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Rubber — Determination of crystallization effects by hardness measurements

Caoutchouc — Détermination des effets de la cristallisation au moyen de mesurages de dureté

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 3387 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This third edition cancels and replaces the second edition (ISO 3387:1994), which has been technically revised. A calibration schedule has been added in Annex A and the normative references updated. It also incorporates the Technical Corrigendum ISO 3387:1994/Cor 1:2000.

Rubber — Determination of crystallization effects by hardness measurements

1 Scope

This International Standard specifies a test based on hardness measurements for determining the progressive stiffening of rubber with time, caused by crystallization. It is limited to materials having an initial hardness at a test temperature of from 10 IRHD to 85 IRHD.

The method is applicable to raw, unvulcanized (compounded) and vulcanized rubber. It is mainly of interest for rubber with a marked crystallization tendency at temperatures experienced in cold climates, such as chloroprene and natural rubber.

The method is not applicable to fast-crystallizing materials which crystallize to a considerable degree within the time-span of 15 min used for conditioning at test temperature.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 48:2010, *Rubber, vulcanized or thermoplastic — Determination of hardness (hardness between 10 IRHD and 100 IRHD)*

ISO 18899:2004, *Rubber — Guide to the calibration of test equipment*

ISO 23529, *Rubber — General procedures for preparing and conditioning test pieces for physical test methods*

3 Principle

One or the other of the following measurements is made on a test piece stored at the desired temperature:

a) the increase in hardness after a specified storage time;

b) the time required for a specified increase in hardness to occur.

4 Apparatus

4.1 Cold chamber, in accordance with ISO 23529, capable of being maintained within ± 2 °C of the specified temperature and using a gaseous heat-transfer medium.

As all final handling and measurements are to be made within the cold chamber, it shall be possible to perform these operations while the test piece temperature remains within the permissible variations. This can be done by providing suitable equipment which permits manipulation of materials within the chamber from the outside (for example, by means of handholes and gloves through the door or wall of the cabinet).

4.2 Hardness gauges, in accordance with ISO 48. Lubricants, if used, shall be of a type not causing friction in the instrument at test temperature.

4.3 Tweezers or tongs, for handling the test pieces.

4.4 Gloves, for handling the test equipment.

4.5 Heated press, for the preparation of raw and unvulcanized (compounded) test pieces.

5 Test pieces

5.1 Dimensions

Tests may be carried out on test pieces of different thicknesses. These do not necessarily give the same values of hardness readings. Tests intended to be comparable shall be made on test pieces of the same thickness.

The upper and lower surfaces of the test piece shall be flat, smooth and parallel to one another. The standard test piece shall be 8 mm to 10 mm thick. Non-standard test pieces may be either thicker or thinner, but in no case shall the test piece be thinner than 4 mm for hardnesses between 35 IRHD and 85 IRHD, or thinner than 6 mm for hardnesses between 10 IRHD and 35 IRHD. The lateral dimensions of both standard and non-standard test pieces shall be such that no test is made at a distance from the edge of the test piece less than the appropriate distance shown in Table 1.

Table 1 — Dimensions of test pieces

Dimensions in millimetres

Total thickness of test piece	Minimum distance from point of contact to edge of test piece
4	7,0
6	8,0
8	9,0
10	10,0
15	11,5
25	13,0

5.2 Preparation

5.2.1 Vulcanized rubber

Test pieces of vulcanized rubber shall be prepared in accordance with ISO 23529. To obtain the necessary thickness, it is permissible to superimpose two pieces of rubber (but no more than two), provided that these have flat, parallel surfaces.

5.2.2 Raw and unvulcanized rubber

Test pieces of raw and of unvulcanized (compounded) rubber shall be prepared by placing a suitable quantity in a preheated mould and then applying heat and pressure (4.5) for a suitable time. The mould, still under pressure, shall be cooled to standard laboratory temperature (see ISO 23529). After 15 min, the pressure shall be released and the test piece removed. It shall be free from blisters and porosity. Values of mould temperature and time of application of pressure required to produce a suitable test piece depend upon the type of rubber. A temperature of 150 °C applied for 3 min has been found suitable for many raw rubbers, while a temperature of 120 °C applied for 3 min has been found satisfactory for many compounded rubbers. However, for some materials, longer times or higher mould temperatures might be necessary to ensure a smooth and flat test piece surface. Under no circumstances shall conditions be used that cause incipient cure or degradation.

5.3 Conditioning

5.3.1 Time-interval between vulcanization and testing

When appropriate, the time interval between vulcanization and testing shall be in accordance with ISO 23529.

5.3.2 Decrystallization and conditioning

Test pieces of vulcanized rubber or test pieces moulded from raw or unvulcanized (compounded) rubber kept for more than 8 h after moulding before testing shall be decrystallized immediately before testing by heating them in an oven at 70 °C for 45 min. They shall then be conditioned at the standard laboratory temperature (see ISO 23529) for at least 30 min and no more than 60 min before testing.

6 Temperature and duration of test

6.1 Temperature

The test shall be carried out at one of the following temperatures (see ISO 23529):

+ 23 °C ± 2 °C (standard laboratory temperature)

+ 27 °C ± 2 °C (standard laboratory temperature)

+ 10 °C ± 2 °C

0 °C ± 2 °C

− 10 °C ± 2 °C

− 25 °C ± 2 °C

− 40 °C ± 2 °C

− 55 °C ± 2 °C

− 70 °C ± 2 °C

If not specified for special reasons, the test shall be carried out at the temperature which is closest to the one where the crystallization rate is at its maximum whenever this is known.

NOTE Generally, crystallization rates are known to have their maxima at the following approximate temperatures:

Rubber polymer	Temperature of maximum crystallization rate °C
Chloroprene rubber	−10
Polyurethane rubber	−10
Natural rubber (1,4-*cis*-polyisoprene)	−25
Dimethyl silicone rubber	−55
1,4-*cis*-polybutadiene	−55

6.2 Duration

Hardness measurements are generally taken after $(24\ ^{0}_{-0,5})$ h and $(168\ ^{0}_{-2})$ h of storage at the test temperature. Intermediate times of reading that enable the hardness to be plotted against time shall be used (48 h and 96 h are suggested). Longer times of storage may be used if the hardness is still increasing at 168 h.

If the hardness increase after $(24\ ^{0}_{-0,5})$ h is more than 10 IRHD above the reading of initial hardness, the test shall be repeated using shorter times of storage (1 h, 2 h, 4 h and 8 h are suggested).

7 Procedure

7.1 Hardness measurement

Carry out the hardness measurement in accordance with ISO 48. The method selected shall be used for the entire test. Make one measurement at either three or five different points distributed over the test piece and take the median of the results. Make each reading at a point at least 4 mm away from points where any previous readings have been made. The same hardness gauge shall be used throughout any one test, the appropriate gauge being determined from the initial hardness at the test temperature. For initial hardnesses between 10 IRHD and 30 IRHD, the instrument specified for method L of ISO 48:2010 shall be used, for initial hardnesses between 30 IRHD and 80 IRHD, the instrument specified for method N of ISO 48:2010 shall be used, and for hardnesses over 80 IRHD, the instrument specified for method H of ISO 48:2010 shall be used. If the hardness increase gives values above 35 IRHD for method L, the hardness readings shall be determined from an extension to ISO 48:2010, Table 5, calculated using the equation given in ISO 48:2010, Annex A.

7.2 Original hardness

First measure the hardness with the test piece and test equipment conditioned at the standard laboratory temperature (see ISO 23529). This measurement gives additional information but is not used in the calculation of crystallization effects and may be omitted for highly plastic samples of unvulcanized rubber.

7.3 Initial hardness at test temperature

Condition the hardness gauge (4.2) and the tweezers or tongs (4.3) in the cold chamber (4.1) at the desired test temperature for at least 60 min.

Place the test piece in the cold chamber at the desired test temperature. After 15 min ± 1 min, take the first hardness reading, using the tweezers or tongs for handling the test piece and the gloves (4.4) for handling the test equipment. If the initial hardness reading is above 85 IRHD, the method is not applicable.

The hardness gauge (4.2) used in this test procedure is normally conditioned and operated inside the cold chamber. Alternatively, a special device may be used where the body of the hardness gauge is placed outside the cold chamber and connected with the indenter in the cold chamber by means of a rod with low heat-conductive capacity, and constructed to avoid the introduction of additional friction.

7.4 Hardness increase due to crystallization

Repeat the hardness measurements, as specified in 7.1, after the specified times of storage at the test temperature.

After all measurements have been completed, it is advisable to dry all apparatus by warming it with circulating air to approximately 40 °C.

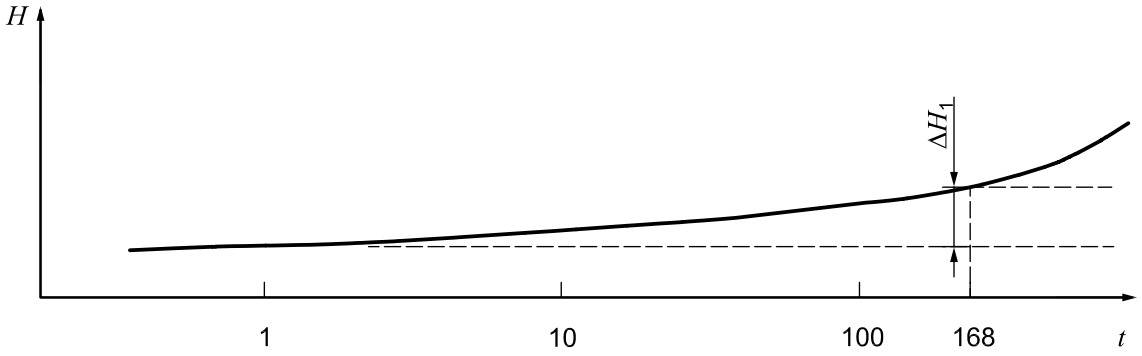
8 Expression of results

8.1 For specification purposes, the hardness increase between the initial hardness reading and the reading taken after $(168\ ^{0}_{-2})$ h storage shall be calculated and stated in the test report — see Figure 1, graph a). If this hardness increase is greater than 10 IRHD, the readings at different times shall be plotted against time (time on logarithmic scale) and a smooth curve fitted to the points. From the curve, the time corresponding to a hardness increase of 10 IRHD shall be obtained by interpolation — see Figure 1, graph b).

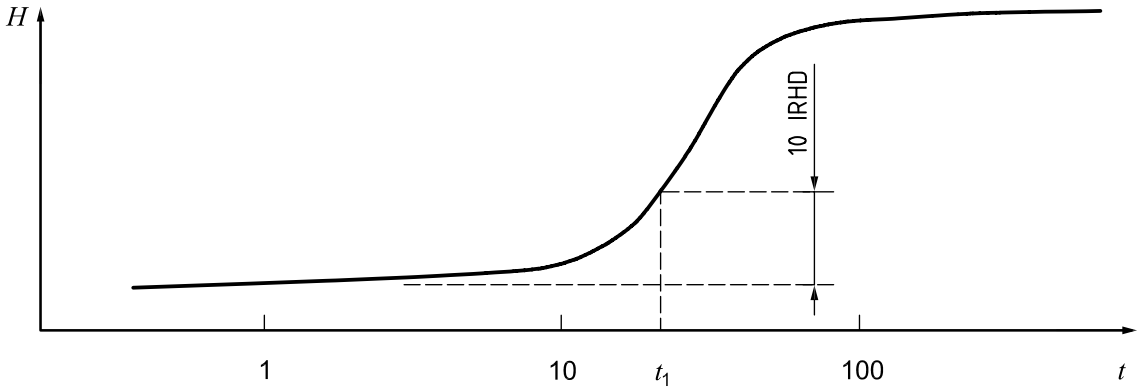
The same procedure is applied, using the shorter time scale, when the hardness increase after $(24\ ^{0}_{-0,5})$ h exceeds 10 IRHD.

The increase in hardness after a specified time or the time for a specified increase in hardness may also be used for reporting of data to comply with requirements in certain specifications — see Figure 1, graph c).

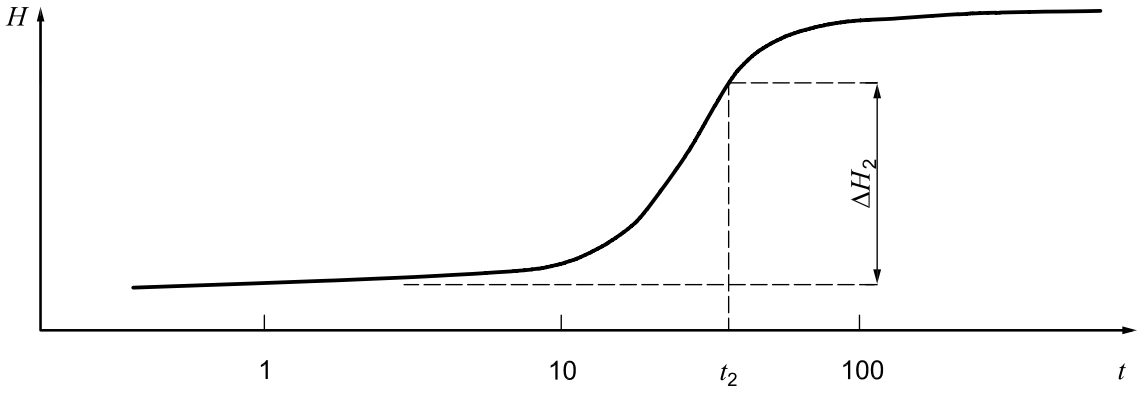
8.2 For other purposes, the time taken for half the hardness increase to occur between the initial and final hardness may be given — see Figure 1, graph d), using the smooth curve of hardness versus time. This assumes that hardness measurements are extended in time to secure the level of final hardness.



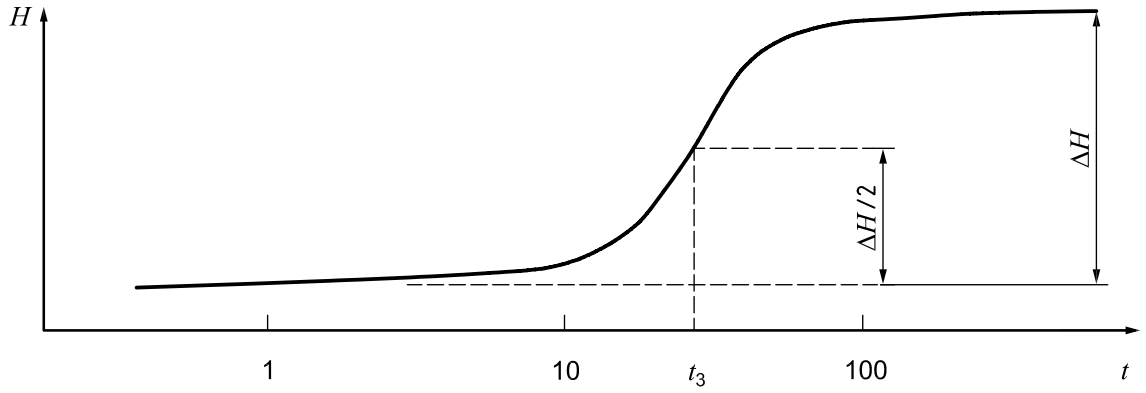
a) Hardness increase after (168 $^{0}_{-2}$) h less than 10 IRHD: report the actual hardness increase, ΔH_1, after (168 $^{0}_{-2}$) h



b) Report time t_1 for 10 IRHD increase to occur



c) Report time t_2 for a specified hardness increase, ΔH_2, to occur, or report hardness increase ΔH_2 after a specified time, t_2



d) Report time t_3 for half the hardness increase between initial and final hardnesses to occur

Key

H	hardness (IRHD)
t	time of storage at test temperature, h

Figure 1 — Different ways of reporting data from smooth curve obtained by plotting hardness readings against time of storage at test temperature

9 Test report

The test report shall include the following information:

a) sample details:

   1) full description of the sample and its origin;

   2) compound details, and cure details, where appropriate;

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

b) test method:

   1) a full reference to the test method used, i.e. the number of this International Standard;

   2) the test procedure used;

   3) the type of test piece used;

c) test details:

   1) the standard laboratory temperature;

   2) decrystallization and conditioning prior to test, if carried out;

   3) the test temperature;

   4) time of storage at the test temperature;

   5) details of any procedures not specified in this International Standard;

d) test results:

   1) the number of test pieces used;

   2) the individual test results;

3) the mean results;

4) date of test.

Annex A
(normative)

Calibration schedule

A.1 Inspection

Before any calibration is undertaken, the condition of the items to be calibrated shall be ascertained by inspection and recorded on any calibration report or certificate. It shall be reported whether calibration is carried out in the “as-received” condition or after rectification of any abnormality or fault.

It shall be ascertained that the apparatus is generally fit for its intended purpose, including any parameters specified as approximate and for which the apparatus does not therefore need to be formally calibrated. If such parameters are liable to change, then the need for periodic checks shall be written into the detailed calibration procedures.

A.2 Schedule

Verification/calibration of the test apparatus is a normative part of this International Standard. However, the frequency of calibration and the procedures used are, unless otherwise stated, at the discretion of the individual laboratory using ISO 18899 for guidance.

The calibration schedule given in Table A.1 has been compiled by listing all of the parameters specified in the test method, together with the specified requirement. A parameter and requirement can relate to the main test apparatus, to part of that apparatus or to an ancillary apparatus necessary for the test.

For each parameter, a calibration procedure is indicated by reference to ISO 18899, to another publication or to a procedure particular to the test method which is detailed; whenever a more specific or detailed calibration procedure than in ISO 18899 is available, it shall be used in preference.

The verification frequency for each parameter is given by a code-letter. The code letters used in the calibration schedule and their meanings are

S standard verification frequency interval as given in ISO 18899, and

U in use.

Table A.1 — Calibration frequency schedule

Parameter	Requirement	Subclause of ISO 18899:2004	Verification frequency guide	Notes
Cold chamber temperature control	±2 °C	18	S	
Decrystallization oven temperature control	70°C ± 1 °C	18	S	
Hardness gauge	As per ISO 48		S	
Heated press temperature	120°C ± 1 °C or 150°C ± 2 °C	18	S	
Heated press pressure	No value specified	16.4 or 16.5	S	
Mould for raw and unvulcanized rubber	Allowing test piece with dimensions in line with Table 1 to be obtained		U	
Thickness gauge	As per ISO 23529	15.1	S	

In addition to the items listed in the table, use of the following, which needs calibrating in accordance with ISO 18899, is implied:

— a timer.

Bibliography

[1] ISO 7619-2, *Rubber, vulcanized or thermoplastic — Determination of indentation hardness — Part 2: IRHD pocket meter method*

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