

MECHANO-CHEMICAL REACTIONS OF POLYMERS. FORMATION OF FREE RADICALS IN STRESSED RUBBER

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Abstract—It has been found that free radicals produced in cross-linked rubbers subjected to high stresses can be detected in E.S.R. either as alkylperoxy radicals or by reacting with a phenol which can give rise to a stable free radical (galvinoxyl). This reaction occurs only during the first $1\frac{1}{2}$ hr of stressing and corresponds to a period of stress relaxation in the rubber. The stable aryloxy radical disappears slowly in the absence of stress by a first order reaction the rate constant of which increases with the application of stress. This is interpreted in terms of a stress activated reaction of galvinoxyl with the rubber network, superimposed on the chain scission reaction and believed to be related to the observed activation of rubber to oxygen by stress.

INTRODUCTION

THE FORMATION of free radicals in uncured rubbers during milling and mastication processes has been inferred by a number of workers from the rheological changes in the polymer^(1,2) and from the chemical reactions which can be initiated in the rubbers under conditions of shear.^(3,4,5,6) More recently direct evidence has been found for macro-radical formation by E.S.R. spectroscopy. The free radicals have been trapped by freezing the masticated polymer in liquid nitrogen below the glass transition temperature,⁽⁷⁾ their reaction with stable free radicals previously introduced into the system^(8,9) has been followed.

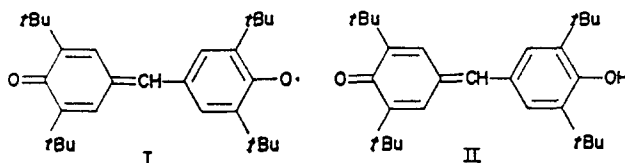
Similar effects have been found during the milling of vulcanized rubbers⁽⁷⁾ and, in the presence of oxygen, the radicals were characterized as alkylperoxy radicals.

When vulcanized rubbers are subjected to mechanical stress, the rate of oxidative degradation is increased, particularly under dynamic conditions.⁽¹⁰⁾ The nature of this activation process is not well understood, although it is known that the rate of antioxidant consumption is accelerated.⁽¹¹⁾ The present work is concerned with an attempt to elucidate the mechanism of mechano-degradation of vulcanized rubber since at present there is little evidence on the mechanism of antifatigue agents which differ in structure from heat ageing antioxidants.

Three methods of following radical formation in stretched peroxide cured rubbers were examined.

- (a) Direct observation of alkylperoxy radicals
- (b) Change in concentration of a stable aryloxy radical (galvinoxyl I) swelled into the rubber
- (c) Formation of aryloxy radicals from a phenol (hydrogalvinoxyl II) swelled into the rubber.

Galvinoxyl I was chosen as the scavenging radical because it is relatively stable in solution both in the absence and in the presence of oxygen and yet it is an extremely effective scavenger for alkyl and alkylperoxy radicals.⁽¹²⁾



EXPERIMENTAL

Preparation of rubber vulcanizate

A peroxide cured rubber was chosen as the chemically simplest cross-linked network available. The rubber composition was

Rubber RSS1	100 g
Dicumyl peroxide (<i>Perkadow S.B.</i>)	2 g

After milling on a warm two-roll mill, the rubber was cured at 160° until maximum torque was achieved in the Monsanto Rheometer (usually 1.5 hr) under which conditions the peroxide had been substantially decomposed. The rubber sheets obtained (2.5 mm thick) were hot acetone extracted for 4–5 days under nitrogen to remove breakdown products of the peroxide.

Square ended dumbbell samples with one end removed (width 4 mm, length 10 cm) were cut from the rubber for suspension in the E.S.R. spectrometer.

Preparation of Galvinoxyl (2,6-di-tert-butyl-4-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-p-tolyloxy)

Galvinoxyl was prepared by a modification of the method of Joshi.⁽¹³⁾

A solution of 4,4'-dihydroxy-3,5,3',5'-tetra-*tert*-butyldiphenylmethane (1.41 g, 0.0033 mole) in ether (15 ml) was added over 30 min to a well stirred solution of potassium ferricyanide (3.95 g; 0.012 moles) and potassium hydroxide (0.6 g) in water (15 ml) and ether (80 ml). The addition was carried out under nitrogen and the mixture was stirred under nitrogen for a further hour. The ether layer was separated, washed several times with water and dried over sodium sulphate. The ether was removed under reduced pressure in a rotary evaporator and the product was recrystallized rapidly several times from absolute ethanol. The melting point of the galvinoxyl was 154.5–155.5°.

Preparation of Hydrogalvinoxyl

Hydrogalvinoxyl was prepared by a modification of the method of Green.⁽¹⁴⁾

0.844 g (2 m-moles) of Galvinoxyl and 0.45 g. (1 m-mole) of 4,4'-dihydroxy-3,5,3',5'-tetra-*tert*-butyldiphenylmethane were added to a constricted dry tube. To the mixture was added 30 ml of freshly distilled and degassed ether. The solution was degassed and the tube sealed under vacuum. Over the course of one week the blue colour changed to yellow. The tube was opened and the ether removed under reduced pressure in a rotary evaporator.

After several recrystallizations from aqueous methanol, the bright yellow product melted at 157–158°.

Preparation of samples for E.S.R. studies

Galvinoxyl and hydrogalvinoxyl were introduced into the purified rubber by swelling in benzene solutions. It was found to be essential to exclude oxygen completely during this process, particularly in the case of galvinoxyl itself since, if the samples were exposed to oxygen before the solvent had been removed, the radical concentration was greatly diminished.

Rubber containing Galvinoxyl

By calculation, it was found that a benzene solution containing 0.2 g galvinoxyl per 100 ml would be required to produce a radical concentration of 10^{-5} moles radical per gram of rubber. This was the order of radical production expected in rubber by chain scission. In practice 0.1 g per 100% benzene was found to be sufficient.

A solution of 0.1 g galvinoxyl in 100 ml benzene was de-oxygenated by passage of nitrogen. The rubber samples, cut to the required shape, were placed in the solution and a continual stream of nitrogen was passed through the solution for 12 hr. After swelling, the samples were removed and dried *in vacuo* at room temperature. The dried samples were stored either *in vacuo* or in nitrogen for as short a period as possible before use.

Rubber containing Hydrogalvinoxyl

In this case, the concentration of the adduct is not so important. The procedure was identical to that for galvinoxyl except that 0.2 g hydrogalvinoxyl per 100 ml of benzene was used.

Application of stress to the samples

The physical properties of the rubber were expected to be poor since the stock was an unfilled one and the maximum extension that could be applied without breaking was 150% (extension ratio $\lambda = 2.5$). Stress was applied either by application of weights between 1 kg and 1.5 kg or by stretching between clamps to the required extension in air at room temperature.

Measurement of radical concentrations from E.S.R. spectra

E.S.R. spectra were obtained using a Hilger-Watts Microspin Spectrometer. All curves were obtained from the rubber samples placed directly into the cavity (General purpose No. W932 operating on H_{011} cylindrical mode) by double modulation.

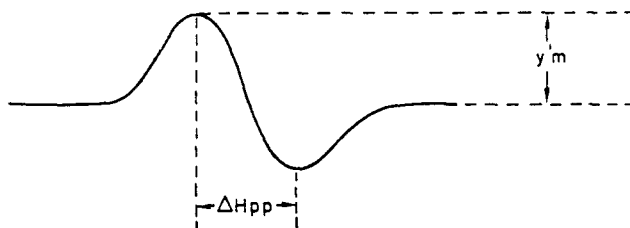
A reference sample with g value different from that of galvinoxyl was used in the cavity with the rubber so both spectra could be recorded simultaneously.

A sealed capillary tube containing a known weight of copper sulphate solution was fastened to the rubber sample for this purpose. This technique was found to be essential for reproducibility of results.

The spectrum obtained from the stressed rubber not containing other additives was the typical asymmetric spectra of the alkylperoxy radical obtained by other workers.⁽⁷⁾ Rubbers containing both galvinoxyl and hydrogalvinoxyl gave partially resolved doublets.

Radical concentration

The radical concentration was calculated by comparing the ratio of $y'm(\Delta H_{pp})^2$ for the rubber to $y'm(\Delta H_{pp})^2$ for the reference sample (10.7 mg of 0.1 M CuSO_4).



The ratios were calibrated by comparing the areas of well resolved spectra, calculated by the summation method of Wyard.⁽¹⁵⁾ It was necessary to estimate the length of rubber actually in the spectrometer cavity. This was calculated approximately using the following technique.

A capillary tube containing standard copper sulphate solution, longer than the estimated length of sample in which radical concentration was being measured, was placed in the E.S.R. cavity and the number of radicals calculated. The capillary tube was then emptied until a length shorter than the estimated length of the sample remained. Again the spectrum was recorded and the number of spins calculated.

The length L of the sample being measured was then calculated from

$$\frac{L}{l} = \frac{N(L)}{N(l)}$$

where $N(L)$ is the number of radicals when the capillary tube was full and $N(l)$ is the number of radicals detected when the capillary tube contained length (l) of copper sulphate solution.

To reduce the error due to the change in Q value of the cavity during the measurement, the operation was carried out with a rubber sample in the cavity.

Stress relaxation

The stress relaxation curves for the rubber were obtained on a "Wallace Stress Relaxometer" using the maximum extension, approx. 100% ($\lambda = 2$), possible on the instrument.

The number of cross-links was determined from the Mooney Rivlin equation after measuring the force F required to give an extension ratio λ .

RESULTS

Effect of stress on acetone extracted, peroxide cured vulcanizates

The unstressed vulcanizates exposed to air showed an initial count of alkylperoxy radicals in the region of 0.5×10^{16} . In one experiment (Fig. 1) the number of alkylperoxy radicals increased even in the absence of stress at the rate of 8×10^{13} radicals/hr./ml. In the stressed state ($\lambda = 2.5$) the number of radicals increased more rapidly initially. The initial rate of radical formation reduced rapidly during the first 4 hr to that found in the absence of stress. Different samples of rubber gave quite

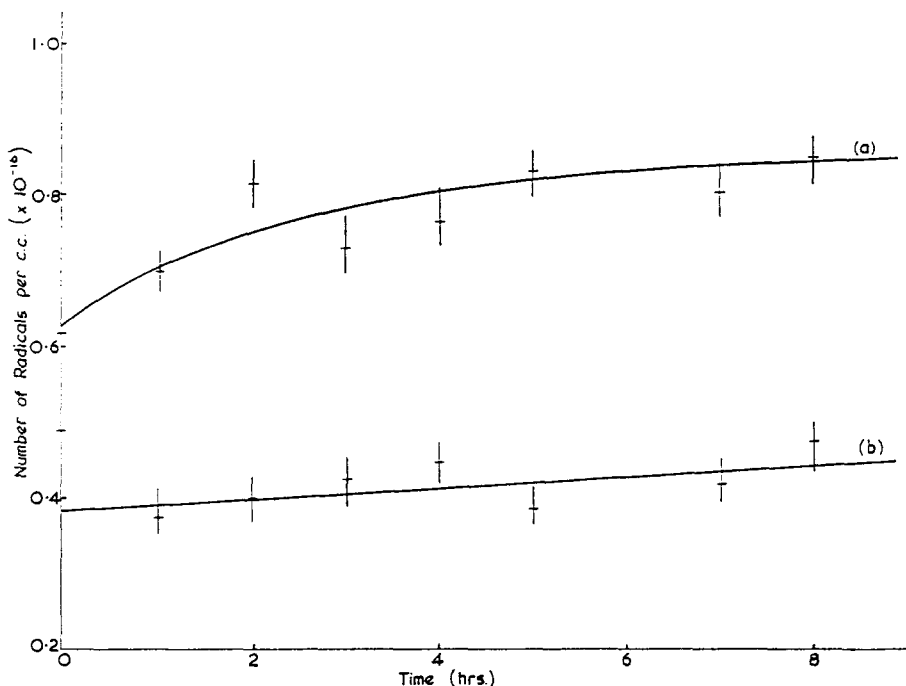


FIG. 1. Variation of radical concentration with time in peroxide cured rubber at room temperature: (a) stressed, $\lambda = 2.5$; (b) unstressed.

different results, as did specimens from the same rubber sample stored for different lengths of time. The cause of this irreproducibility has not yet been determined but it appears likely that both the initial state of the vulcanizate (including the possible presence of minor radical scavengers) and its age control its behaviour under stress.

Effect of stress on purified peroxide cured vulcanizates containing galvanoxyl

In the absence of stress, samples of rubber containing galvinoxyl showed an initial increase in concentration of the aryloxy radical species on exposure to oxygen (see

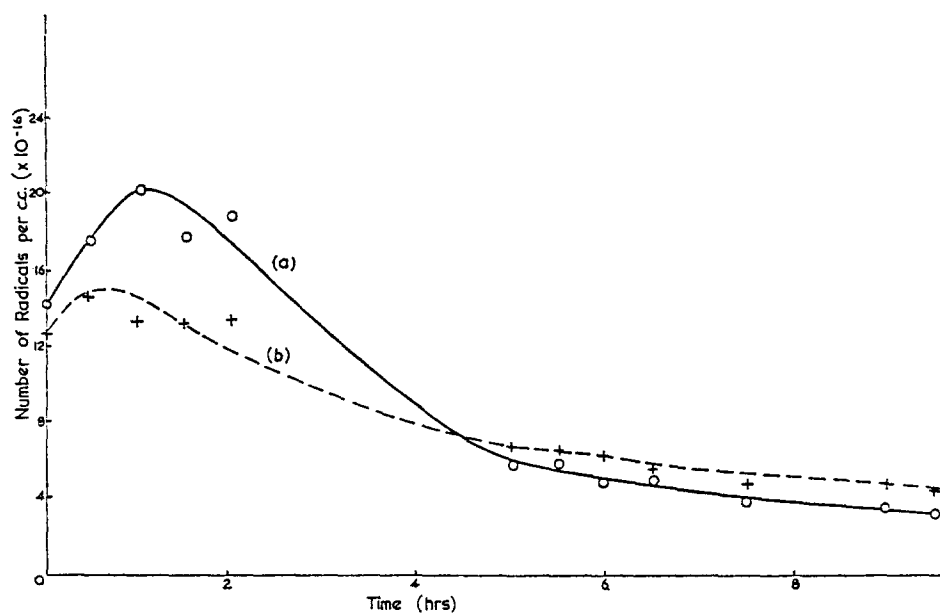


FIG. 2. Variation of radical concentration with time in peroxide cured rubber containing galvinoxyl: (a) stressed, $\lambda = 2.5$; (b) unstressed.

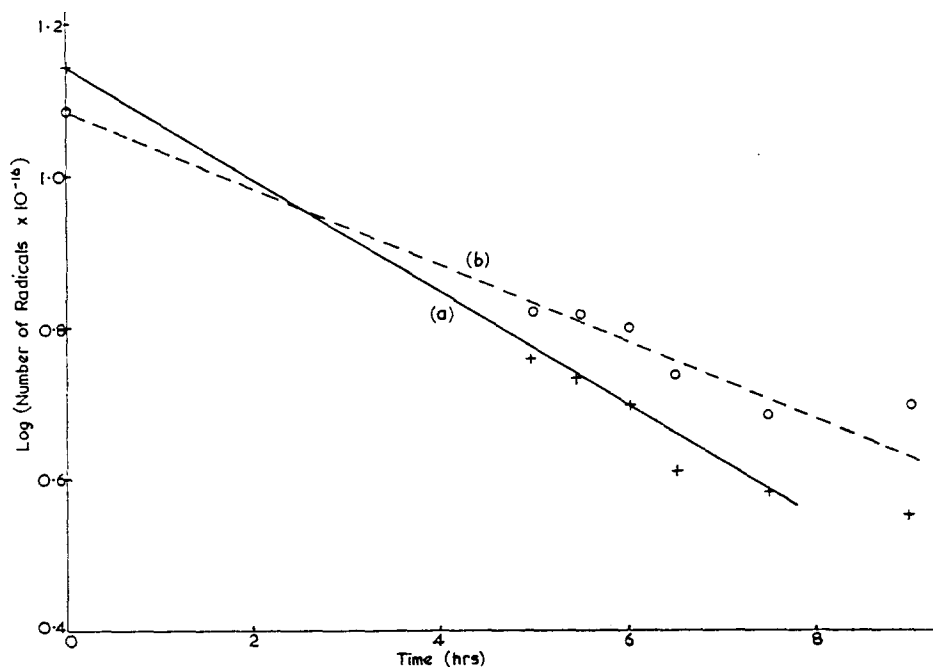


FIG. 3. Variation of log (galvinoxyl concentration) with time in Fig. 2 (ignoring the initial increase): (a) stressed, $\lambda = 2.5$; (b) unstressed.

Fig. 2) but after about 1 hr the radical concentration decayed exponentially (see Fig. 3). Under stress ($\lambda = 2.5$) the rates of both radical formation and radical decay were greater (Fig. 2). Again the rate of decay was exponential but with a higher first order rate constant. The two rate constants were

$$\begin{aligned}k_{(\text{stressed})} &= 0.168 \text{ hr}^{-1} \\k_{(\text{unstressed})} &= 0.122 \text{ hr}^{-1}\end{aligned}$$

Using $k_{(\text{unstressed})}$, it was calculated that the initial radical concentration after swelling would have been 4.5×10^{18} per cc if decay had occurred with this rate constant from the time of sample preparation. This agrees well with the value of 5.58×10^{18} radicals/ml calculated from the conditions of swelling and is evidence for reaction between the rubber network and galvinoxyl, which appears to be independent of the presence of oxygen.

Effect of stress on purified, peroxide cured vulcanizates containing hydrogalvinoxyl

At the beginning of the experiment, the rubber contained an initial concentration of galvinoxyl about 10 times lower than that obtained by swelling in galvinoxyl. This decayed exponentially in the absence of applied stress (Figs. 4 and 5). Under stress ($\lambda = 2.5$), galvinoxyl was formed during the initial 1.6 hr followed by the usual exponential decay.

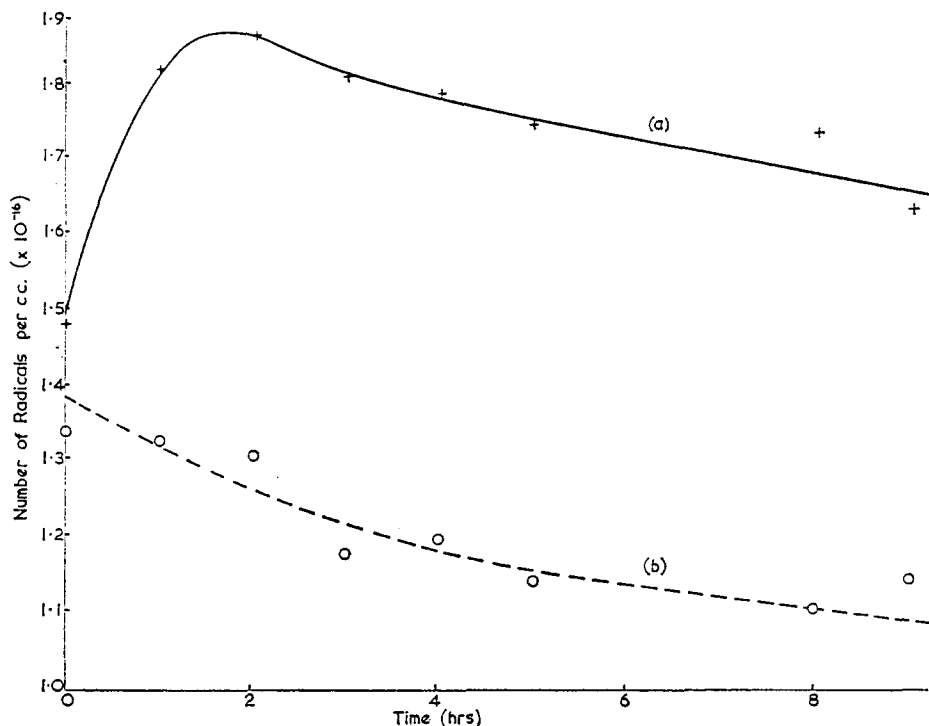


FIG. 4. Variation of radical concentration with time in peroxide cured rubber containing hydrogalvinoxyl: (a) stressed, $\lambda = 2.5$; (b) unstressed.

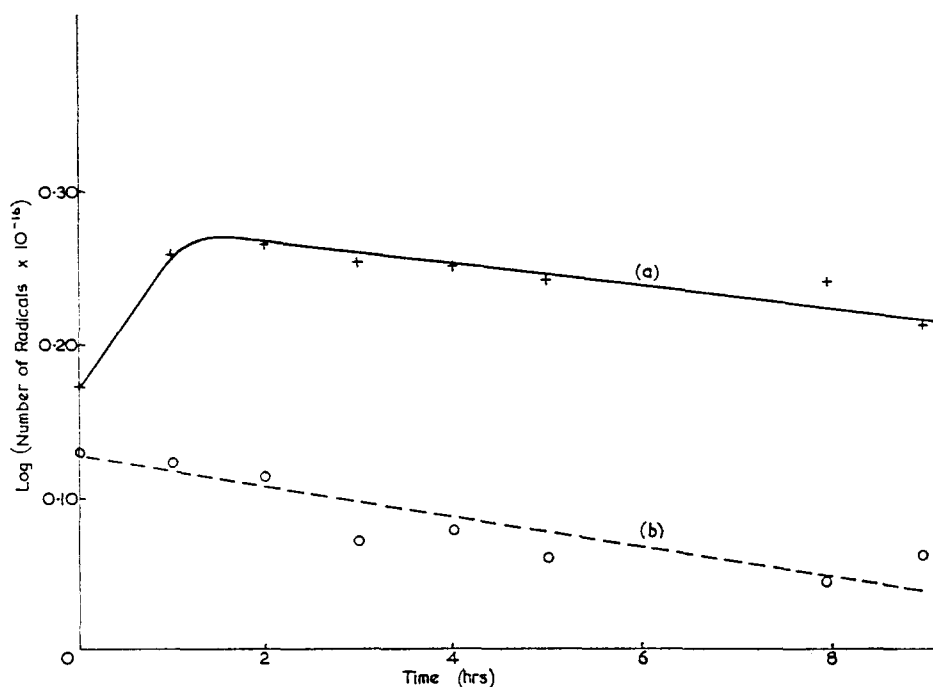


FIG. 5. Variation of log (galvinoxyl concentration) with time in peroxide cured rubber containing hydrogalvinoxyl: (a) stressed, $\lambda = 2.5$; (b) unstressed.

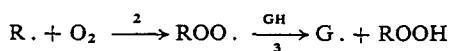
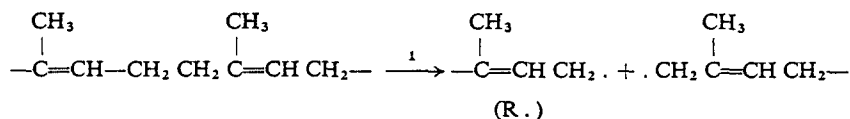
The increase in radical concentration during the initial period was $0.392 \times 10^{16}/\text{ml}$. This is a composite process since the radical generation process is superimposed on an exponential decay which would have led to a reduction of 0.061×10^{16} radicals/ml. The total increase was therefore $0.453 \times 10^{16}/\text{ml}$.

Stress relaxation measurement of broken cross-links

The amount of stress relaxation was very small and took place essentially during the first 1.5 hr. After this time, about 2 per cent stress relaxation had taken place corresponding to about 120×10^{16} cross-links breaking.

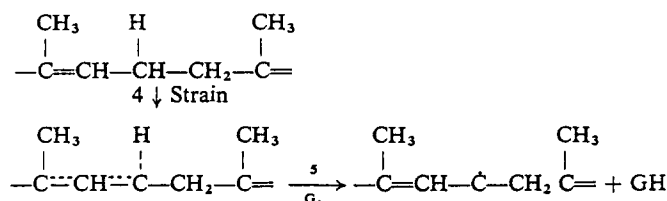
DISCUSSION

The main features of the process of degradation by stress of peroxide cured rubber are fairly clear. Two distinct processes seem to be occurring. There is an initial chain scission process (1) which gives rise to alkylperoxy radicals (2) which in the presence of excess hydrogalvinoxyl (GH) are converted to hydroperoxides with the formation of the aryloxy radical (3)



The period of radical generation corresponds to an initial period of stress relaxation in the polymer which again ceases at quite a low degree of relaxation. This probably corresponds to the redistribution of stresses in the network by scission of the most highly strained cross-links.

A second process is superimposed upon chain-scission. This is reflected in the faster consumption of galvinoxyl in stressed than in unstressed rubber and oxygen appears not to affect this reaction. It is not clear from the available evidence what this process is. The most likely possibility is that hydrogalvinoxyl is one of the products of the reaction with unstressed rubber—a process which has been proposed as a transfer mechanism which reduces the effectiveness of phenolic antioxidants.⁽¹⁶⁾ The reaction with strained rubber may be an activated form of this, since straining of the double bond and distortion of the tetrahedral angle will also weaken the C—H bond on adjacent carbon atoms.



By the same mechanism, however, disappearance of galvinoxyl may involve either addition to the activated double bond or attack at a weakened C—C single bond. Further work is required to clarify this.

It seems likely, however, that the activation of rubber to oxygen under stress is associated with the reaction of oxygen with rubber, activated by strain in one of the above ways. A direct consequence of this would be the increased consumption of antioxidant observed in stressed rubber.⁽¹¹⁾

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Résumé—On a montré que les radicaux libres produits lorsque l'on soumet des caoutchoucs réticulés à de fortes tensions peuvent être détectés par RPE soit sous la forme de radicaux peroxyalcoylés soit après réaction avec un phénol qui peut conduire à un radical libre stable (galvinoxyle). Cette réaction n'a lieu que durant la première $1\frac{1}{2}$ hr de tension et correspond à une période de relaxation de tension dans le caoutchouc. Le radical stable aryloxy disparaît lentement en absence de force de tension selon une réaction du premier ordre dont la constante de vitesse augmente avec l'application de la force. Ceci peut être interprété en disant que la réaction du galvinoxyle avec le réseau du caoutchouc, activée par l'application de la tension, se superpose à la réaction de rupture de chaîne. On pense que cela peut être relié à l'activation du caoutchouc vis-à-vis de l'oxygène que l'on observe par application d'une tension.

Sommario—Si è trovato che i radicali liberi che si producono in gomme con legami incrociati sottoposte ad elevate tensioni, possono venir rivelati nella E.S.R. sia come radicali alchilperossidici che mediante reazione con un fenolo che può dar luogo ad un radicale libero stabile (galvinossile). Tale reazione avviene solamente durante la prima $1\frac{1}{2}$ ora di tensione e corrisponde ad un periodo di cedimento nella gomma. Il radicale stabile arilossico sparisce lentamente in assenza di tensione mediante una reazione di primo ordine, la cui costante di velocità aumenta con l'applicazione di tensione. Ciò si interpreta come reazione attivata da tensione tra il galvinossile e la struttura reticolare della gomma, reazione che si sovrappone a quella relativa alla scissione della catena e che si crede essere in relazione all'attivazione della reazione gomma/ossigeno dovuta alla tensione.

Zusammenfassung—Es wurde festgestellt, daß freie Radikale, die in vernetzten Kautschuken unter der Einwirkung hoher Belastung gebildet werden, durch E.S.R. nachgewiesen werden können entweder als Alkylperoxy-Radikale oder durch eine Reaktion mit einem Phenol die zu einem stabilen freien Radikal (Galvinoxyl) führen kann. Diese Reaktion findet nur während der ersten $1\frac{1}{2}$ Stunden der Belastung statt und entspricht einer Periode der Relaxation im Kautschuk. Das stabile Aryloxy-Radikal verschwindet langsam bei Abwesenheit von Belastung nach einer Reaktion erster Ordnung, deren Geschwindigkeitskonstante bei Belastung zunimmt. Dies wird gedeutet als eine durch Belastung aktivierte Reaktion des Galvinoxyls mit dem Kautschuk Netzwerk, die der Kettenspaltungsreaktion überlagert ist und wahrscheinlich in Beziehung steht mit der beobachteten Aktivierung von Kautschuk gegenüber Sauerstoff unter Belastung.