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British Standard

Methods of testing vulcanized rubber

Part A44. Determination of resistance to ozone cracking (dynamic strain test)

[ISO title : Rubber, vulcanized – Resistance to ozone cracking –
Part 2 : Dynamic strain test]

Méthodes d'essai des élastomères vulcanisés
Partie A44. Détermination de la résistance au craquelage par l'ozone
(essai de déformation dynamique)

Prüfverfahren für vulkanisierte Elastomere
Teil A44. Bestimmung der Beständigkeit gegen Ozonrißbildung
(dynamisches Prüfverfahren)

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 1431/2-1982 'Rubber, vulcanized – Resistance to ozone cracking – Part 2 : Dynamic strain test' published by the International Organization for Standardization (ISO).

A static strain test for determining resistance to ozone cracking is described in BS 903 : Part A43 which is identical with ISO 1431/1.

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 drawn especially to the following.

The comma has been used 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 'this part of ISO 1431' appear, referring to this standard, they should be read as 'this Part of BS 903'.

Cross-references

International standard	**Corresponding British Standard**
	BS 903 Methods of testing vulcanized rubber
ISO 37-1977	Part A2 : 1971 Determination of tensile stress-strain properties (Technically equivalent)
ISO 471-1977	Part A35 : 1978 *Standard temperatures, humidities and times for the conditioning* and testing of test pieces (Identical)
ISO 1431/1-1980	Part A43 : 1982 Determination of resistance to ozone cracking (static strain test) (Identical)
ISO 4661-1977	Part A36 : 1978 Preparation of test pieces (Identical)

It is intended that the international standard 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 a British Standard as BS 903 : Part A45. 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)).

Additional information. In UK practice, the standard laboratory temperature is 23 ± 2 °C (see clause **7**).

Compliance with a British Standard does not of itself confer immunity from legal obligations.

British Standard

Methods of testing vulcanized rubber

Part A44. Determination of resistance to ozone cracking (dynamic strain test)

1 Scope and field of application

This part of ISO 1431 specifies a method intended for use in estimating the resistance of vulcanized rubbers to cracking when exposed, under dynamic 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 the 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 of 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 static strain conditions are specified in ISO 1431/1. A reference method for estimating the ozone concentration will form the subject of ISO 1431/3.

2 References

ISO 37, *Rubber, vulcanized — Determination of tensile stress-strain properties.*

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

ISO 1431/1, *Rubber, vulcanized — Resistance to ozone cracking — Part 1 : Static strain test.*

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

3 Definition

For the purposes of this part of ISO 1431, the following definition applies.

dynamic strain : A strain (normally a tensile strain) with a sinusoidal nature varying with time at some selected repetition rate or frequency.

The maximum strain and the repetition rate are used to describe the dynamic strain conditions.

4 Principle

Exposure of test pieces, either under continuous dynamic strain or under alternate periods of dynamic and static 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.

Two 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 dynamic strain or combination of dynamic and static strains.

b) Determination of the time to the first appearance of cracks at any given dynamic strain or combination of dynamic and static strains.

5 Apparatus (see the figure)

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 lamp is used, the amount of ozone produced can be controlled by adjusting either 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 the ozone content shall be provided.

The reference method for estimating the ozone concentration will form the subject of ISO 1431/3. 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 the gas flow.

This shall be capable of adjusting the average velocity of the 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 rate 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 value 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 Dynamic testing apparatus.

This shall be constructed of a material (for example aluminium) that does not readily decompose ozone.

Its essential features are its stationary parts, provided with grips for holding one end of each of the test pieces in a fixed position, and similar but reciprocating parts, for holding the other end of each test piece. The travel shall be such that initially the minimum distance between the grips gives zero strain and the maximum distance gives the specified maximum strain.

The reciprocating parts shall be so arranged that their motion is in a straight line and in the direction of the common centre line of each opposing pair of grips. Corresponding planes in the upper and lower grips shall remain parallel to each other throughout the motion.

The eccentric which actuates the reciprocating parts shall be driven by a constant speed motor to give a frequency of 0,5 ± 0,025 Hz. If necessary, a timing device may be provided which stops the apparatus after a period of dynamic exposure and starts it again after the rest period.

The grips shall hold the test pieces firmly, without any slipping or tearing, and shall enable adjustment to be made to the test pieces to ensure accurate insertion. Each test piece shall be held in such a way that both sides are in contact with the ozonized air and its length is in the direction of the air flow.

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 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 test 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 dumb-bell 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. Dumb-bell test pieces in accordance with ISO 37 may also be used.

7 Conditioning

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

For non-product 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 may be used.

Samples and test pieces shall be stored in the dark, in an essentially ozone-free atmosphere during the period between vulcanization and testing; 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 also be used, as far as possible, for products. For evaluations intended to be comparable, the storage time and conditions 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 100 ± 10 pphm or 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 by volume. 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 partial pressures of ozone. At standard conditions of atmospheric pressure and temperature (101 kPa, 273 K), a concentration of 1 pphm is equivalent to an ozone partial pressure of 1,01 mPa.

Further guidance will be given in ISO 1431/3.

8.2 Temperature

The preferred temperature of test is 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 normally be not 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 Maximum elongation

Tests shall normally be carried out with the maximum elongation of the dynamic straining cycle at one or more of the following levels :

5 ± 1, 10 ± 1, 15 ± 2, 20 ±2, 25 ± 2, 30 ± 2 %

9 Procedure

9.1 General

Adjust the rate of flow and temperature of the ozonized gas and its ozone concentration to that required. Place each test piece, mounted at zero strain, in the dynamic testing apparatus, and by moving the reciprocating part of the apparatus adjust the maximum travel between the grips to give the required maximum elongation. Move the reciprocating part to the position of minimum travel and check that the test piece has returned to zero strain.

After inserting in the test chamber, start the dynamic testing apparatus. Maintain the test conditions at the required levels. No adjustment shall be made during the test to the minimum and maximum travel between the grips. Thus, no adjustment shall be made for any changes in zero and maximum strain caused by development of set in the test piece.

Periodically stop the machine with the test piece held at the maximum elongation and examine for the development of cracking by means of a lens of magnification about X 7, 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 in their clamps from the chamber for a short period. 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 should be ignored.

There are essentially two permissible types of dynamic exposure, continuous and intermittent. In the first type, the test pieces are continuously cycled between zero and maximum strain, whilst in the second type, periods of dynamic cycling are interspersed with periods of static strain exposure.

9.2 Continuous dynamic exposure

Two alternative procedures for exposure of test pieces are permissible.

9.2.1 Procedure A

Cycle the test pieces between zero and 10 % elongation at 0,5 Hz and examine them after 72 h for the development of cracking (alternative maximum elongations and alternative exposure periods may be given in the material specification).

9.2.2 Procedure B

Cycle the test pieces between zero and one or more of the maximum elongations given in 8.4 at 0,5 Hz. If only one elongation is used, this shall be 10 % 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 maximum elongation.

NOTE — It is sometimes satisfactory to omit examination at 16 h.

9.3 Intermittent dynamic exposure

Cycle the test pieces between zero and the specified maximum elongation for the specified period. With the test pieces held at the maximum elongation, continue exposure in the static condition in the same ozonized atmosphere. Repeat the sequence of alternate dynamic and static exposure periods as necessary.

Unless otherwise specified, the maximum strain shall be 10 %. For certain products, intermittent dynamic exposure tests may show better correlation with service performance than continuous dynamic exposure tests. The time sequence of dynamic and static exposure periods shall be given in the product specification.

Two alternative procedures for evaluation are permissible.

9.3.1 Procedure A

Examine the test pieces at the end of the specified sequence of dynamic and static exposure periods. Note the presence or absence of cracks.

9.3.2 Procedure B

Examine the test pieces at the end of each sequence of dynamic and static exposure periods and, if necessary, at suitable intervals during each sequence. Note the total time until the first appearance of cracks.

10 Expression 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 the ozone resistance at the specified maximum strain.

If required, the results of a continuous dynamic exposure test may also be expressed in terms of the number of cycles to the first appearance of cracks.

11 Test report

The test report shall include 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) a reference to this part of ISO 1431,

  2) the type of exposure (continuous or intermittent),

  3) the procedure used (A or B),

  4) the test piece dimensions;

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 that specified,

  5) the air flow rate,

  6) the maximum strain(s) on the test pieces,

  7) the duration of the test,

  8) for intermittent dynamic exposure only, the duration of the alternate dynamic and static exposure periods,

  9) any non-standardized procedures;

d) test results :

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

2) for procedure A only, whether cracking occurred (if required, the nature of any cracking may also be given),

3) for procedure B, the times or the number of cycles to the first appearance of cracks;

e) date of test.

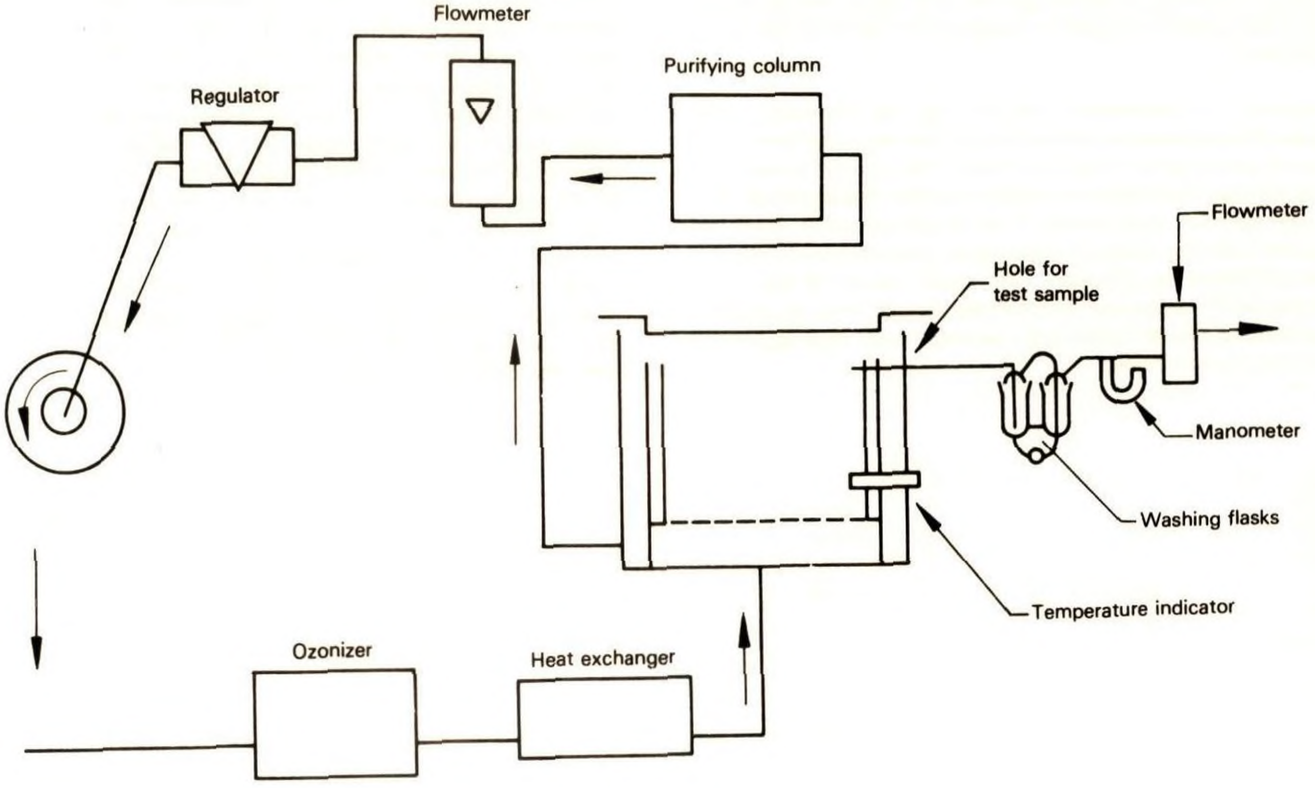

Figure — Schematic diagram of the apparatus

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 strain to which the rubber can be exposed for a given exposure period without cracking, 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.

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.

Under dynamic strain conditions a distinction should be made between ozone cracking and the cracking resulting from fatigue failure. Ozone attack is the sole cause of crack initiation at cyclic strains below a characteristic strain known as the mechanical fatigue limit. Once this limit is exceeded, the rate of crack growth increases rapidly and is mainly the result of mechanical fatigue, assisted in many rubbers by the presence of atmospheric oxygen. In this region the effect of ozone is small and becomes increasingly negligible at higher strains. Mechanical fatigue can also occur at low strains once ozone cracks reach a certain size. For these reasons, the ranking order of different rubbers can vary according to the magnitude of the strain, so that the test conditions used should, as far as possible, match those anticipated in service.

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Committees responsible for this British Standard

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Institution of Water Engineers and Scientists
Malaysian Rubber Producers' Research Association
Ministry of Defence
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