INTERNATIONAL STANDARD ISO 1431

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION •МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Vulcanized rubbers — Determination of resistance to ozone cracking under static conditions

First edition — 1972-03-15

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UDC 678.01 Ref. No. ISO 1431-1972 (E)

Descriptors : cracks, cracking (fracturing), resistance, vulcanized elastomers, ozone.

Price based on 5 pages

FOREWORD

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International Standard ISO 1431 was drawn up by Technical Committee ISO/TC 45, *Rubber and rubber products.*

It was approved in January 1970 by the Member Bodies of the following countries:

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Printed in Switzerland

Vulcanized rubbers — Determination of resistance to ozone cracking under static conditions

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for estimating the relative resistance of vulcanized rubbers to cracking when exposed, under static strain, to air containing ozone but in circumstances where the effects of direct sunlight are excluded.

2 PRINCIPLE

Exposure, in a closed chamber, of test pieces, held under static strain at a fixed temperature, to an atmosphere containing a fixed concentration of ozone; examination of the test pieces at intervals, to determine the time at which cracks first appear.

3 APPARATUS (See Figure 1)

3.1 Closed test chamber, thermostatically controlled to within ± 2 °C of the working temperature, lined with or constructed of material that does not readily decompose ozone and having a volume of at least 0.1 m^3 such that the ratio of the total exposed surface area (in cm^2) of test pieces, supporting clamps and rotating frame to the volume of the chamber (in cm^3) does not exceed 1 : 10, and preferably having a small window through which the surface of the test piece can be observed.

3.2 Source of ozonized air: this is either

a) a silent discharge tube, or

b) an ultra-violet lamp.

The ozonized air shall be free from nitrogen oxides, oil, dust and other contaminants and shall be brought to a relative humidity of not more than 65 % at the test temperature. From this source the ozonized air shall be fed into the chamber via a heat exchanger to adjust its temperature to the temperature required in the test chamber.

3.3 Means of adjusting the concentration of ozone produced by the ozonizer.

This means may be automatic but this is not essential. When an ultra-violet light source is used, control is obtained by adjusting the voltage applied to the tube or shielding part of the tube exposed to the air flow. When a silent discharge generator is used, the concentration is obtained by adjusting the voltage applied to the generator, the dimensions of the electrodes, and the air or oxygen metering device; a two-stage dilution of the ozonized air can also be used. The adjustment shall be such that it will maintain the concentration within ± 5 parts per hundred million of the working concentration when this is 50 parts per hundred million, or within ± 20 parts per hundred million when the working concentration is 200 parts per hundred million.

3.4 Means of sampling the ozonized air from the vicinity of the test pieces in the chamber and **means of estimating its content of ozone.**

The estimation of the ozone concentration should preferably be carried out using the method described in the Appendix. Other methods, such as the Brewer/Milford method[1], may be used provided that they give results identical to those obtained using the preferred method, within the specified tolerances.

3.5 The use of a **mechanically rotated frame** mounted in the test chamber and upon which the clamps for holding the stretched pieces are mounted is considered desirable but not essential. When such a rotating frame is included it shall be perforated to provide a free flow of ozonized air and shall rotate at 2 rev/min. Where no rotating frame is included, provision shall be made to provide uniform ozone concentration throughout the chamber. Precautions shall be taken to avoid any slipping or tearing of the pieces in the grips.

The clamps for the test pieces shall be made of a material such that the surface absorption of ozone is kept to a minimum. The grips shall enable the test pieces to be fixed in such a way that both sides of them are in contact with the ozonized air and with their length in the direction of movement of the latter.

3.6 Means of adjusting the average velocity of flow of ozonized air in the test chamber to a value of not less than 8 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.

4 TEST PIECE

Each 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 grips before stretching. The part of the test piece held in the grips and the cut edges, including 1 mm on the upper and lower sides, shall be carefully coated, by dipping or brushing, with an ozone-resistant lacquer (such as one based on chlorosulphonated polyethylene). Silicone grease shall not be used.

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[1] Brewer, A.W. and Milford, J.R., (proc. Roy. Soc. A 1960, 256, No. 1287, 470).

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The surface of the test piece shall be a freshly moulded one, not cut or buffed, preferably vulcanized between sheets of highly polished aluminium foil which shall be retained on the test piece until prepared for test. For test pieces cut from finished goods, the test piece shall be such that an undamaged surface is exposed for test.

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

5 CONDITIONING OF TEST PIECES

A period after vulcanization of a minimum of 16 h and a maximum of 4 weeks shall elapse before the test pieces are conditioned prior to exposure. With unknown samples the minimum only is possible. Where the samples are vulcanized between sheets of highly polished aluminium foil, the latter shall be retained on the sample until it is prepared for conditioning.

The conditioning period shall be between 48 and 96 h at the relevant extension (see 6.3) in a substantially ozone-free atmosphere maintained at the standard laboratory temperature and protected against direct sunlight, after which the test pieces shall be mounted in the chamber.

5.1 For all test purposes the minimum time between vulcanization and testing shall be 16 h.

5.2 For non-product tests the maximum time between vulcanization and testing shall be 4 weeks and for evaluation intended to be comparable, the tests, as far as possible, shall be carried out after the same time interval.

5.3 For product tests, whenever possible, the time between vulcanization and testing shall not exceed 3 months. In other cases tests shall be made within 2 months of the date of receipt by the customer of the product.

6 TEST CONDITIONS

6.1 Ozone concentration

Tests shall normally be carried out at an ozone concentration of 50 ± 5 parts per hundred million by volume. For very special purposes, such as when highly resistant polymers are being tested, a higher concentration such as 200 ± 20 parts per hundred million by volume may be used.

6.2 Temperature

The temperature of test shall be 30 ± 2 °C. Where this temperature may be difficult to maintain, other temperatures, such as 40 ± 2 °C, may be used but results obtained will differ from those obtained at 30 ± 2 °C.

6.3 Elongation

Tests shall normally be carried out with test pieces stretched by one or more elongations of 10, 20 and 40 %.

7 PROCEDURE

The ozone concentration shall be adjusted to that required. 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.

The test pieces shall preferably be examined for the development of cracking by means of a lens of magnification of about 7 X mounted in the window of the chamber. For this purpose the test pieces shall be illuminated at the time of the examination by a suitably arranged light. If the chamber does not have a window, the test pieces shall be removed from the chamber in their clamps and examined in the stretched condition using a 7 X magnification lens. The test pieces shall not be handled or bumped when carrying out the examination.

The test pieces shall preferably be examined at intervals such as 2, 4, 8, 16, 24, 48, 72, 96 h and, if necessary, at suitable intervals thereafter.

8 TEST REPORT

The test report shall include the following information:

a) the ozone concentration and method of estimation;

b) the temperature of test;

c) the elongation of the test pieces;

d) the average minimum time at which cracks appear;

e) the test piece dimensions and whether they were moulded or cut.

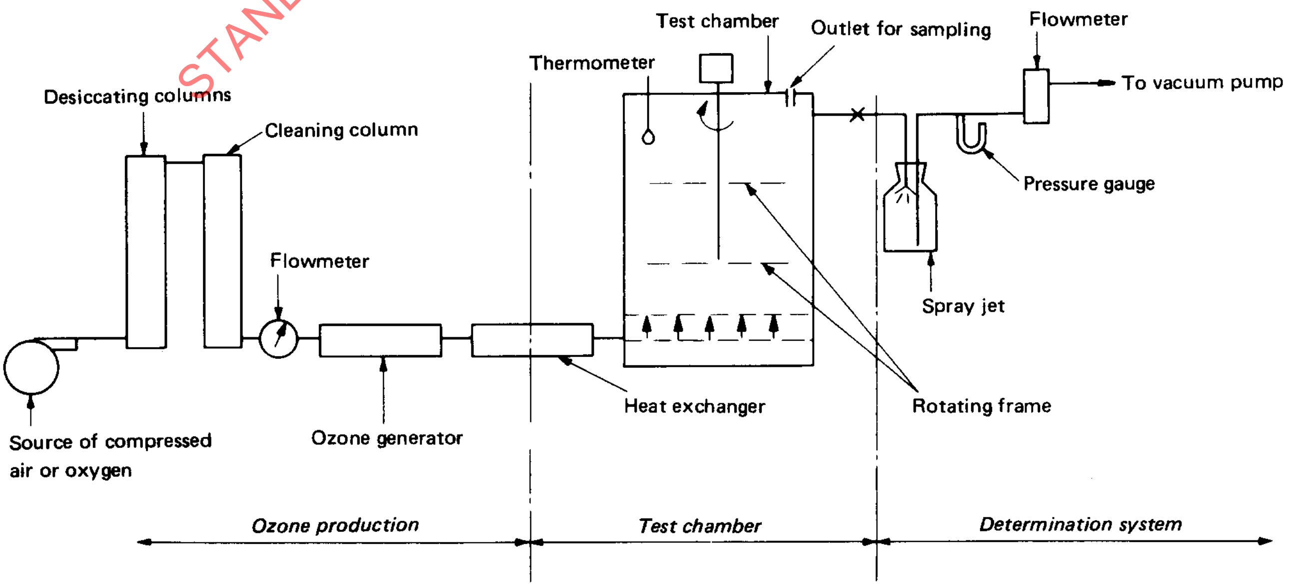

FIGURE 1 – Schematic diagram of apparatus for ozone cracking resistance test

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APPENDIX

METHOD FOR MEASURING OZONE CONCENTRATION

A.0 INTRODUCTION

Apparatus for measuring the concentration of ozone in the test chamber shall be provided.

A method for analysis that is satisfactory but not necessarily mandatory is absorption of the ozone in buffered potassium iodide solution and titration of the liberated iodine with a standard solution of sodium thiosulphate.

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A.1 REAGENTS

Reagent grade chemicals and distilled water should be used in all tests.

A.1.1 Buffer solution

Prepare a 0.025 M solution of anhydrous disodium hydrogen phosphate (Na_2HPO_4), and a 0.025 M solution of anhydrous potassium dihydrogen phosphate (KH_2PO_4).
To prepare the buffer solution having a pH of 6.7 to 7.1, add 1.5 volumes of the first solution to 1 volume of the second solution. Shake thoroughly. If considered necessary to prevent growth of algae, 1 ml of toluene may be added to the solution.

A.1.2 Crystallized potassium iodide (KI), freshly prepared.

A.1.3 Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) solution, 0.020 N.

This solution may be standardized by using a standard 0.020 N potassium bromate ($KBrO_3$) solution to oxidize an excess quantity of potassium iodide (KI) in acid solution. Titrate the liberated iodine immediately with the sodium thiosulphate solution.

The titration equipment for the microammeter method (see A.2.2.1) may be used to determine the end-point in this titration. Store the prepared 0.020 N sodium thiosulphate solution in a brown bottle in a cool dark place.

Redetermination of the normality of the solution should be carried out weekly.

A.1.4 Sodium thiosulphate solution, 0.002 N.

Prepare by pipetting 10 ml of 0.020 N solution into a 100 ml volumetric flask and diluting to the mark.

A.2 APPARATUS

A.2.1 Spray-jet device

A.2.1.1 *Type 1*

In the apparatus shown in Figure 2, the glass tube A is approximately 10 mm in diameter and 100 mm long terminating at B in a short length of capillary tubing with a bore of 1 to 2 mm. Concentric within A is a small glass tube C. Figure 2 (a) is an enlarged view of this part. The end of C is first carefully heated in a blowpipe flame until the bore is reduced in size so as just to admit a wire or drill 0.75 mm in diameter.

At this thickened end two flats are ground off on a sheet of fine alumina abrasive paper as at D in Figure 2 (b). When in position in tube A, end D fits snugly against the hole in capillary B. A rubber tubing connection at E holds the two tubes in position. F is a trap about 50 mm in diameter, and 100 mm long, and G is an enlargement in the exit tube about 38 mm diameter, containing glass wool to trap spray passing F. F is connected to the side tube of A. H is a 1 l three-neck Woulff bottle or round-bottom chemically resistant flask in which A and F are secured by standard taper ground joints. A occupies the centre opening with B protruding just below the neck and J reaching to within 12.5 mm of the bottom of the bottle. The third opening serves to introduce and remove the reagent. A is connected through plasticized short connecting pieces of polyvinyl chloride tubing and glass tubing to a rotameter graduated for an air flow from 0 to 1.0 m^3/h.

The entrance to the rotameter is connected with glass tubing to the sampling tube, and the exit of F is connected to a vacuum line. When the apparatus is properly regulated and a vacuum is applied at F, most of the reagent enters F, furnishing a head of reagent at B where the entering air resolves it into a fine mist which fills the entire bottle. The absorption flask should be mounted in a light-tight box to protect it from light while a run is being made.

A.2.1.2 *Type 2*

A modification of the spray-jet method is in current use on some commercial ozone chambers. This involves absorbing the ozone in a buffered potassium iodide solution which contains a measured amount of standard sodium thiosulphate solution.

It has the advantage over the unmodified spray-jet method in that no iodine is volatilized and no empirical factor is therefore necessary to correct for this loss.

To use this modified method it is necessary to alter slightly the equipment shown in Figure 2. A round-bottom flask with a bottom drain cock should be used with four necks or outlets. Two of these are used as depicted in Figure 2 to house the spray-jet and the upper reservoir return tube, and the other two contain a pair of platinum electrodes and a burette for adding sodium thiosulphate solution. The modified apparatus is shown in Figure 3. A sufficient quantity of buffer solution containing 15 g of potassium iodide is added so that a pool of solution fully covers the electrodes when an air stream is drawn through the apparatus. As iodine is liberated, the current increases and the null indicator or microammeter (see A.2.2) will indicate this increase. A reference point on the scale is chosen and as soon as the indicator reaches this point a stop watch is started. Immediately afterwards a known volume of 0.002 N sodium thiosulphate solution is added from the burette and the time for the current again to reach its original or reference value is noted. For low ozone concentrations, 1 to 2 ml of sodium thiosulphate solution are sufficient; for higher concentrations, correspondingly more is added. This is the preferred method when using the spray-jet to remove ozone from the air-ozone stream.

The air sample should be drawn directly from the ozone chamber. Special precautions to draw air from various levels of the chamber are not necessary since adequate circulation will be maintained if the preceding chamber specifications are met. Glass lines only should be used to convey the air-ozone stream to the absorbing device. Plasticized plactics are to be avoided except as short connecting pieces for joining glass tubing.

A.2.2 Titration apparatus

A.2.2.1 *Microammeter method*

The solution and washings from spray-jet Type 1 absorption method may be titrated in a 250 ml wide-mouth flask, or beaker of equal size.

An air or magnetic stirrer should be used. The titrating equipment consists of a microburette, microammeter of 0 to 20 μA range, a heavy-duty dry cell of 1.5 V, one 1 000 Ω and one 30 000 Ω resistor, and two platinum electrodes approximately 2.5 mm in diameter and 25 mm in length. The resistors are connected in series across the 1.5 V battery, and the potential across the 1 000 Ω resistor is applied to the electrodes.

The microammeter is connected in series with proper consideration for polarity with the electrodes in this secondary circuit. The platinum electrodes are embedded in glass tubing in the usual manner.

A.2.2.2 *Null indicator method*

A special null meter can be employed that utilises a one-transistor amplification stage and represents a ten-fold increase in end-point sensitivity. This null meter may be used with any ozone absorption device. The initial reading is taken for the buffered potassium iodide solution with a potential of 100 mV applied to the electrodes. This potential is automatically applied by the circuitry in the null meter. After absorbing the ozone in the buffered solution, the free iodine is titrated with standard sodium thiosulphate solution. The end-point is the original or initial meter reading.

A.3 PROCEDURE (For spray-jet device Type 1)

Dissolve 15 g of potassium iodide (A.1.2) in 75 ml of buffer solution (A.1.1). Add this to the absorber flask, adjust the jet to produce a fine mist, and turn on the vacuum pump.

Adjust the flow to 0.25 to 0.30 m^3/h. After completion of the absorption run, titrate the solution and washings with 0.002 N sodium thiosulphate solution (A.1.4). Add the sodium thiosulphate solution to the buffered solution of liberated iodine until zero current or the initial current value is reached.

Add the sodium thiosulphate solution dropwise when nearing the end-point, and wait after the addition of each drop to ensure complete reaction.

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