Table 1.

Chloride		$(\Delta\varphi/\Delta T)_5 - (\Delta\varphi/\Delta T)_2$
HCl NaCl KCl	m = 1	0.31 0.32 Average: 0.32 0.32 mV/degree
HCl NaCl KCl	m = 0.01	0.33 0.32 Average: 0.30 0.32 mV/degree

For the isothermal cell

$$\text{Ag; AgCl, MCl}_{\text{aq}}, \text{Hg}_2\text{Cl}_2\text{; Hg} \qquad (6)$$

we obtain $(d\Delta\varphi/dT)_{is} = 0.34$ mV/degree at 25°C.

As the thermoelectric force of the thermocouple silver-mercury is small (about 0.01 mV/degree[10]), we again find that the relation (3) holds within the limits of experimental error.

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Received June 20, 1955.

Oxidative Stress Relaxation of Natural Rubber Vulcanized with Di-*Tertiary*-Butyl Peroxide

SVEIN ORE

Central Institute for Industrial Research, Oslo, Norway

It has been shown by Farmer and Moore[1] that natural rubber can be vulcanized with di-*tert.*-butyl peroxide (DTBP). Presumably the free radicals formed by the unimolecular decomposition of the peroxide abstract some of the more labile (*e. g.* α-methylenic) hydrogen atoms leading to direct C—C crosslinks between the rubber molecules, *tert.*-butanol and acetone being the main reaction products.

This preliminary communication presents some of the results of an investigation of the oxidative stress relaxation of the following types of DTBP vulcanizates: (A). First grade pale crepe, DTBP, and some carbon black (MPC) mixed on the mill and vulcanized in a press. The carbon black was added to minimize the deleterious effect of impurities. (B). Purified rubber vulcanized: 1. In aqueous heating media. 2. In the press. 3. In DTBP vapour.

(A). In Fig. 1 is plotted on a logarithmic scale the relaxation curves for a vulcanizate with 20 % MPC vulcanized for 15 minutes at 160° and relaxed in air at 90—140° (modulus 2.57 kg/cm² at an extension ratio of 1.2). A rapid initial rate of relaxation due primarily to peroxidic reaction products, was eliminated by preheating the samples *in vacuo* for 30

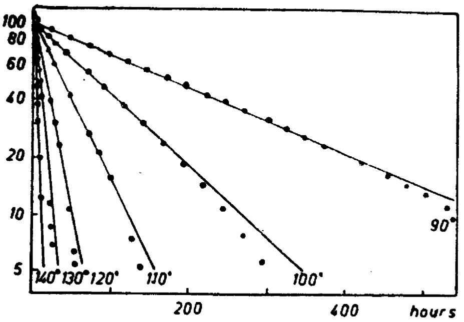

Fig. 1. Relaxation curves. Ordinate: % of original stress. Abscissa: hours.

min. at 150°. This treatment also serves to remove the physical relaxation. From the relaxation curves shown in Fig. 1 an energy of activation of 22.7 kcal is calculated for the relaxation process. The same relaxation rates are obtained when only 5 % MPC is used. The relaxation rate is nearly inversely proportional to the initial modulus of the sample, corresponding to a rate of oxidation nearly independent of the degree of vulcanization. With no preheating *in vacuo* there would also in addition to the normal initiation of oxidation chains by hydroperoxide decomposition, be an initiation by some non-volatile peroxidic materials formed during the vulcanization process and the amount of which will depend on the degree of vulcanization.

When approximately 75 % of the stress is relaxed, the relaxation curves of the preheated samples start deviating from linearity, apparently mainly because of the consumption of natural antioxidant in the oxidation. A closer examination shows that this occurs somewhat earlier when the degree of vulcanization is higher, corresponding to a consumption of natural antioxidant during vulcanization with DTBP. Acetone extraction of the samples before heat-treatment *in vacuo* has practically no influence on the relaxation rates. The antioxidants left are therefore probably proteins and possibly some of the normally extractable antioxidants which have been chemically bound to the rubber during the vulcanization.

The rate of crosslinking was measured by intermittently subjecting the relaxing sample to a small additional stress and measuring the corresponding increase in elongation. This method gives (as confirmed by tests on a pure gum sulphur vulcanizate) the same value for the rate of crosslinking as do the ordinary "intermittent stress relaxation" measurements on a separate sample, and the former method seem to have certain advantages. The rate of crosslinking was found to be 25—30 % of the rate of scission in the whole temperature range studied, *i. e.* with the same energy of activation. If the samples were acetone extracted, however, the rate of crosslinking was 45—50 % at 90° and reached 25—30 % at the higher temperatures. This may be a combined effect of the acetone-extractable substances acting as a plasticizer and the crosslinking capacity of the carbon black, although there was only a small difference between the effect when 20 % and when 5 % MPC was used.

(B). In order to avoid the use of additives such as carbon black a purified rubber was used in the following experiments, in which the effect of the degree and mode of vulcanization and of the pretreatment of the samples on their oxidation and relaxation behaviour was studied. The rubber was extracted from first grade pale crepe by a modification of the method of Bloomfield and Farmer [2] and should according to this be free of the "oxide fraction". The nitrogen content was about 0.035 %. Films of 0.05 mm thickness were prepared from solution and vulcanized at 150° for 30 min.

By the vulcanization in distilled water in an oxygen free atmosphere followed by extraction with acetone, the peroxidic material formed in the samples was still sufficient to be the dominating oxidation chain initiator at the beginning of the relaxation process. This peroxidic material seems to be chemically combined with the rubber and can preferably be destroyed by heating the sample *in vacuo*. Results of experiments on samples in which such a more nearly complete removal of the

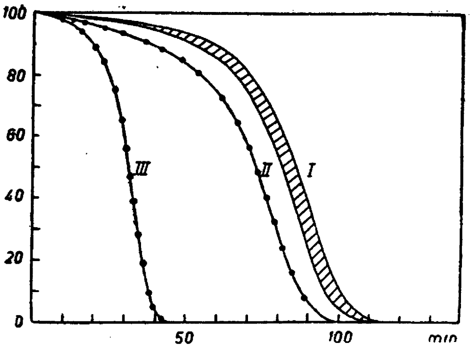

Fig. 2. Relaxation curves. Ordinate: % of original stress. Abscissa: minutes.

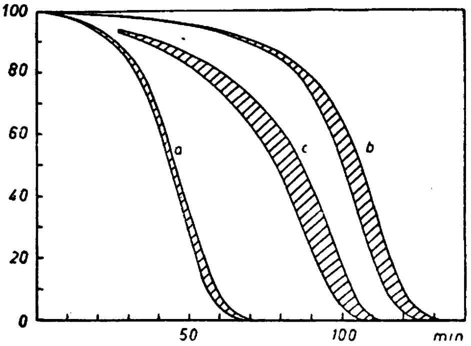

Fig. 3. Relaxation curves. Ordinate: % of original stress. Abscissa: minutes.

peroxidic material has been carried out, will be published later. In the experiments described here a relatively mild heat treatment of 10 min. at 120° was used. This reduced the initial relaxation rate by approximately 50 %. The hatched area I shown in Fig. 2 covers the relaxation curves (on a linear scale) of eight vulcanizates of modulus varying from 2.4 to 4.7 kg/cm^2 (at an extension ratio of 1.25), the upper curve corresponding to the higher modulus. Relaxation was carried out in dry oxygen at 90°. Without preheating, a modulus of 2.7 gives the relaxation curve II. Several factors play a part in determining the dependence of the curves I on modulus: The dependence of the concentration of the peroxidic material on the degree and conditions of vulcanization, the dependence of the oxidation rate on this concentration, and the consumption of natural antioxidant as a function of degree and mode of vulcanization.

The curve III represents a preheated sample of modulus 2.7 kg/cm^2 relaxed at 100°. The activation energy calculated from the relaxation curves differs little from the value obtained for the inhibited relaxation of the whole crepe vulcanizates described above. In accordance with the network theory the amount of oxygen absorbed (preliminary gravimetric measurements) at 99 % relaxation is proportional to the degree of vulcanization. There was no measurable crosslinking at 90°.

Fig. 3 shows the relaxation (at 90°) of samples vulcanized a) in water and with 5 % stearic acid in the rubber, b) in 2 *N* NaOH, and c) in pure DTBP vapour. (The ranges of moduli covered by the areas shown are not as large as in Fig. 2.) Apparently the stearic acid promotes the deactivation of the proteins, giving a less inhibited reaction, whereas the addition of NaOH to the water mainly serves to reduce the water concentration in the rubber, thus reducing the rate of deactivation by the DTBP. So efficient is this osmotic effect that a dry sample vulcanized in a press gave exactly the same relaxation curve.

It is interesting to observe the effect of incorporating 0.2 % copper stearate in the samples of a) before preheating. There is a marked reduction in the initial relaxation rate, presumably because of a more complete destruction of the peroxidic material *. In the later stages, however, the catalytic and antioxidant-inactivating effect of the copper stearate becomes apparent, giving a much faster rate than uncatalyzed samples.

By the vulcanization in DTBP vapour for 30 min. at 150°, the rubber became seriously overvulcanized at the surface. As should be expected, the curves c) in Fig. 3 show that the antioxidant-free stage is reached comparatively late in this case.

This investigation is being completed and extended to comprise accurate oxygen absorption measurements in order that the relation between this pure scission reaction and the detailed shape of the relaxation curve may be studied.

This work has been made possible by the kind assistance and financial support from *The British Council, The Rubber Development Board, The Rubber Producers Research Association, The Norwegian Council for Scientific and Industrial Research* and the *"Fridtjof Nansens Fond".*

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Received July 14, 1955.

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* *Note added in proof:* This marked effect of copper stearate indicates that these peroxidic materials are rubber hydroperoxides. They may possibly be formed at the moment the cooled sample (with a certain amount of free radicals) is removed from the press or the autoclave and exposed to the air.

Separation of Corticosteroids by Countercurrent Distribution

HANS CARSTENSEN

Institute of Physiology, University of Upsala, Upsala, Sweden

The separation of adrenal cortical steroids by physical methods has been attempted mainly by paper chromatography [1,2]. Countercurrent distribution has been applied by Voigt [3] in order to fractionate some nitrogen-containing, highly polar substances in adrenocortical extracts, supposed to be of steroidal nature. Talbot *et al.*[4] have recently reported the use of countercurrent distribution for fractionation of urinary corticosteroids. They seem, however, not to have achieved a satisfactory separation. Engel *et al.*[5] found that a 150 transfer countercurrent distribution was insufficient to separate urinary metabolites of corticosterone. The present experiments show that most corticosteroids may be