temperature in circumstances where the effects of direct light are excluded.

Great caution is necessary in attempting to relate standard test results to service performance since the relative ozone resistance of different vulcanizates can vary markedly according to conditions, especially ozone concentration and temperature. In addition, tests are carried out on thin test pieces deformed in tension and the significance of attack for articles in service may be quite different owing to the effects of size and the type and magnitude of deformation. Explanatory notes on the nature of ozone cracking are given in the annex.

Methods for determining resistance to ozone cracking under dynamic strain conditions and combined dynamic and static strain conditions will form the subject of Part 2 of this International Standard. A reference method for estimating the ozone concentration will form the subject of Part 3 of this International Standard.

2 References

ISO 471, *Rubber — Standard temperatures, humidities and times for the conditioning and testing of test pieces.*

ISO 4661, *Rubber — Preparation of test pieces.*

3 Definitions

3.1 threshold strain : The highest tensile strain at which a vulcanizate can be exposed to air containing a given concentration of ozone without ozone cracks developing on it after a given exposure period.

Threshold strain must be distinguished from limiting threshold strain, defined in 3.2

3.2 limiting threshold strain : The tensile strain below which the time required for the development of ozone cracks increases very markedly and can become virtually infinite.

4 Principle

Exposure of test pieces under static tensile strain, in a closed chamber at a constant temperature, to an atmosphere containing a fixed concentration of ozone. Examination of the test pieces for cracking at certain intervals.

Three alternative evaluation procedures are described for selected values of ozone concentration and exposure temperature :

a) Determination of the presence or absence of cracks after exposure for a fixed period of time at a given strain.

b) Determination of time to the first appearance of cracks at any given strain.

c) Determination of the threshold strain for any given exposure period.

5 Apparatus (See figure 1)

5.1 Test chamber.

This shall be a closed, non-illuminated chamber, thermostatically controlled to within ± 2 °C of the test temperature, lined with, or constructed of, a material (for example aluminium) that does not readily decompose ozone. Dimensions shall be such that the requirements of 5.5 are met. The chamber may be provided with a window through which the surface of the test pieces can be observed.

5.2 Source of ozonized air

Either of the following apparatus may be used :

a) an ultra-violet lamp;

b) a silent discharge tube.

The use of oxygen is necessary when using the discharge tube in order to avoid the formation of nitrogen oxides. The ozonized oxygen or air may be diluted with air to attain the required ozone concentration. Air used for generation of ozone or dilution shall first be purified by passing it over activated charcoal and shall be free from any contaminants likely to affect the ozone concentration, cracking or estimation of ozone.

The temperature of the source shall be kept constant to within ± 2 °C.

The ozonized air shall be fed from the source into the chamber via a heat exchanger to adjust its temperature to that required for the test and shall be brought to the specified relative humidity (see 8.3).

5.3 Means for adjusting the concentration of ozone.

This may be, but does not have to be, automatic. When an ultra-violet light source is used the amount of ozone produced can be controlled by adjusting the voltage applied to the tube or the gas flow rates, or by shielding part of the tube exposed to the gas flow. When a silent discharge tube is used, the amount of ozone produced can be controlled by adjusting the voltage applied to the generator, the dimensions of the electrodes, the oxygen flow rate, or the diluent air flow rate. A two-stage dilution of the ozonized air can also be used. The adjustments shall be such that they will maintain the concentration within the tolerances given in 8.1. In addition, after each occasion that the test chamber is opened for insertion or inspection of test pieces, the ozone concentration shall return to the test concentration within 30 min. The concentration of ozone entering the chamber shall at no time exceed the concentration specified for the test.

5.4 Means of determining the ozone concentration.

A means of sampling the ozonized air from the vicinity of the test pieces in the chamber and means of estimating its ozone content shall be provided.

The reference method for estimating the ozone concentration will form the subject of Part 3 of this International Standard. However, other methods, such as electrochemical or colorimetric methods, may be used, provided they are calibrated against the reference method. Glass pipelines should be used to convey the ozonized air to the measuring device. Plastics are to be avoided except as short connecting pieces for joining glass tubing. The entire sampling line shall be purged prior to its use for ozone estimation by passing a high concentration of ozone through it for sufficient time to oxidize any contaminants.

5.5 Means of adjusting gas flow.

This shall be capable of adjusting the average velocity of flow of ozonized air in the test chamber to a value of not less than 8 mm/s and preferably to a value between 12 and 16 mm/s, 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 %. The gas flow rate is the volume throughput of ozonized air in unit time and this shall be sufficiently high to prevent the ozone concentration in the chamber being significantly reduced owing to ozone destruction by the test pieces. The rates of destruction will vary according to the rubber being used, the test conditions and other details of the test. As a general guide, it is recommended that the ratio of the exposed surface area of the test pieces to the gas flow rate should not exceed 12 $s \cdot m^{-1}$, but this may not always be low enough. In cases where there is doubt, the effects of destruction should be checked experimentally and, if necessary, the test piece area should be decreased. A diffusing screen or equivalent device should be used to assist thorough mixing of incoming gas with that in the chamber.

5.6 Test piece carrier.

Clamps shall be provided for holding the test pieces at the required elongation with both sides in contact with the ozonized air in such a manner that the length of the test piece is substantially parallel to the gas flow. The clamps shall be made of a material which does not readily decompose ozone (for example aluminium).

The use of a mechanically rotating carrier mounted in the test chamber and upon which the clamps or frames for holding the test pieces are mounted is recommended to equalize the effect of different ozone concentrations in the chamber. In one example of a suitable carrier, the test pieces move at a speed between 20 to 25 mm/s in a plane normal to the gas flow and each follow consecutively the same path in such a manner that the same position within the chamber is visited by the same piece every 8 to 12 min, and the area swept by the piece (shown shaded in figure 2) is at least 40 % of the available cross-sectional area of the chamber.

6 Test piece

The test piece shall consist of a straight strip of width not less than 10 mm, thickness 2,0 ± 0,2 mm and length not less than 40 mm between the grips before stretching.

It shall be cut from freshly moulded sheet or, if required, from a finished product in accordance with ISO 4661. It shall have an undamaged test surface; ozone resistance shall not be assessed on surfaces that have been cut or buffed. Comparisons of different materials are only valid if the cracking is assessed on surfaces of similar finish produced by the same method.

The ends of the test piece held in the grips may be protected with an ozone-resistant lacquer. Care shall be taken in selecting a lacquer to ensure that the solvent used does not appreciably swell the rubber. Silicone grease shall not be used. Alternatively, the test piece may be provided with modified ends, for example by the use of lugs, to enable it to be extended without causing excessive stress concentration and breakage at the grips during ozone exposure.

For each test condition at least three pieces shall be used.

NOTES

1 It is recommended that test sheets are vulcanized between highly polished aluminium foil which is left on the rubber until the test pieces are prepared. This provides protection against handling and ensures a fresh test surface at the time of testing.

2 It is sometimes impracticable to cut the standard test pieces. In such cases one form of test piece which may be used is the T 50 dumbbell with a length of 50 mm and width 2 mm. When used to detect the onset of cracking these test pieces have been shown to give approximately equivalent results to the standard test pieces at the same percentage elongations.

3 As an alternative to the exposure of test pieces at several different strains, a test piece in the form of an annulus has been used which is strained to produce a continuous range of extensions. This method has been found to give approximately equivalent results to the standard test pieces when used to determine threshold strain.

7 Conditioning

7.1 Conditioning in the unstrained state

For all test purposes, the minimum time between vulcanization and straining the test pieces shall be 16 h.

For non-products tests, the maximum time between vulcanization and straining the test pieces shall be 4 weeks.

For product tests, wherever possible, the time between vulcanization and straining the test pieces shall not be more than 3 months. In other cases, tests shall be made within 2 months of the date of receipt of the product by the customer.

Test pieces and test sheets shall not, between the time of vulcanization and insertion in the cabinet, be allowed to come into contact with vulcanizates of a different composition. This is necessary to prevent additives which may affect the development of ozone cracks, such as antiozonants, from migrating by diffusion from one vulcanizate into adjacent vulcanizates.

It is recommended that aluminium foil be placed between test pieces and sheets of different compositions, but any other method which prevents migration of additives can be used.

Samples and test pieces shall be stored in the dark, in an essentially ozone-free atmosphere during the period between vulcanization and stretching; the normal storage temperature should be the standard laboratory temperature (see ISO 471), but other, controlled, temperatures may be used if appropriate for particular applications. These storage conditions should be used, as far as possible, for products. For evaluations intended to be comparable, the storage time and conditions shall be the same.

7.2 Conditioning in the strained state

After stretching, the test pieces shall be conditioned for a period of between 48 and 96 h in an essentially ozone-free atmosphere in the dark; the temperature for this conditioning shall normally be the standard laboratory temperature (see ISO 471), but other temperatures may be used if appropriate for particular applications. The test pieces shall not be touched or otherwise disturbed in any way during the conditioning period. For tests intended to be comparable, the conditioning time and temperature shall be the same.

8 Test conditions

8.1 Ozone concentration

Unless otherwise specified, the test shall be carried out at an ozone concentration of 50 ± 5 parts per hundred million by volume (pphm). If a lower concentration is required for testing rubbers known to be used under low ambient ozone concentrations, an ozone concentration of 25 ± 5 pphm is recommended. If highly resistant polymers are being tested, a test concentration of 200 ± 20 pphm is recommended.

NOTE — It has been found that differences in atmospheric pressure can influence ozone cracking when test pieces are exposed to constant ozone concentrations expressed in parts per hundred million. This effect may be taken into account by expressing the ozone content in the ozonized air in terms of the partial pressure of ozone, i.e. in millipascals, and making comparisons at constant ozone partial pressures. At standard conditions of atmospheric pressure and temperature (101 kPa, 273 K) a concentration of 1 pphm is equivalent to a partial pressure of 1,01 mPa.

Further guidance will be given in Part 3 of this International Standard.

8.2 Temperature

The preferred temperature of test shall be 40 ± 2 °C. Other temperatures such as 30 ± 2 °C or 23 ± 2 °C may be used but the results obtained will differ from those obtained at 40 ± 2 °C.

8.3 Relative humidity

The relative humidity of the ozonized air should not normally be more than 65 % at the test temperature.

Very high humidity can influence the results; for products intended for use in damp climates, the test shall be carried out at a relative humidity in the range 80 % to 90 %.

8.4 Elongation

Tests should normally be caried out with test pieces stretched to one or more of the following elongations :

5 ± 1 — 10 ± 1 — 15 ± 2
20 ± 2 — 30 ± 2 — 40 ± 2
50 ± 2 — 60 ± 2 — 80 ± 2 %.

9 Test procedure

9.1 General

Adjust the rate of flow and temperature of the ozonized gas and its ozone concentration to that required and place the strained test pieces, suitably conditioned, in the test chamber. Maintain the test conditions at the required levels.

Periodically examine the test pieces for the development of cracking by means of a lens of magnification about 7X, the test pieces being illuminated at the time of examination by a suitably arranged light source. The lens may either be mounted in a window in the chamber wall, or the test pieces may be removed from the chamber for a short period, in their clamps. The test pieces shall not be handled or bumped when carrying out the examination.

NOTES

1 Attention is drawn to the highly toxic nature of ozone. Appropriate measures should be taken to minimize the exposure of the operator.

2 Cracking on surfaces which have been cut or buffed shall be ignored.

Three alternative procedures for exposure of test are permissible.

9.2 Procedure A

Strain the test pieces at 20 % elongation and examine them after 72 h for the development of cracking. An alternative elongation and an exposure period may be given in the appropriate material specification.

9.3 Procedure B

Strain the test pieces at one or more of the elongations given in 8.4. If only one elongation is used, this shall be 20 % unless otherwise specified. Examine the test pieces after 2,4,8,16,24,48,72 and 96 h and, if necessary, at suitable intervals thereafter and note the time until the first appearance of cracks at each elongation.

9.4 Procedure C

Strain the pieces at no fewer than four of the elongations given in 8.4. Examine the test pieces after 2,4,8,16,24,48,72 and 96 h and, if necessary, at suitable intervals thereafter and note the time until the first appearance of cracks at each elongation so that the threshold strain can be estimated.

NOTE — For procedures B and C it is sometimes satisfactory to omit examination at 16 h.

10 Expresion of results

10.1 Procedure A

Report the results as no cracking or cracking. If cracking has occurred and an estimate of the degree of cracking is required, a description of the cracks (for example appearance of single cracks, the number of cracks per unit area and the average length of the ten largest cracks) may be given, or a photograph of the cracked test piece may be taken.

10.2 Procedure B

Take the time to the first appearance of cracks as the measure of ozone resistance at the specified strain.

10.3 Procedure C

Indicate the range within which the threshold strain is found to lie by reporting the highest strain at which cracking was not detected and the lowest strain at which cracking was observed after the specified exposure period. If replicate tests give different results quote the extreme range observed, for example, if three test pieces are used at each of 10, 15 and 20 % strains and one cracks at 10 % only, one at 15 % and all three at 20 %, the quoted range should be 10 to 20 %. Graphical presentation may be used to assist interpretation of the results.

NOTES

1 A method that has been found useful is to plot the logarithm of strain against the logarithm of the time to first cracking — both the longest time at which no cracks are seen and the earliest time when cracks are observed may be plotted. Where possible, a smooth curve may be drawn taking into account the gap between the longest time with no cracks and the earliest time with cracks at each strain to assist estimation of the threshold strain for any time within the test period (see figure 3). For some rubbers the curve may approximate to a straight line but this should not be assumed since it can lead to large errors in estimating threshold strain. Unless otherwise specified, the threshold strain at the longest test period should be reported.

2 With some rubbers, a linear plot of strain against time to first cracking will enable the existence of a limiting threshold strain to be observed.

11 Test report

The test report shall contain the following information :

a) sample details :

 1) a full description of the sample and its origin;

 2) compound details, cure-time and temperature, where appropriate;

 3) method of preparation of test pieces, for example whether moulded or cut;

b) test method :

 1) the reference of this International Standard;

 2) the procedure used (A, B or C);

 3) the test piece dimensions;

 4) whether a rotating carrier was used;

c) test details :

 1) the ozone concentration and the method of estimation;

 2) the temperature of test;

 3) the temperature of conditioning, if other than the standard laboratory temperature;

 4) the humidity, if other than specified;

 5) the air flow rate;

 6) the strain(s) on the test pieces;

 7) the duration of the test;

 8) any non-standard procedures;

d) test results :

 1) the number of the test pieces tested at each strain;

 2) for procedure A only, whether cracking occurred. If required the nature of cracking may also be given;

 3) for procedure B only, the times to the first appearance of cracks;

 4) for procedure C only, the observed range of threshold strain for a suitable exposure period or periods, or the limiting threshold strain;

e) the date of test.

Annex

Explanatory notes

Cracks develop in rubber only on surfaces subjected to tensile strain. The pattern of cracks, and the severity of cracking, vary according to the magnitude and nature of the applied strain. The strain on an article in service will vary from a minimum at one point, which need not necessarily be zero, to a maximum at some other point. The pattern of cracks at all extensions in this range should be considered when ozone resistance is being measured.

The first criterion for describing a material as ozone resistant is total freedom from cracking. Thus, the higher the threshold strain for a given exposure period or the higher the limiting threshold strain or the longer the time before cracks appear on a test piece at a given elongation, the better is the ozone resistance.

However, an alternative criterion may be necessary when ozone cracks below a certain limit of size are permitted on the rubber over a given range of strains. This criterion is based on the concept that one vulcanizate can be described as more ozone resistant than another if the ozone cracks on it are less severe over the range of extensions encountered in service, which should be specified. The visual nature of the ozone cracks which develop in the test piece should then be reported so that the whole relationship between strain and severity of cracking is determined.

The way in which ozone cracking depends on strain is not a simple relationship. The number of cracks on a test piece is related to their size and this relationship depends on the threshold strain for a given exposure period and the elongation applied to the test piece, for any given material.

Thus no ozone cracking will occur for a given exposure period at strains between zero and the threshold (by definition). A few cracks, which will be large, will be found at strains slightly above the threshold, and the cracks will become more numerous and smaller at progressively higher strains. At very high strains the cracks may sometimes be so small as to be invisible to the naked eye.

Cracks will coalesce as the exposure increases, particularly when they are very numerous on the surface of the test piece. This will result in the length of some cracks being increased, but without a proportionate increase in depth. Coalescence is probably due to a tearing process as well as ozone attack, and will sometimes result in a number of larger cracks being scattered among the general mass of small dense cracks which often cover the test piece surface at high strains.

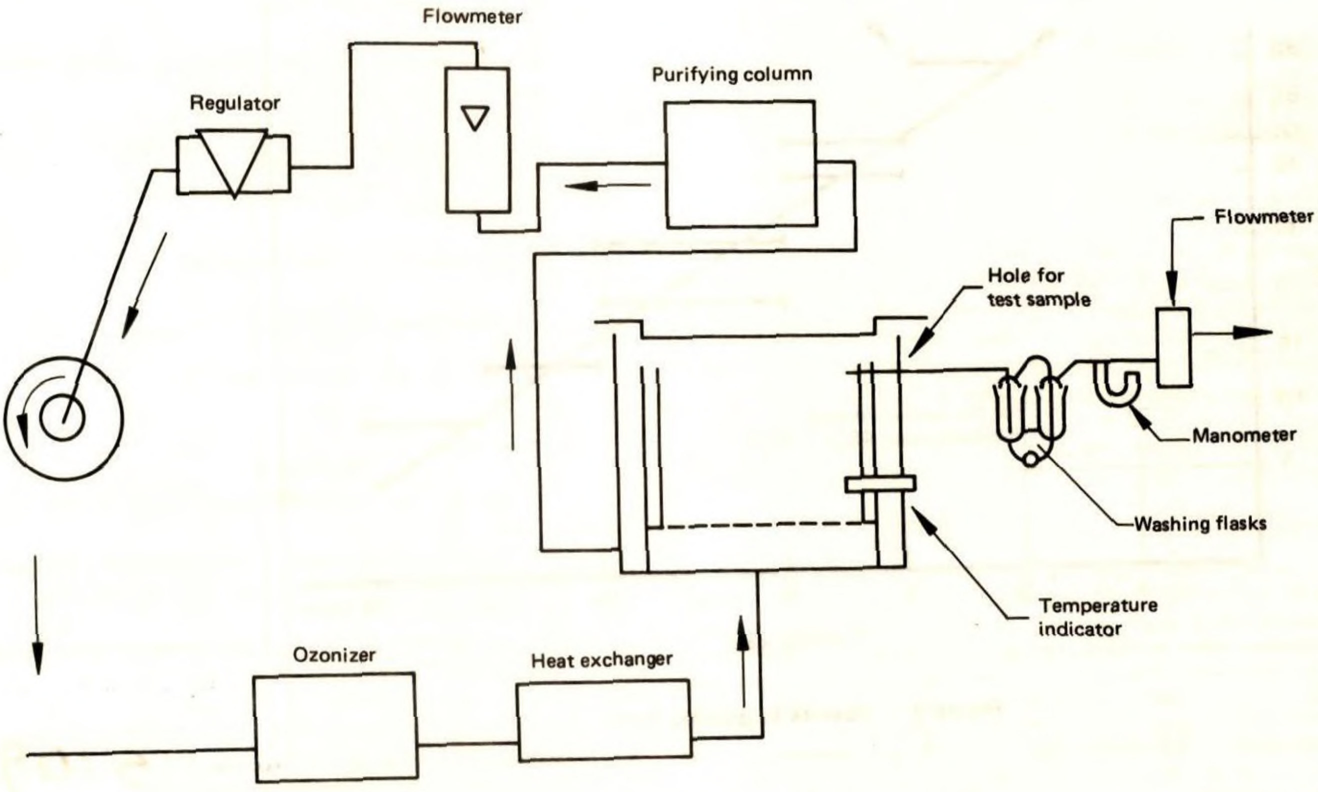

Figure 1 — Schematic diagram of the apparatus

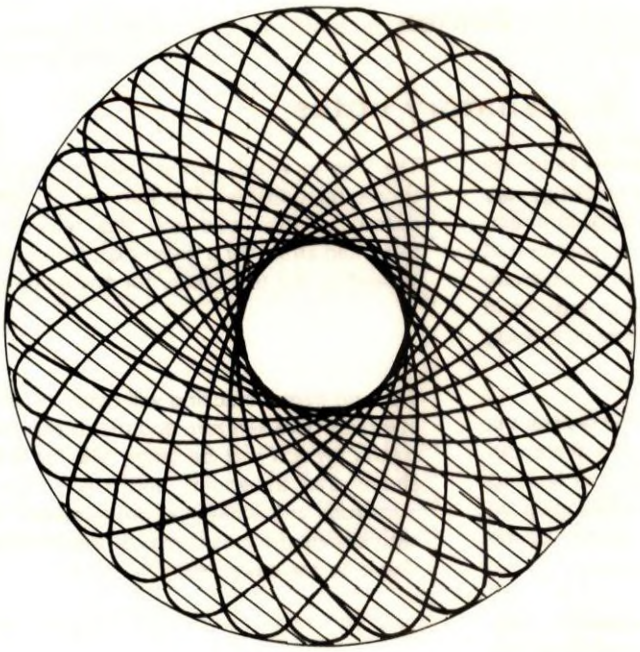

Figure 2 — Path of test piece and swept area (shaded)

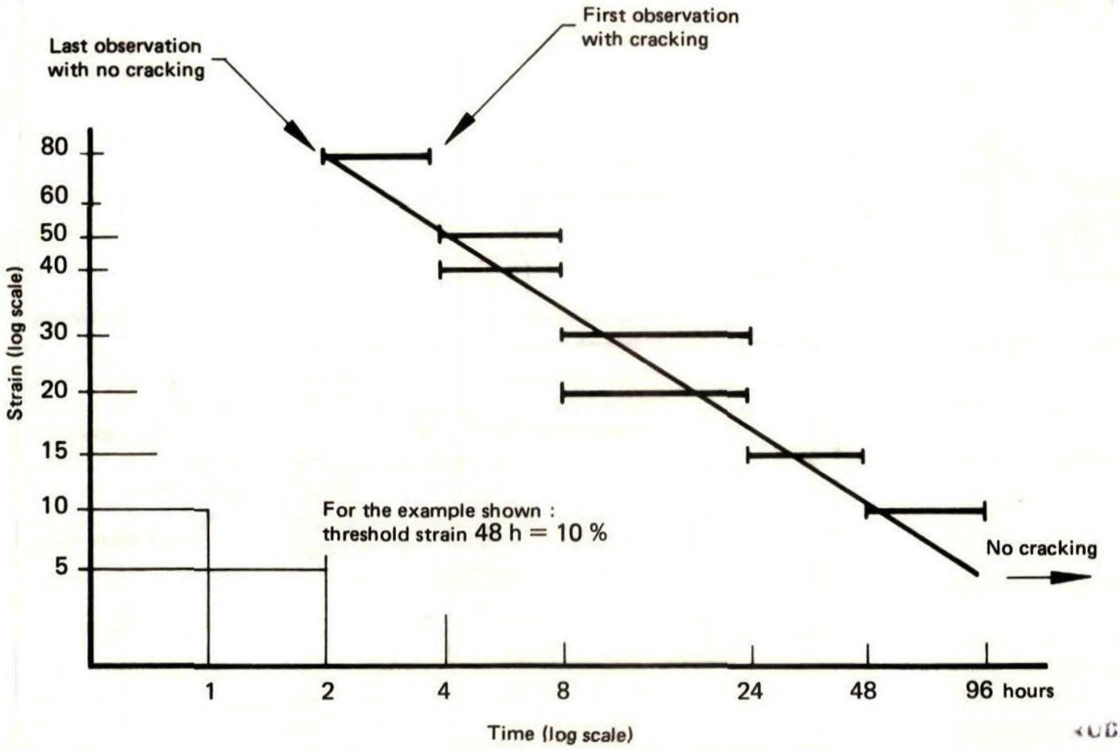

Figure 3 — Results in graphic form

Standards publications referred to

See national foreword.

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This British Standard, having been prepared under the direction of the Rubber Standards Committee, was published under the authority of the Board of BSI and comes into effect on 26 February 1982.

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Cooperating organizations

The Rubber Standards Committee, under whose direction this British Standard was prepared, consists of representatives from the following:

British Association of Synthetic Rubber Manufacturers
*British Rubber Manufacturers' Association
Department of Industry (Chemicals and Textiles)
Institution of Production Engineers
Medical Sterile Products Association
*Ministry of Defence
Plastics and Rubber Institute
*Rubber and Plastics Research Association of Great Britain
Rubber Growers' Association
Society of Motor Manufacturers and Traders Limited
*The Malaysian Rubber Producers' Research Association

The organizations marked with an asterisk in the above list, together with the following, were directly represented on the Technical *Committee entrusted with the preparation of this British Standard:*

British Railways Board
ERA Technology Ltd.
Institution of Mechanical Engineers
Institution of Water Engineers and Scientists
National College of Rubber Technology
Scientific Instrument Manufacturers Association
Shoe and Allied Trades Research Association
Individual expert

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