The Mechanism of Radiation Damage to Elastomers.
I. Chain Scission and Antirad Action

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INTRODUCTION

The mechanisms by which high energy radiation affects the properties of elastomers are not completely defined. However, it is accepted that two of the most important secondary events are the crosslinking and scission of polymer chains. These crosslinks and scissions lead to marked changes in polymer properties. Depending on which is predominant, elastomers are either crosslinked with a resulting increase in modulus and decrease in elongation, or undergo scission to a low-modulus, weak material.

Since these property changes are deleterious to most elastomer uses, their prevention is a matter of considerable interest. Born[1] discovered certain substances which have been termed radiation protective agents or antirads. These materials when incorporated into a variety of elastomers served to protect these polymers against the deleterious property changes caused by irradiation.

An essential step in understanding the mechanism by which these antirads are effective is the establishment of (1) whether they prevent scission, crosslinking, or both, (2) whether they act by an antioxidant-like mechanism, or are effective in the absence of oxygen, and (3) whether there are major differences in mechanism from one antirad to the next, or whether they vary only in degree of effectiveness.

The present study was undertaken to obtain more extensive information concerning the effects of antirads upon chain scission induced by high energy gamma radiation. Stress relaxation measurements were chosen as the measure of chain scission.
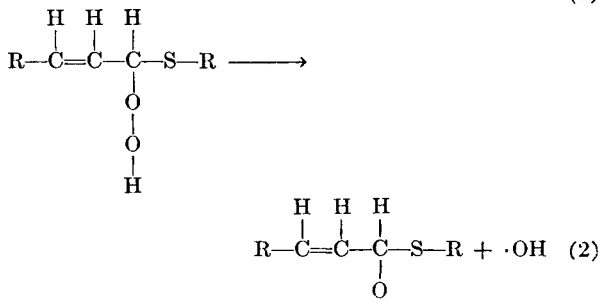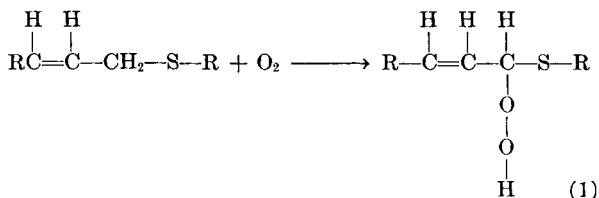
When a rubber sample is stretched to a given strain and held fixed at this strain, the stress gradually decreases. This phenomenon is termed stress relaxation. At elevated temperatures, this stress decay of sulfur-vulcanized natural rubber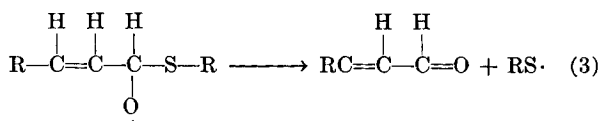 approximates an exponential law, as was shown in the pioneering work by Tobolsky and co-workers.[2,3] That this is an oxidative effect can be shown by the three-decade decrease in the rate of stress decay, when oxygen is excluded from the relaxing system. At room temperature the rate of relaxation is much less. A large portion may be due to simple decay of secondary or van der Waals interchain forces.

Recent investigators have shown that the relaxation of sulfur-vulcanized natural rubber at elevated temperatures in air may be adequately represented by the sum of two exponential terms. Le Foll[4] ascribes this to an initial rapid relaxation of secondary interchain forces, followed by a slower oxidative chain scission. Berry,[5] on the other hand, has proposed a mechanism whereby the two exponential terms are related to a relatively slow oxidation of the crosslinks followed by more rapid scission:

$$X + O_2 \xrightarrow{\;k_1\;} P$$
$$P \xrightarrow{\;k_2\;} \text{scission}$$
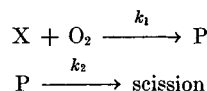
That this mechanism may be operative is borne out by the observations of Bateman and Cunneen.[6] They propose the following mechanism for the oxidation of organic sulfides which they studied:

(1)

(2)

$$R-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}-S-R \longrightarrow R\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}=O + RS\cdot \quad (3)$$

$$2RS\cdot \longrightarrow RSSR \quad (4)$$

It can be readily seen that step (1) of Bateman and Cunneen's mechanism corresponds to the k_1 process of Berry. Further, Berry's k_2 process involves steps (2), (3), and (4) of Bateman and Cunneen.

EXPERIMENTAL PROCEDURES

As the base recipe for this study, the following ASTM compound was selected.[7]

	Parts by weight
Natural rubber	100
Stearic acid	3
Zinc oxide	5
Sulfur	3
Benzothiazyl disulfide	1
Phenyl-2-naphthylamine	1
EPC carbon black	50

To this control recipe were added five parts of eleven selected antirads: (1) N-phenyl-N'-o-tolylethylenediamine (FLX); (2) N-cyclohexyl-N'-phenyl-p-phenylenediamine (Antiox 4010), (3) 6-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline (Santoflex B), (4) N,N'-dioctyl-p-phenylenediamine (UOP-88), (5) 2-naphthylamine, (6) 1,4-naphthoquinone, (7) phenylhydroquinone, (8) 2-naphthol, (9) N,N'-diphenyl-p-phenylenediamine (35%) + phenyl-1-naphthylamine (65%) (Akroflex C), (10) N,N'-dicyclohexyl-p-phenylenediamine, and (11) p-quinone. The antirads were chosen from those either showing maximum antirad effectiveness during Born's empirical study[1] or having structural variations of interest. It is recognized that the solubility limit was exceeded for some of these antirads in the rubber. This fact makes comparisons of antirad effectiveness unreliable, but it in no way affects the mechanistic conclusions of this work.

The compounds were mixed as described in standard ASTM procedures. All of the samples were cured to optimum cures as determined by physical properties. The 0.025-in.-thick cured sheets were cut into 1.25-in. × 0.25-in. strips for testing.

Relaxation measurements were made on the Multilaxometer which has been described previously.[1] Experiments were made both in air and in nitrogen, both with and without irradiation. A Co-60 gamma source was used which provided a

uniform gamma radiation flux of 1.35×10^7 ergs/g.$^{-1}$ (C) hr.$^{-1}$ (1.58×10^5 R. hr.$^{-1}$).

RESULTS AND DISCUSSION

The types of results which were obtained are shown in Figures 1 and 2. Stress relaxation was plotted as log (S/S_0) vs. t, where S is the stress at time t and S_0 is the stress at $t = 0$. The rates of stress relaxation (k) were then taken directly as the slope of the linear portion of the curves (expressed as hours^{-1}). The rates of relaxation under irradiation have been corrected for the relaxation which would be noted without irradiation by simple subtraction of the rates.

It is assumed that the ratio of the stress at fixed elongation of a rubber sample before and after a given continuous stress relaxation is the same as the ratio of load-bearing chains (ν) before and after the same relaxation. If this is true, then the number of load-bearing chains broken or the number of scissions can be calculated directly if the number of load-bearing chains is known initially.[8]

Other research work[9] has shown that the effective molecular weight between crosslinks (M_c) for the
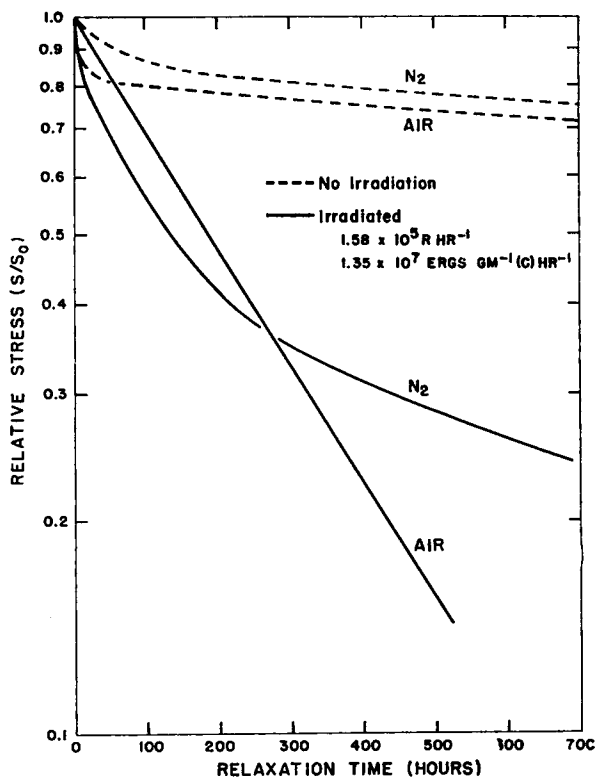

Fig. 1. The stress relaxation of carbon black-loaded natural rubber containing 1 part phenyl-2-naphthylamine (control).
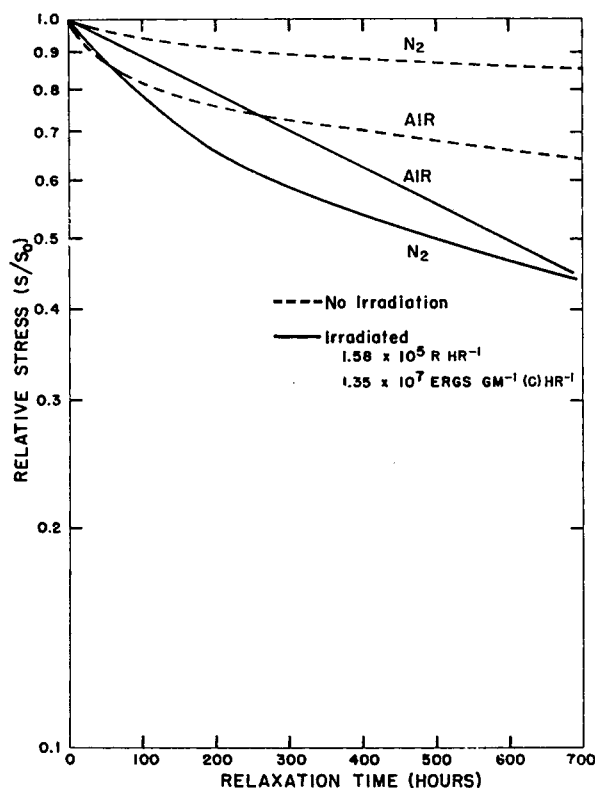
Fig. 2. The stress relaxation of carbon black-loaded natural rubber containing 5 parts N-cyclohexol-N'-phenyl-p-phenylenediamine.

natural rubber stock employed in these experiments, containing 50 pphr of EPC black, may be represented by the following relationship:

$$\frac{1}{M_c} = \frac{M_{100}}{73.7 \times 10^4} \quad (1)$$

where M_{100} is the modulus (expressed in psi) at 100% elongation.

If the original molecular weight between crosslinks is known, and it is noted that the number of crosslinks per gram is given by N/M_c, the number of scissions per 100 e.v. energy absorption (G_s) may be readily determined:

$$G_s = \frac{kN}{RM_c(6.58 \times 10^{17})} \quad (2)$$

where k is the rate constant (hour^{-1}) for the decrease in crosslinks described earlier.

$$-\frac{ds}{dt} = \frac{d}{dt}k \quad (3)$$

$$\log\left(\frac{S}{S_0}\right) = kt \quad (4)$$

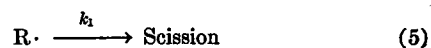## TABLE I
The Effect of Antirads on Scission

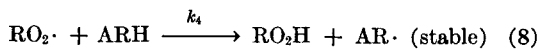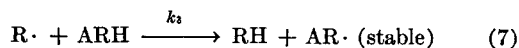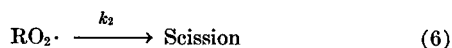| Antirad (5 pphr)	G (events/100 e.v.)	
	Scissions in	
	N$_2$	Air
None (1 pphr phenyl-2-naphthylamine)	2.7	13
N-Phenyl-N'-o-tolylethylenediamine	1.8	4.3
N-Cyclohexyl-N'-phenyl-p-phenylene-diamine	1.2	1.4
6-Phenyl-2,2,4-trimethyl-1,2-dihydro-quinoline	1.9	4.2
N,N'-Dioctyl-p-phenylenediamine	1.5	5.0
2-Naphthylamine	1.6	5.6
1,4-Naphthoquinone	2.0	5.6
Phenylhydroquinone	2.2	5.4
2-Naphthol	1.3	4.1
N,N'-Diphenyl-p-phenylenediamine (35%) + phenyl-1-naphthylamine (65%)	1.4	3.7
N,N'-Dicyclohexyl-p-phenylenediamine	1.5	3.0
p-Quinone	2.8	7.8

In eq. (2), N is Avogadro's number and R is the radiation dose in megaroentgens. The conversion factor of 1 megaroentgen exposure being equivalent to the absorption of 6.58×10^{19} e.v./g. was used. To obtain this value, a weight absorption coefficient for the stock of 2.89×10^{-2} cm.^{2}/g. was calculated, and the new air absorption value of 87.7 ergs/g. of air for one roentgen was assumed.[10]

The yields of scissions are listed in Table I. These results reveal several interesting facts. The first is that in the presence of air, the antirads serve in all cases to decrease the yield of chain scission. The yields of chain scission in air are only 11 to 60% as great in the presence of antirads as in their absence. As has been reported previously, the effectiveness of radiation in causing chain scission is greatly reduced in the absence of air. This is true whether antirads are present or not.

The most interesting observation, however, is that the antirads are effective in the absence of air, as well as in its presence. In the absence of air, the yields of chain scission are 45 to 82% as great in the presence of antirads as in their absence. Only in the case of p-quinone is the antirad ineffective in the absence of air.

Qualitatively these observations could be explained by assuming the following mechanisms (ARH = antirad):

$$\text{R}\cdot \xrightarrow{k_1} \text{Scission} \quad (5)$$

$$RO_2 \cdot \xrightarrow{k_2} \text{Scission} \qquad (6)$$

$$R \cdot + ARH \xrightarrow{k_3} RH + AR \cdot \text{ (stable)} \qquad (7)$$

$$RO_2 \cdot + ARH \xrightarrow{k_4} RO_2H + AR \cdot \text{ (stable)} \quad (8)$$

Irradiation, whether in the presence or absence of air, will yield $R \cdot$ radicals, but in air these will be converted to $RO_2 \cdot$ radicals by the very rapid reaction:

$$R \cdot + O_2 \xrightarrow{k_5} RO_2 \qquad (9)$$
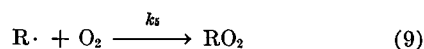
Thus, in air, $RO_2 \cdot$ radicals will predominate in the system, whereas, in the absence of air, $R \cdot$ radicals will predominate. Evidence from the large body of polymer oxidation research indicates that $k_2 > k_1$. Consequently, it would be expected and is actually observed that the yield of chain scission is less in the absence of air than in its presence. Any reactions of the type (7) or (8) will decrease the radical concentration and thus the rate of chain scission by reactions (5) or (6). If we assume that $k_4 > k_3$, then the decreased effectiveness of antirads in the absence of air is easily explained. Indeed, evidence from other reactions would indicate that the $RO_2 \cdot$ radical may be more energetic.

It should be pointed out that in stress relaxation, every load-bearing chain which undergoes scission contributes to the total relaxation unless the broken chain radical ends reunite before they can migrate away from each other under the applied stress. But, if they do migrate away from each other, they may undergo various fates. Through oxidation, hydrogen abstraction, reaction with various other materials present, or disproportionation, these free radical ends may be stabilized in a permanent or nontransient broken form. On the other hand, by combination with other free radical ends or addition to unsaturated sites present in the polymer matrix, the free radical ends may reunite with main chains and essentially disappear. Thus the chain scissions measured by stress relaxation may be both transient and nontransient in nature. Yields of chain scission measured in this way may be considerably larger than those measured by rates of gel formation or related techniques, since these latter methods measure only the nontransient chain scissions.

CONCLUSIONS

The effect of antirads on chain scission as measured by stress relaxation is one of inhibition both in the presence of air and to a lesser extent in its ab-

sence. This can be explained by assuming a reactivity of the antirads with $RO_2 \cdot$ radicals yielding stable products, and a somewhat decreased reactivity with $R \cdot$ radicals. A greater tendency of $RO_2 \cdot$ radicals to lead to chain scission than $R \cdot$ radicals seems to be indicated.

References

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3. A. V. Tobolsky, R. D. Andrews, and E. E. Hanson, *J. Appl. Phys.*, **17**, 352 (1946).
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10. Based on electron absorption coefficients from C. M. Davisson and R. D. Evans, *Rev. Mod. Phys.*, **24**, 79 (1952) and ICRU recommendations.

Synopsis

The effect of antirads on the gamma radiation yields of scission in black loaded natural rubber stocks has been studied. The yield of chain scission has been measured by stress relaxation methods. The antirads were found to decrease the rate of chain scission, both in air and under nitrogen, with the antirad effectiveness being greater in the former case. The presence of oxygen accelerated the radiation induced chain scission. These results may be explained if it is assumed that (1) $RO_2 \cdot$ radicals lead to chain scission more readily than do $R \cdot$ radicals, and (2) $RO_2 \cdot$ radicals react with antirads leading to stabilized products more readily than do $R \cdot$ radicals.

Résumé

On a étudié l'effet des antirads sur les rendements de scission sous l'influence des radiations gamma sur les stocks de caoutchouc naturel chargé de noir. Le rendement en scission de chaîne a été mesuré par la méthode de relaxation à la tension. Les antirads décroissent la vitesse de rupture de chaîne, à l'air et sous azote, avec une efficacité plus grande dans le 1ᵉʳ cas. La présence d'oxygène accélère la rupture de chaîne induite par les radiations. Ces résultats peuvent être expliqués si on admet que (1) les radicaux $RO_2 \cdot$ provoquent plus facilement une rupture de chaîne que les radicaux $R \cdot$ et (2) que les radicaux $RO_2 \cdot$ réagissent avec les antirads en formant plus facilement des produits stabilisés que les radicaux $R \cdot$.

Zusammenfassung

Der Einfluss von Strahlenschutzstoffen auf die Spaltungs-ausbeute bei Gammabestrahlung von russgefüllten Natur-kautschuk wurde untersucht. Die Kettenspaltungsaus-beute wurde nach der Spannungsrelaxationsmethode gemes-sen. Es wurde gefunden, dass die Schutzstoffe sowohl unter Luftals auch unter Stickstoff die Geschwindigkeit der Kettenspaltung herabsetzen, wobei ihre Wirksamkeit im ersteren Fall grösser ist. Die Gegenwart von Sauerstoff beschleunigte die strahlungsinduzierte Kettenspaltung. Die hier mitgeteilten Ergebnisse können durch die Annahme erklärt werden, dass (1) RO₂· Radikale leichter zur Ketten-spaltung führen als R· Radikale und (2) RO₂· Radikale mit den Schutzstoffen leichter unter Bildung stabilisierter Pro-dukte reagieren als das bei R· Radikalen der Fall ist.