

## LONG-TERM STABILITY OF RUBBER HARDNESS REFERENCE BLOCKS

Anton Štiber, Konrad Herrmann, Zoran Šušterič

ZAG, Laboratory for metrology, Ljubljana, Slovenia  
PTB, Laboratory for hardness measurement, Braunschweig, Germany;  
SAVATECH d.o.o., Kranj, Slovenia

**Abstract** - Methods for hardness measurement on elastomers are characterized by a set-up where indenters with various defined geometries are pressed under defined test forces into the surface of testing material. The hardness value represents the resistance of the material to the rigid indenter and is calculated from the indentation depth of the indenter in the to be tested material. The test methods IRHD and Shore are the most common methods used in the field of rubber hardness measurements. Appropriate hardness measuring instruments are spread world wide. A periodic verification has to be carried out to assure the accuracy of these measuring instruments. Direct and indirect verification methods are recommended to be used. For the indirect method rubber hardness reference blocks are used. This indirect verification method is especially appropriate for the daily check of hand held rubber hardness testers. On the other side the direct verification of test force, depth measuring system and indenter geometry is suited for the periodic calibration of rubber hardness testers. For the rubber hardness reference blocks their accurate hardness reference value and the long-term stability are the most important characteristics.

In this paper the long-term behaviour of hardness of rubber blocks which at present are available on the market and are made by different producers is presented. For the measurements the Shore and IRHD hardness standard devices in the PTB have been used. In order to determine the relationship between hardness and time under the specified conditions a regression analysis of the obtained measurement results was carried out.

The results of this analysis can be used for the improvement of quality assurance systems in the field of rubber hardness measurements.

**Keywords:** Hardness, rubber reference blocks, long-term stability

### 1. HARDNESS OF RUBBER

Hardness of a material is generally defined as material's resistance to introduction of foreign bodies into its surface layers. At given temperature, it depends on material's physical properties, as well as on shape and properties of indenter. In fact, like moduli of elasticity, hardness may be envisioned as a measure of the material's stiffness. For crystals, e.g. metals, where indentation deformations are

very small, hardness and elasticity moduli are nearly proportional to each other, especially if the ratio between elastic and plastic deformation work is constant. On the other hand, stiffness of amorphous polymers, like rubbers, is usually much lower and deformations in the vicinity of the indenter are large, highly in the nonlinear region. This, however, results in likewise courses of hardness and elasticity moduli, but not in exact proportionality between them.

For practical purposes (products) rubber is used in crosslinked (vulcanized) state, i.e. in a form of three dimensional network made by intermolecular covalent linkages. These linkages thermally stabilize the raw rubber and make it highly elastic. Hardness increases with increasing linkage density. Besides, several other components that are normally added to rubber, such as reinforcing fillers (carbon black, silica) and softeners (oils), have a strong impact to its hardness. Whereas hardness increases with increasing content of fillers, it decreases with increasing amount of softeners. The latter are also the cause for rubber hardening with time. Though slowly, the softeners, which are not chemically bonded to rubber molecules, migrate by diffusion to rubber surface, where they evaporate. So, the gradual time loss of softeners causes rubber hardness to increase.

Hardness of rubber also depends on temperature. By raising temperature the free volume of rubber increases and the effective potential barriers for molecular conformations decrease, making the network less stiff and thus causing drop of its hardness. Temperature dependence of rubber hardness is of Arrhenius type with the usual activation energies of a few kJ/mol.

For measuring hardness of rubber the scales Shore A and IRHD are normally used, rarely the scale Shore D. Indenters' shape and dimensions, as well as indentation force are standardized.

### 2. DESCRIPTION OF MEASURING METHODS

There are several hardness scales for Shore and IRHD methods stipulated in standards. Shore A and D scales are defined in standards ISO 7619 and ISO 868 while IRHD scales N, H, L and M are defined in standard ISO 48.

These methods are used for the determination of the hardness of vulcanized or thermoplastic rubbers, plastics

and ebonite on samples with flat surfaces. Methods differ primarily in indenter geometry and in the magnitude of the indenting force.

*IRHD (International Rubber Hardness Degree) method*

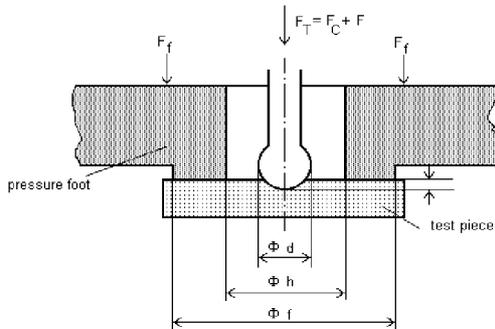


Fig. 1: Measurands of indenter and pressure foot

Hardness value is expressed in International Rubber Hardness Degree. Application ranges of methods on IRHD scales, ball diameters and forces are as follows:

- Low-hardness...method L: 10 IRHD - 35 IRHD ball 5 mm...0,3(contact force)/5,7(tot. force)N
- Normal test...method N: 35(30) IRHD - 85(95) IRHD ball 2,5 mm...0,3/5,7 N
- High-hardness...method H: 85 IRHD - 100 IRHD ball 1 mm.....0,3/5,7 N
- Microtest...method M: 35(30) IRHD - 85(95) IRHD ball 0,395 mm...8,3/153,3 mN

*Shore method*

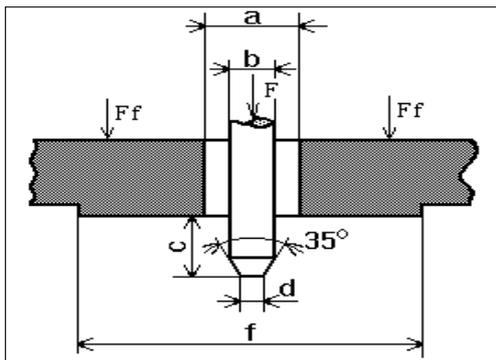


Fig. 2 Measurands of cone indenter and pressure foot at Shore A scale.

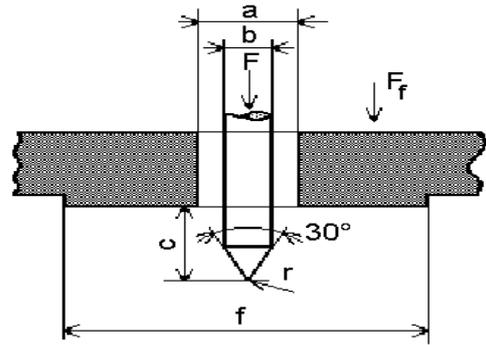


Fig. 3 Measurands of cone indenter and pressure foot at Shore D scale.

Application ranges of methods on Shore scales, main dimensions and forces are as follows:

- Normal hardness...method A: 0 – 100 Shore indenter (b/d=1,25/0,79 mm;  $\alpha=35^\circ$ ) $F_{max}=8,05$  N
- High hardness..... method D: 0 – 100 Shore indenter (b/r=1,25/0,1 mm;  $\alpha=30^\circ$ ). $F_{max}=44,5$  N

3. PERIODIC LONG - TERM HARDNESS MEASUREMENT

Several series of measurement – recalibrations have been carried out since 1994 to establish changes in hardness during the time. Three sets of Shore A, two sets of IRHD N and two sets of IRHD M reference blocks were used. The sets were made by the following producers: SHORE Instruments, HAMPDEN EQUIPMENT LTD, RAPRA and WALLACE. The sets of blocks were stored and kept between each recalibration in laboratory for Metrology in Ljubljana under normal temperature condition between 19 °C and 25 °C and humidity between 30 % and 70 %.

Recalibrations were carried out on reference standards on PTB Physikalisch Technische Bundesanstalt in Braunschweig where rubber hardness reference standards are set up. The rubber hardness standard device is of the type U7294A made by Bareiss Co. in Oberdischingen (Germany).

On this device corresponding measuring heads for the above mentioned rubber hardness scales were used.

For each set of blocks the following measurement results were obtained:

TABLE I. Shore A calibration blocks

Calibrated in/by	USA	UK	PTB	PTB	PTB	PTB	PTB
date	1994	1996	1997	2000	2001	2002	2003
Reading time s	1	3	3	3	3	3	3
Hardness values							
set Nr. 1, ID1320301							
white	32,8	33	33,9	33,9	33,1	34,3	35,1
yellow	44,2	43	44,1	42,8	42,0	42,8	42,9
blue	52,8	51	52,2	51,1	50,0	51,5	50,6
green	63,3	60	62,0	61,0	60,2	61,7	60,7
red	72,1	70	71,5	70,6	69,7	72,2	70,7
brown	79,6	76	79,1	78,9	78,0	79,5	77,9
black	93,9	94	95,2	95,1	94,8	95,9	94,6
set Nr. 2, ID1320306							
white	33,0	36	37,1	37,6	37,1	37,1	37,6
yellow	41	45	46,5	46,8	46,5	46,2	46,8
blue	50	54	56,1	57,1	56,3	56,0	56,7
green	58	62	63,8	65,8	64,8	64,3	65,7
red	75	83	83,7	84,9	83,9	85,2	85,8
orange	84	91	93,8	94,7	93,8	94,7	95,0
set Nr. 3, ID1320307							
yellow		38	39,8	40,7	40,1	40,7	41,1
blue		50	50,8	51,8	51,6	51,6	52,5
white		58	59,0	60,3	60,7	60,4	61,4
green		67	68,0	70,0	70,0	69,9	70,6
red		77	78,0	79,3	79,5	79,5	80,3
orange	-	87	87,0	87,7	87,9	87,6	88,8

TABLE II. IRHD Normal calibration blocks

Calibrated in/by	UK	PTB	PTB	PTB	PTB	PTB
date	1995	1997	2000	2001	2002	2003
Reading time s	30	30	30	30	30	30
Hardness values						
set Nr. 4, ID1320305						
A	41	40,6	41,6	42	41,5	42,2
B	52	51,2	52,5	52,7	51,9	53,3
C	62	61,7	63,3	63,8	62,3	64,7
D	72	72,4	74,4	74,8	72,2	75,4
E	82,5	82,2	84,1	84,4	82,3	85,1
F	92	90,9	92,3	92,5	90,6	92,6
set Nr. 5, ID1320303						
A	41,5	41,3	41,7	41,7	41,4	42,1
B	56,5	55,2	56,8	56,6	55,2	56,9
C	65,5	64,5	65,7	65,7	64,5	66,2
D	74,5	72,9	75,2	75,0	73,0	75,4
E	86,5	85,5	87,9	87,8	85,7	87,9
F	92,5	92,3	94,2	94,0	92,6	94,0

TABLE III. IRHD Micro calibration blocks

Calibrated in/by	UK	PTB	PTB	PTB	PTB
date	1995	2000	2001	2002	2003
Reading time s	30	30	30	30	30
Hardness values					
set Nr. 6, ID1320302					
A	41,5	42,6	42,4	42,9	42,9
B	57,5	58,7	58,3	58,6	59,0
C	69,5	69,3	71,7	71,6	72,5
D	79,5	80,3	82,8	82,4	82,6
set Nr. 7, ID1320304					
A	42	43,0	42,4	42,5	45,1
B	58	57,2	57,0	57,7	58,5
C	69,5	69,0	70,0	71,1	70,6
D	81	80,3	81,6	81,9	81,4

The graphic presentation of the values for the Shore A blocks is depicted in the Fig. 4 to 6.

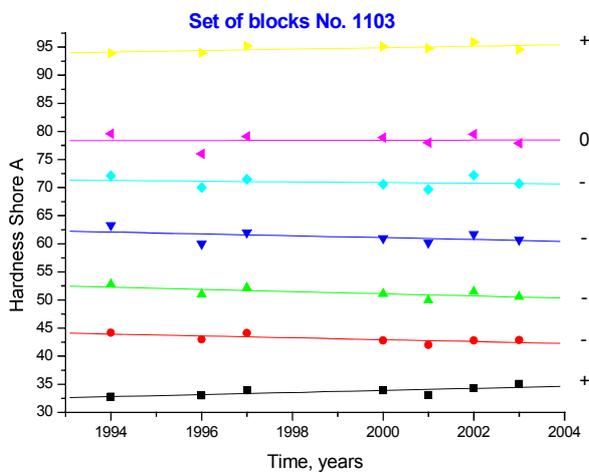


Fig. 4 Hardness change of the set No.1 of Shore A rubber blocks over time.

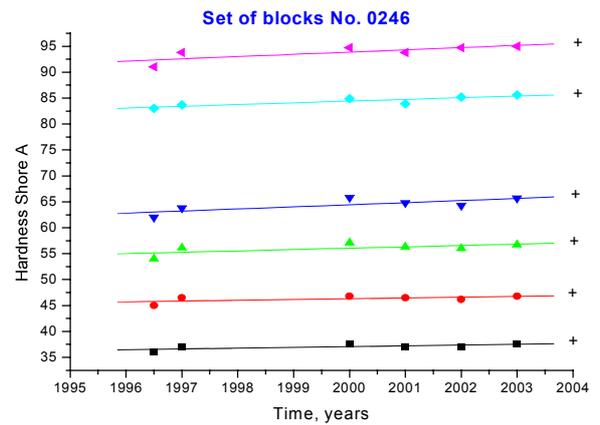


Fig. 5 Hardness change of the set No.2 of Shore A rubber blocks over time

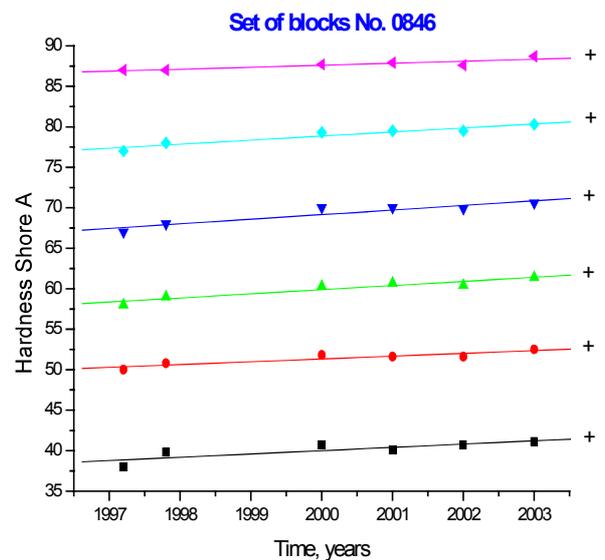


Fig. 6 Hardness change of the set No.3 of Shore A rubber blocks over time

Next in the Fig. 7 and 8 the hardness change of sets of IRHD normal rubber blocks is shown.

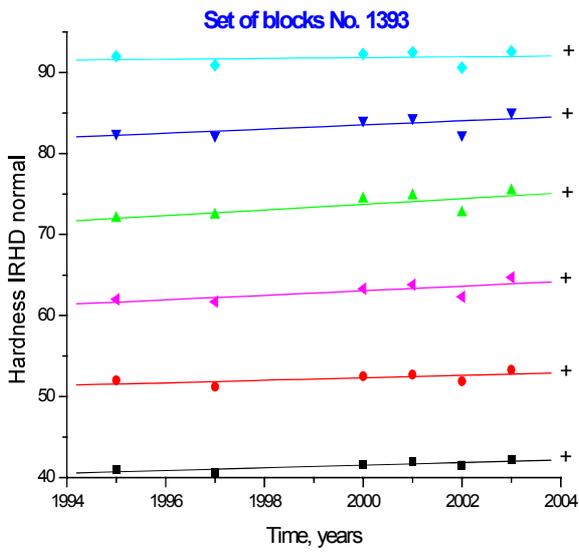


Fig. 7 Hardness change of the set No.4 of IRHD normal rubber blocks over time

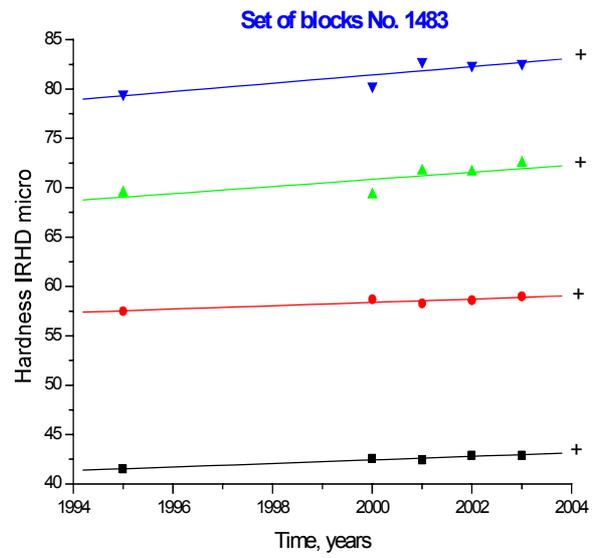


Fig. 9 Hardness change of the set No.6 of IRHD micro rubber blocks over time

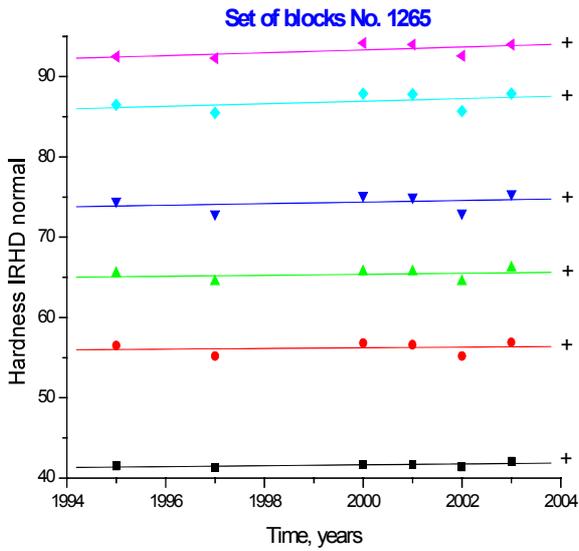


Fig. 8 Hardness change of the set No.5 of IRHD normal rubber blocks over time

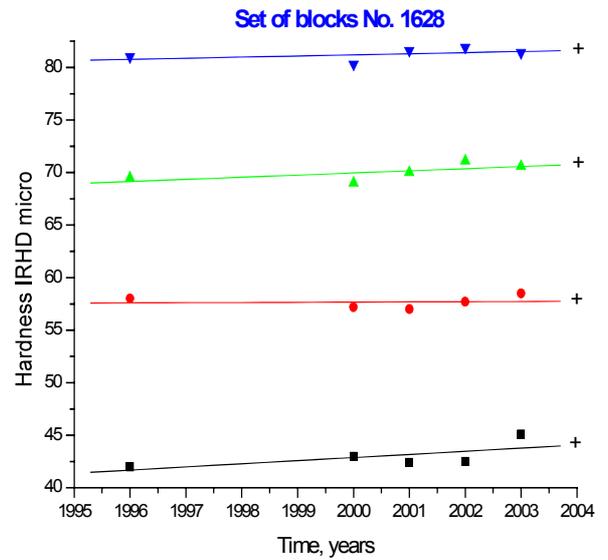


Fig. 10 Hardness change of the set No.7 of IRHD micro rubber blocks over time

Finally, the Fig. 9 and 10 show the hardness change over time for two sets of IRHD micro rubber blocks.

#### 4. EVALUATION OF THE RESULTS

The signs + or – on the right side of the figures indicate the tendency of the hardness change. With the exception of the Shore A set No.1 which showed several cases of hardness decrease, in general the hardness reference blocks show a hardness increase over time. This confirms the theory of hardness change over time for rubber products and, between them, rubber blocks.

To find out the reason for unusual decreasing tendency of hardness of the set Nr.1 additional spectral analysis was carried out. Two blocks out of the set was analysed. White block which hardness increases and blue block which hardness decreases. No significant differences between them were found out. Both were made of a kind of silicon rubber like Silopren VS. Long term elasticity and stability of such type of rubber is known. There are several possible effects which make hardness decreasing like loss of vinyl components, absorption of softeners, meltenders and others. No mentioned effects were discovered.

For the regression analysis a linear formulation was used. Although the measurement values deviate to both sides of the regression straight lines, obviously a non-linear formulation is not justified. The variation of the measurement values cannot be clearly assigned to a hardness change of the block or to the measurement uncertainty of the device.

Next arises the question on the amount of hardness change over time.

The tables IV to VI summarize the yearly hardness changes for the different sets of rubber blocks.

Table IV.

Yearly hardness changes for the Shore A sets of rubber blocks

Set No.	Nominal hardness values						
	30	40	50	60	70	80	90
1	0,19	-0,2	-0,2	-0,2	-0,1	0,0	0,13
2	0,15	0,16	0,26	0,41	0,33	0,43	-
3	-	0,41	0,35	0,51	0,57	0,50	0,25

Table V.

Yearly hardness changes for the IRHD normal sets of rubber blocks

Set No.	Nominal hardness values					
	40	50	60	70	80	90
4	0,16	0,15	0,28	0,35	0,25	0,05
5	0,06	0,04	0,06	0,10	0,16	0,18

Table VI.

Yearly hardness changes for the IRHD micro sets of rubber blocks

Set No.	Nominal hardness values			
	40	60	70	80
6	0,18	0,17	0,36	0,42
7	0,30	0,02	0,20	0,11

From the tables IV to VI the conclusion can be drawn that the yearly hardness change for the Shore A blocks is larger than that for the IRHD normal and IRHD micro blocks. A clear dependency of the hardness change on the nominal value of the hardness cannot be observed. But, the hardness

change seems to be somewhat smaller for low and high hardnesses than for middle values of hardness. Under the condition that a tolerance for the Shore and IRHD rubber hardness measurement of U = 1 Shore resp. 1 IRHD is required, the hardness change should not occupy more than 25 % of the total uncertainty, the usage time of the blocks should not be longer than 6 months. This usage time seems to be reasonable if one considers that for the daily check of rubber hardness testers the block will be used up and must be replaced by a new one.

#### 5. CONCLUSIONS

The investigation of the long-term stability of rubber hardness reference blocks yielded that blocks of sufficient quality are existing which guarantee for a stability of the hardness value over six months. This also confirms the result of a previous investigation on the properties of rubber hardness reference blocks.[5] From this can be derived that the validity of the hardness value of a rubber hardness reference block should be not longer than six months. This usage time is reasonable if the block is used for the daily check of rubber hardness testers, because after this time the block is used up. Further, the investigation revealed that between rubber blocks from different manufacturers remarkable differences can arise. This means that in future rubber hardness reference blocks with improved quality should be offered. By its results this investigation can contribute to this quality improvement.

In this way besides the direct calibration of rubber hardness testers according to the draft standard ISO/CD 18898 [6] preconditions for the indirect calibration and verification of testers with rubber hardness reference blocks are created.

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#### Authors:

- Mr. A. Stibler ZAG Ljubljana, Dimiceva 12, 1000 Ljubljana, Slovenija, E-mail: anton.stibler @ zag.si  
 Dr. K. Herrmann PTB Berlin, POB 1132, D-12562 Berlin, Germany, E-mail: konrad.herrmann@ptb.de  
 Dr. Z. Šušterič SAVATECH d.o.o., Škofjeloška c. 6, 4000 Kranj, Slovenija, E-mail: zoran.susteric@sava.si