Rubber Chemistry. — *"Influence of high temperatures on the stress-strain curve of vulcanised rubber."* By A. VAN ROSSEM and H. VAN DER MEYDEN.

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§ 1. *Introductory. Purpose of the Investigation.*

While the influence of the temperature on the properties of metals and alloys has been studied thoroughly — a recent bibliography [1]) on this subject contains the titles of 216 investigations — the influence of the temperature on the physical properties of rubber has been the subject of only a few limited investigations.

In 1910 P. BREUIL [2]) made a first attempt to study the influence of temperature on the properties of vulcanised rubber, but the dynamometer which he used was inaccurate and his results were far from conclusive.

Later this subject was studied by WORMELEY [3]) and also by DINSMORE [4]) but only in relation to the testing of vulcanised rubber and therefore over a limited range of temperatures (9—35° and 21—35° respectively). Both investigators came to the conclusion that the testing temperature had a strong influence on the results of the tensile tests and suggested, in order to obtain comparative results, tests at constant temperature.

In a recent investigation, LE BLANC and KRÖGER [5]) studied the influence of low temperatures on the stress-strain curve and the sub-permanent set of vulcanised rubber and also carried out some experiments at temperatures higher than the normal. This investigation will be referred to later.

In spite of the limited attention which has been paid to this subject, the study of the physical properties of rubber at elevated temperatures is highly important, from a theoretical, as well as from a practical standpoint, which is obvious from following considerations:

1. Structure theories of vulcanised rubber will be greatly influenced by the knowledge of the properties of this material at high temperatures.
2. For an elucidation of the hot vulcanisation process a thorough

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[1]) Proceed. Am. Soc. Test. Mat. 24 (II), 128 (1924).

[2]) Le Caoutchouc et la Gutta Percha 7, 4073 (1910).

[3]) The Rubber Industry, 1914, p. 246.

[4]) Cf. Report of the Physical Testing Committee of the Division of Rubber Chemistry of the American Chemical Society. Ind. Eng. Chem. 17, 535 (1925).

[5]) Kolloid-Zeitschr. 37, 205 (1925).

knowledge of the properties of the rubber at the temperature of vulcanisation will be a necessity. It is often stated that the vulcanised rubber after removal from the hot moulds is quite brittle. This proves that the properties of rubber at the temperature of vulcanisation are different from those of the same rubber at the ordinary temperature.

3. During use, various rubber articles, such as motor car tyres, steam hoses, hot water bottles, etc. are exposed to high temperatures. For the testing of those articles, it is desirable to have an insight into the changes of the properties which take place at high temperatures.

The following part of our study deals only with the influence of high temperatures up to 147° on the stress-strain curve of vulcanised rubber. Elsewhere [1]) the results of this investigation will be published in details. It is our intention to give here a short account of the most important results.

§ 2. *Experimental part.*

For the above mentioned tensile tests with metals at high temperature, the grips of the dynamometer and the test piece are surrounded by an oven, kept at constant high temperature. It is probable, that the complicated technique, which would be necessary to carry out such tests with rubber, has deterred various investigators from this subject.

The technique used in our tensile experiments at high temperatures is a very simple one. The tensile tests were all carried out with rings on the ordinary dynamometer of SCHOPPER. The pulleys, supporting the rings, are heated at the temperature required for the experiment and quickly mounted on the dynamometer, for which procedure 30 seconds are sufficient. Subsequently the ring, which is also heated at the temperature of the experiment, is quickly mounted on the pulleys, which takes about 5 seconds, and the tensile test is immediately started. During the test the ring will cool, but this decrease in temperature will be partly compensated by development of heat during the tensile test. For this reason the temperature of the ring will not be strictly constant during the experiment, but the results described below are so striking that this is no objection in coming to a general conception of the influence of high temperature.

It may be pointed out, that owing to generation of heat during the tensile test, such tests under normal conditions are neither carried out at constant temperature.

The pulleys of the SCHOPPER-dynamometer are heated in an oven and the rubber rings are mounted on a wooden cylinder which is immersed in a mercury bath kept at constant temperature.

Deviations of temperature of the mercury bath were $\pm$ 0.5, and it was shown, that the time, necessary for heating the rings to the desired temperature was 1 minute.

[1]) Journ. Soc. Chem. Ind. 45, 67 T (1926).

Preliminary experiments, which will not be described here, showed, that when studying tensile properties of vulcanised rubber at high temperatures three principal factors must be considered, i.e.:

a. the degree of vulcanisation;

b. the temperature at which the rings are heated and tested;

c. the time, during which the rings are heated.

The principal purpose of a systematic study of the phenomena should therefore be concentrated on the influence of each of these factors.

The first part of these experiments were carried out with rings consisting of a rubber-sulphur mix. From a mix, consisting of 92½ parts of First Latex Sheet (N°. 351 Institute) and 7½ parts of sulphur, a number of slabs were vulcanised in the oilbath at 147° during 60, 90 and 120 minutes time of cure. The vulcanisation coefficient [1]) of these slabs were 2.1, 3.2 and 4.2 respectively. Rings, punched from the slabs were heated at various temperatures, 70°, 100°, 130° and 147°, during progressive time, and tested at the same temperature in the way described above.

In Table 1 are compiled the results of the tensile tests of rings with a vulcanisation coefficient 3.2 and in Figure 1 are reproduced the stress-strain curves of rings, tested at 100° and 147°. The figures are the average of two corresponding tests, except in those cases where brittleness of the rubber occurred and differences in duplo-tests are inevitable.

From Table 1 and Fig. 1 the following can be concluded:

1. When rings are tested at increased temperature the stress-strain curve is shifted towards the elongation axis, in other words, the rubber becomes softer. The higher the temperature of testing, the greater is the shifting of the curve. When testing the rings at high temperatures the elongation at break is increased and especially with rings of low vulcanisation coefficients this phenomenon is striking.

2. Apart from the shifting of the curve a striking phenomenon becomes appearant. When the heating is continued for some time, the tensile and the elongation at break show a sharp decrease, in other words the rings have become brittle.

The time of heating, necessary to cause brittleness of the rings, at a certain vulcanisation coefficient is highly dependent from the temperature. With rings of a vulcanisation coefficient 3.2 brittleness appears at 70°, after heating during 2 $\times$ 24 hours, at 100° after 15 minutes. At 130° and 147° the rings are already brittle after heating only 1 minute.

The same phenomenon was observed with rings of vulcanisation coefficient 2.1 and 4.2 respectively.

In Table 2 the results of those experiments are compiled. From these figures it is obvious, that the time of heating necessary to cause brittleness

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[1]) The quantity of combined sulphur, calculated on 100 parts of rubber.

TABLE 1.
Results of tensile tests with rings heated at 70°, 100°, 130° and 147° during progressive time. (Vulcanisation coefficient 3.2).

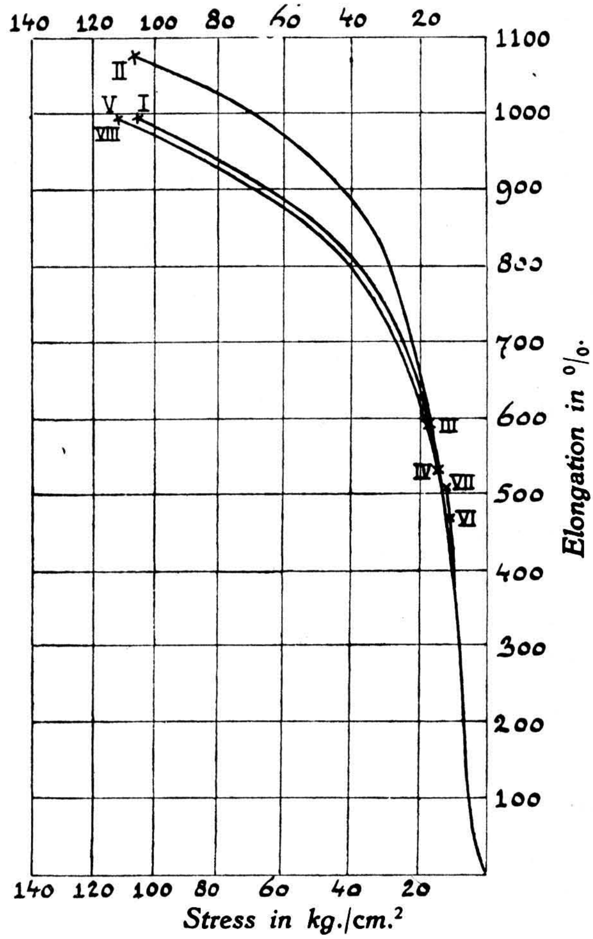
Temperature and time of heating.	Tensile strength in kg./cm².	Elongation at break in %.	Load in kg./cm². for an elongation of 850 %.
Not heated 26° C.	107	990	49
Series at 70° C.			
15 min. at 70° C.	104	1049	37
2 hrs. „ 70 „	109	1040	40
4 „ „ 70 „	113	1040	41
24 „ „ 70 „	112	999	49
2 × 24 hrs at 70° C.	20	568	—
Series at 100° C.			
5 min. at 100° C.	107	1080	34
15 „ „ 100 „	18	595	—
1 hr. „ 100 „	14	532	—
1 „ „ 100 „ , subsequently 1 hr. at 25° C.	112	995	51
Series at 130° C.			
1 min. at 130° C.	12	460	—
5 „ „ 130 „	13	500	—
5 „ „ 130 „ , subsequently 1 hr. at 25° C.	114	1107	48
Series at 147° C.			
1 min. at 147° C.	12	465	—
5 „ „ 147 „	14	512	—
5 „ „ 147 „ , subsequently 1 hr. at 25° C.	115	996	51

decreases quickly with increasing temperature and vulcanisation coefficient.

Rings with vulcanisation coefficient of 4.2 are already brittle after heating 1 min. even at 70°.

3. The brittleness of the rubber is not lasting, in other words, rings which had become brittle through heating, recover their normal tensile

Fig. 1.
Stress-strain curves of rings heated at 100° and 147° C.
(Vulcanisation coefficient 3.2)



I	Blank, not heated (26° C.).				
II	5 min.	at	100° C.		
III	15 ,,	,,	100	,,	
IV	1 hr.	,,	100	,,	
V	1 ,,	,,	100	,,	subsequently 1 hr. at 25° C.
VI	1 min.	,,	147	,,	
VII	5 ,,	,,	147	,,	
VIII	5 ,,	,,	147	,,	subsequently 1 hr. at 25° C.

properties after cooling. The stress-strain curves of the cooled rings are practically coincident with the original (blank) ones. This is shown in Fig. 1 for rings with a vulcanisation coefficient of 3.2, after heating at 100° and 147°, and subsequent cooling during 1 hour at ordinary temperature.

The same holds true for rings with other vulcanisation coefficients.

Similar experiments were carried out with rings vulcanised from mixes of rubber and sulphur with 10 vol % of various compounding ingredients

TABLE 2.

Relation between occurrence of brittleness, temperature and vulcanisation coefficient.

Temperature of heating.	Time of heating after which brittleness occurs.		
	Vulcanisation coefficient 2,1.	Vulcanisation coefficient 3,2.	Vulcanisation coefficient 4,2.
70° C.	longer than 7×24 hrs.	after 2 × 24 hrs.	after 1 min.
100 „	after 24 hrs.	after 15 min.	„ 1 „
130 „	„ 1 hr.	„ 1 „	„ 1 „
147 „	„ 5 min.	„ 1 „	„ 1 „

e.g. : barytes, zinc oxide and carbon black. With rings from these vulcanised mixes similar phenomena were observed. From the extensive series of experiments with various compounding ingredients the figures obtained with a mix with zinc oxide may be given here as an example.

A mix consisting of 92½ parts of rubber, 7½ parts of sulphur and 57 parts of zinc oxide, Diamond N. (10 % of volume calculated on the rubber) was vulcanised at 147° C. during 50, 90 and 120 min.

The rings, punched from the slabs which showed a vulcanisation coefficient of 1.5, 2.8 and 4.0 respectively were heated during progressive time in a mercury bath at 70°, 100°, 130° and 147°, and tested at the same temperature. The results of the series of tensile tests with rings of a vulcanisation coefficient 4.0 are compiled in Table 3. The stress-strain curves obtained at 100° and 147° are reproduced in Fig. 2.

From Table 3 and Fig. 2 the following can be concluded :

1. At 100° the curve is shifted towards the elongation axis (II). Prolonged heating causes brittleness of the rubber ; the endpoint of the stress-strain curve is displaced downwards (III). After cooling, the rings recover their original tensile properties (IV). At 147° the brittleness occurs already after a heating of two minutes (V), the curve returns after cooling to its original position (VI). The changes in physical properties on heating rings with 10 % of volume zinc oxide are essentially the same as those obtained with vulcanised rubber without compounding ingredients. At temperatures of 70° and 100° a difference in the time of heating necessary to cause brittleness, is distinctly visible, while at high temperatures this time is the same, as is shown in Table 4.

Elsewhere the results of the experiments carried out with rubber with various compounding ingredients tested at high temperatures will be published in detail.

TABLE 3.

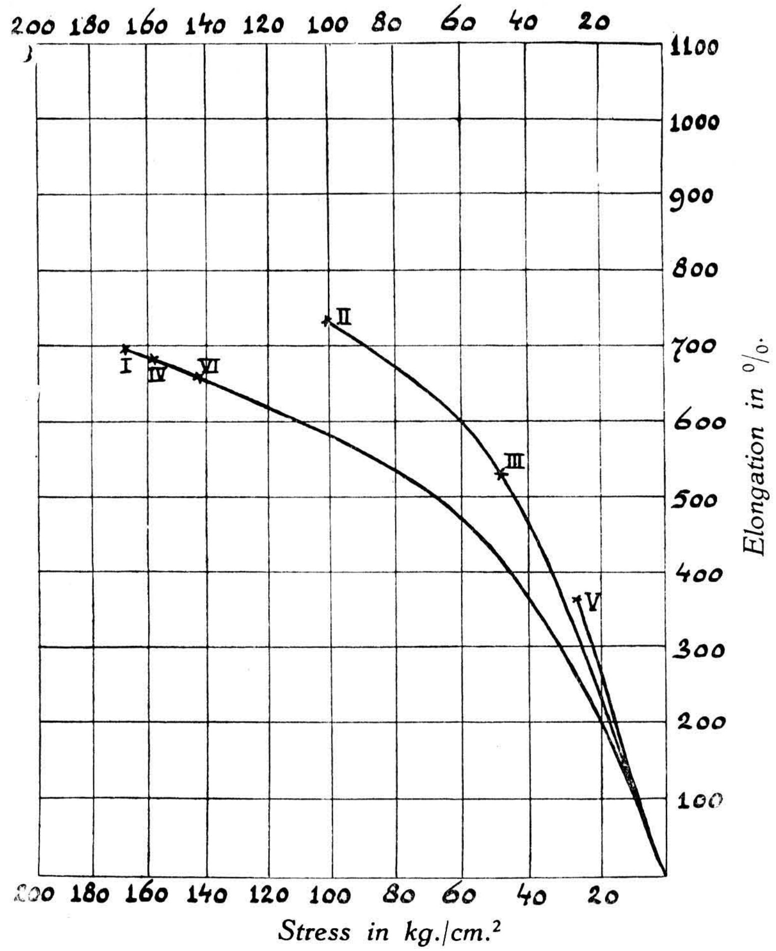
Results of tensile tests with rings with 10 % of volume zincoxide, heated at 70°, 100°, 130° and 147° C. (Vulcanisation coefficient 4.0).

Temperature and time of heating.	Tensile strength in kg./cm².	Elongation at break in %.	Load in kg./cm². for an elongation of 600 %.
Not heated 19°C.	169	699	109
Series at 70° C.			
2 min. at 70° C.	131	740	70
30 „ „ 70 „	133	742	70
24 hrs. „ 70 .	126	700	83
(not continued).			
Series at 100° C.			
2 min. at 100° C.	100	730	59
30 .. .. 100 „	48	530	—
30 „ „ 100 .,			
subsequently 1 hr. at 20° C.	159	681	113
Series at 130° C.			
2 min. at 130° C.	44	560	—
2 „ „ 130 „			
subsequently 1 hr. at 20° C.	162	687	109
Series at 147° C.			
2 min. at 147° C.	26	355	—
2 „ „ 147 „			
subsequently 1 hr. at 19° C.	143	659	109

§ 3. *Concluding remarks.*

In the first place we wish to check our results with those obtained by LE BLANC and KRÖGER (loc. cit.). As mentioned before these investigators have studied especially the influence of low temperature on the stress-strain curve of vulcanised rubber, but they have carried out also some experiments at higher temperature (till 80°). They used a special testing apparatus which was connected with the SCHOPPER-dynamometer. The rings were heated in alcohol. At elevated temperatures this method seems objectionable. They carried out tensile tests with a rubber-sulphur mix,

Fig. 2.
Stress-strain curves of rings, containing 10 % of vol. zincoxide, tested at 100° and 147° C.
(Vulcanisation coefficient 4.0).



I Blank, not heated (19° C.).
II 2 min. at 100° C.
III 30 „ „ 100 „
IV 30 „ „ 100 „ subsequently 1 hr. at 20° C.
V 2 „ „ 147 „
VI 2 „ „ 147 „ subsequently 1 hr. at 19° C.

with progressive time of cure, without mentioning vulcanisation coefficients. Rings with low degree of vulcanisation were heated to 55° and the figures show clearly a shifting of the tensile curve towards the elongation axis. Rings with higher degrees of vulcanisation were always found to be brittle. They conclude from their results :

„Bemerkenswert ist, dasz bei Temperaturen über 30° wirklich gute Eigenschaften überhaupt nicht erhalten werden können. Am günstigsten liegen die Verhältnisse in dieser Beziehung bei den ausvulkanisierten

Produkten. Jenseits von 60° ergeben sich nur wenige Kilo Belastungsfähigkeit, offenbar infolge der Zunahme des Wärmeinhalts über einen kritischen Betrag, wodurch einmal bei längerem Erwärmen die bekannte Desaggregation merkbar einsetzt und anderseits die Kräfte die dem Zerreiszen entgegenwirken, geschwächt werden."

TABLE 4.
Brittleness of rings with and without 10 % of vol. zincoxide.

Temperature of heating.	Time of heating,* after which brittleness occurs.	
	Rings without zincoxide Vulcanisation coefficient 4.2.	Rings with 10% of vol. zincoxide Vulcanisation coefficient 4.0.
70° C.	after 1 min.	after longer than 24 hrs.
100 „	„ 1 „	after 30 min.
130 „	„ 1 „	„ 2 „
147 „	„ 1 „	„ 2 „

This conclusion is in contradiction with our results. With a low coefficient of vulcanisation excellent tensile properties could be recorded even at 100° and at 130°, when the period of heating was not too long.

LE BLANC and KRÖGER have left out of consideration the time of heating, which is of paramount importance. For this reason they did not get a complete survey of the influence of high temperatures on the stress-strain curve.

Finally we wish to make a few remarks in relation to the cause of the described phenomena. It is not our intention now to put forward an explanatory theory of the phenomena just described, but only to point out a few directions in which the experimental study will be continued. The important observation of brittleness at high temperature gives us cause to the following points.

1. It is well known that overvulcanisation causes brittleness at ordinary temperature. In this respect the brittleness at high temperature might be attributed to overvulcanisation due to prolonged heating. This is not the case as is obvious from determinations of vulcanisation coefficients before and after heating in the mercury bath which proved to be the same. Moreover it was a priori improbable that overvulcanisation should be caused by heating during one or two minutes at 147°.

2. When vulcanised rubber is heated in air at high temperature, oxidation takes place, which causes a decrease in physical properties, determined at ordinary temperature (dry heat or ageing test). In our experiments the air was not in contact with the rubber, because the rings were heated in a mercury bath, and therefore oxidation is improbable.

3. Brittleness at high temperature must be ascribed in our opinion to another cause than brittleness at room temperature from overvulcanisation.

Brittleness at high temperature is likely to stand in close relation with an increase of plasticity at high temperature [1]).

Two methods of further investigation propose themself to verify the correctness of these suppositions :

a. A closer study of the sub-permanent set at high temperature, because this property stands in relation with the plasticity.

b. Direct measurement of the plasticity of rubber at high temperatures.

Finally attention may be drawn to the possibility that a closer study of the conduct of vulcanised rubber at high temperature leads to a new method of carrying out ageing experiments.

The investigation of the properties of vulcanised rubber at high temperature is continued in the directions here described.

Netherland Government Rubber Institute.

Delft, December 1925.

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[1]) It is sometimes pointed out wrongly that a high degree of plasticity is always accompanied by a high elongation. This is not the case as is obvious from a plastic material as putty.