

Stress Relaxation of Unaccelerated Natural Rubber-Sulfur Vulcanizates Before and After Treatment with Triphenylphosphine

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Synopsis

The aerobic and anaerobic stress relaxation of unaccelerated natural rubber-sulfur vulcanizate networks has been examined before and after treatment with triphenylphosphine, a reagent which converts polysulfidic crosslinks into di- and monosulfide crosslinks. This treatment reduces the rate of anaerobic stress relaxation and makes the network more susceptible to protection by zinc dibutyldithiocarbamate against aerobic stress relaxation. Aerobic stress relaxation of the network after treatment with triphenylphosphine remains nonautocatalytic, indicating that it still contains the precursor of an antioxidant, and crosslinking continues to occur during aging, showing that the presence of polysulfide groups is not a sole prerequisite for such network formation.

I. INTRODUCTION

Extracted, fully cured natural rubber (NR) vulcanizates derived from a tetramethylthiuram disulfide (TMTD)-zinc oxide system show completely different stress-relaxation behavior from unaccelerated and conventionally accelerated NR-sulfur vulcanizates.¹ The aerobic stress relaxation of a NR-TMTD-ZnO vulcanizate network involves autocatalytic oxidative scission of the polyisoprene main chains, a process which is readily retarded by phenolic antioxidants and especially by metal dialkyldithiocarbamates. In the absence of antioxidant, crosslink formation on oxidative aging is negligible relative to network degradation, while stress relaxation is insignificant under anaerobic conditions. Contrasting with this, the aerobic stress relaxation of extracted unaccelerated NR-sulfur vulcanizates and of certain conventionally accelerated NR-sulfur vulcanizates is not autocatalytic, and considerable crosslinking occurs concurrently with network degradation; phenolic antioxidants are only moderately effective in preventing stress relaxation, while metal dialkyldithiocarbamates may, initially, enhance network degradation and thereafter be only moderately effective protective agents; there is also considerable stress relaxation *in vacuo*, except for vulcanizates which have been cured for extended times.² These differences in stress-relaxation behavior must be due to differences in the structures of the vulcanizate network, and, in order to establish the

interrelationship between them, resort is now being made to the use of chemical reagents (chemical probes)^{3,4} which modify the structures of the vulcanizate networks in a known way, and to the preparation of networks of well-defined structure. A comparison of the anaerobic and aerobic stress-relaxation behavior of these vulcanizate networks should reveal which structural features of the network, viz., the crosslink, the main polyisoprene chain, or structural modifications of the latter, are responsible for particular types of aging.

This paper describes a study of the stress-relaxation behavior of unaccelerated NR-sulfur vulcanizate networks before and after treatment with triphenylphosphine. This reagent converts polysulfidic crosslinks present in the original vulcanizate into mono- and disulfide crosslinks, without affecting cyclic monosulfides^{4,5} which are important modifications of the main chain of this type of vulcanizate.^{3,6}

II. EXPERIMENTAL METHODS

Preparation of Vulcanizates

Unaccelerated NR-sulfur vulcanizates were prepared both from smoked sheet (RSS1) and from highly purified (HP) NR (United States Rubber Co.). The rubbers were hot acetone-extracted under nitrogen for 24 hr., dried *in vacuo*, and then compounded with 10 parts of sulfur phr according to the method described elsewhere.³ Vulcanization was effected at 140°C. for 4 or 6 hr. to give sheets 0.2 mm. thick. The vulcanizates were hot acetone-extracted under nitrogen for 24 hr., then dried and stored *in vacuo* in the dark.

Treatment of Vulcanizate Networks with Triphenylphosphine

The general method used has been described previously.⁴ Briefly, it consists of treating the swollen vulcanizate network with a solution of triphenylphosphine in dry benzene *in vacuo* at 80°C. for 96 hr. (or, in one case, 232 hr.). The treated samples are then continuously extracted with cold benzene under nitrogen in the dark for 24 hr., then dried and stored *in vacuo* at room temperature. In certain experiments benzene was replaced by dry acetone as the reaction and extraction solvent. Control experiments were also made in which the samples were heated in benzene, in the absence of triphenylphosphine, under the specified reaction conditions. Table I details the combined sulfur (S_c) values for the untreated acetone-extracted samples and for those heated in solvent with and without triphenylphosphine.

Measurement of Stress Relaxation

The principle and method of measuring stress relaxation of extended rubber samples have been described elsewhere.⁷ The continuous stress-relaxation measurements were obtained by use of an automatically operated

TABLE I

Combined-Sulfur Values (S_c) of Unaccelerated NR-Sulfur Vulcanizate Networks Before and After Treatment at 80°C. *in vacuo* in the Presence or Absence of Triphenylphosphine

Vulcanizate Network	S_0 , % ^a	Treatment	S_c after treatment, % ^a	Com-bined S removed by treat-ment, % ^c
RSS1	4.45, 4.47	—	—	—
RSS1	4.45, 4.47	Benzene, 96 hr.	4.40, 4.41	1
RSS1	4.45, 4.47	Benzene/Ph ₃ P, 86 hr.	3.59, 3.59	19
RSS1	4.45, 4.47	Benzene/Ph ₃ P, 232 hr.	3.44, 3.47	23
Highly purified NR	3.53 —	Acetone/Ph ₃ P, 96 hr.	2.52, —	29

^a Determined by dry combustion of sample (ca. 50–100 mg.) and estimation of sulfate ion complexometrically with Ba⁺⁺/EDTA.³

relaxometer,⁸ and the intermittent measurements by means of a manually operated apparatus. The results are presented as plots of $\log f/f_0$ against time, f being the stress in a strip at time t and f_0 that at zero time. Additives were introduced into the vulcanizates by swelling the samples overnight in 0.2% solutions of the additive in ethyl acetate and subsequently drying the samples *in vacuo* at room temperature.

III. EXPERIMENTAL RESULTS

The continuous aerobic stress relaxation at 80°C. of an acetone-extracted smoked sheet sulfur vulcanizate (4 hr. cure at 140°C.), is not autocatalytic, but gives an almost linear plot of $\log f/f_0$ against time (Fig. 1). The corresponding intermittent relaxation is appreciably slower and continuous relaxation *in vacuo* slower still. In the presence of 2,2'-methylene bis(4-methyl-6-*tert*-butylphenol) (Antioxidant 2246) continuous relaxation in air is reduced almost to the vacuum rate, but this is not so in the presence of zinc dibutyldithiocarbamate (ZBC) (Fig. 1).

The above (control) samples, after being heated for 96 hr. at 80°C. in benzene *in vacuo*, show stress relaxation at 80°C. similar to that of the controls, except that the rate of intermittent relaxation in air is markedly reduced (Fig. 2).

The control samples and the samples which had been heated in benzene at 80°C. were subsequently heated unswollen for 96 hr. at 80°C. at 10⁻⁴ mm. Hg pressure. The resulting vulcanizate networks show aerobic stress-relaxation behavior appreciably different from that of their precursors (Fig. 3; cf. Figs. 1 and 2); in particular, the reheated control sample undergoes a faster continuous stress relaxation than its precursor, and the reheated, benzene-treated sample relaxes significantly faster than its pre-

cursor under intermittent conditions. Further, ZBC is now much more effective as a protective agent against aerobic continuous stress relaxation.

After heating the control samples with triphenylphosphine in benzene for 96 hr. at 80°C. *in vacuo*, the continuous stress relaxation in air at 80°C. is initially autocatalytic, but after 50 min. it attains a rate which decreases exponentially with time and which is somewhat faster than that of the

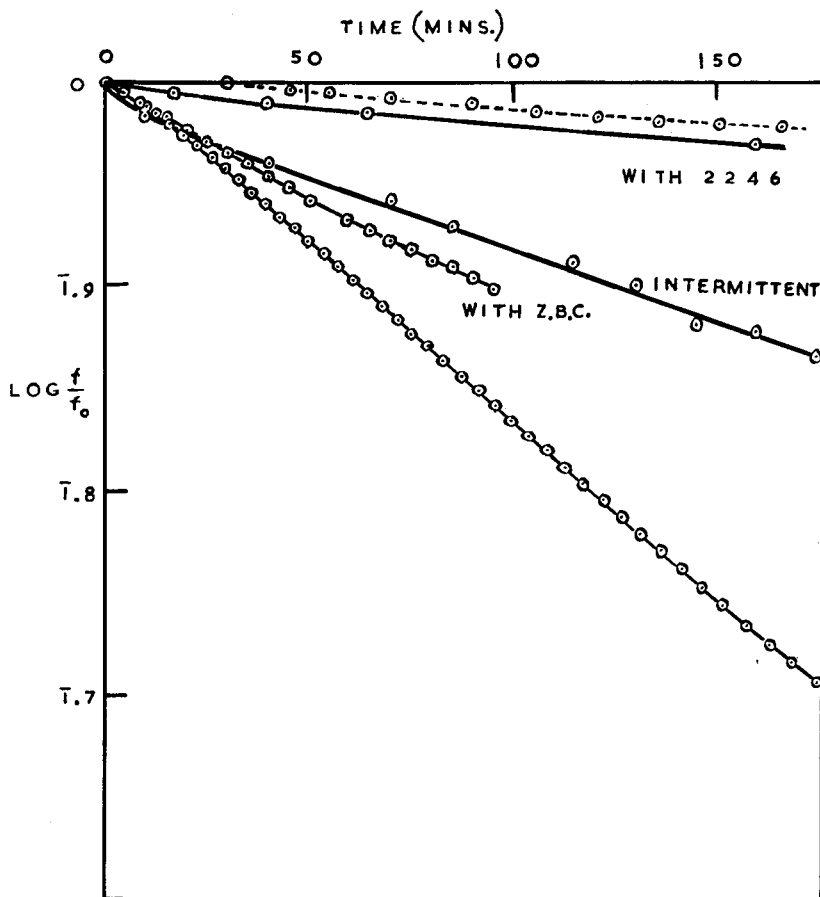


Fig. 1. Stress relaxation at 80°C. of an acetone-extracted unaccelerated sulfur vulcanizate of smoked sheet (cured 4 hr. at 140°C.). (In this and all other figures aerobic relaxation is represented by full lines and vacuum relaxation by dotted lines. Except where specified otherwise, all data refer to continuous stress-relaxation measurements.)

control (Fig. 4). The intermittent stress relaxation in air of the triphenylphosphine-treated samples proceeds at a rate approaching that of the continuous relaxation and at an appreciably faster rate than that of the corresponding control samples. Both Antioxidant 2246 and ZBC reduce the relaxation rate in air to a very low value, which approaches that of the very slow continuous relaxation observed *in vacuo* (Fig. 4). The effect of ZBC

contrasts with its behavior in the corresponding control sample (Fig. 1).

A control sample which had been treated with triphenylphosphine in benzene for 232 hr. at 80°C. shows less sign of autocatalysis during aerobic continuous stress relaxation than does the sample treated for 96 hr. (Fig. 5). Other features of the stress relaxation are similar to those of Figure 4.

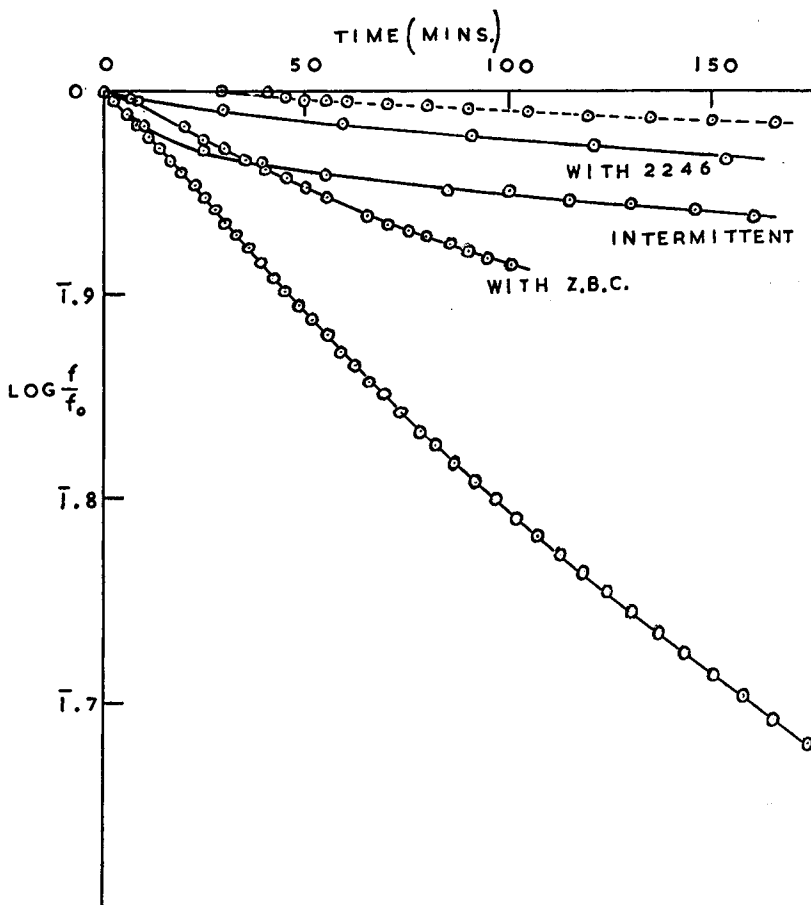


Fig. 2. Stress relaxation at 80°C. of an acetone-extracted unaccelerated sulfur vulcanizate of smoked sheet (cured 4 hr. at 140°C.) heated for 96 hr. at 80°C. in benzene *in vacuo*.

The sulfur vulcanizate network prepared from highly purified NR cured for 6 hr. at 140°C., undergoes stress relaxation in air somewhat more rapidly than the network derived from smoked sheet, but the general characteristics of the relaxation remain the same (Fig. 6; cf. Fig. 1).

After treatment with triphenylphosphine in acetone for 96 hr. at 80°C. the rate of continuous aerobic stress relaxation is markedly increased and is initially autocatalytic, although the autocatalysis persists only for about

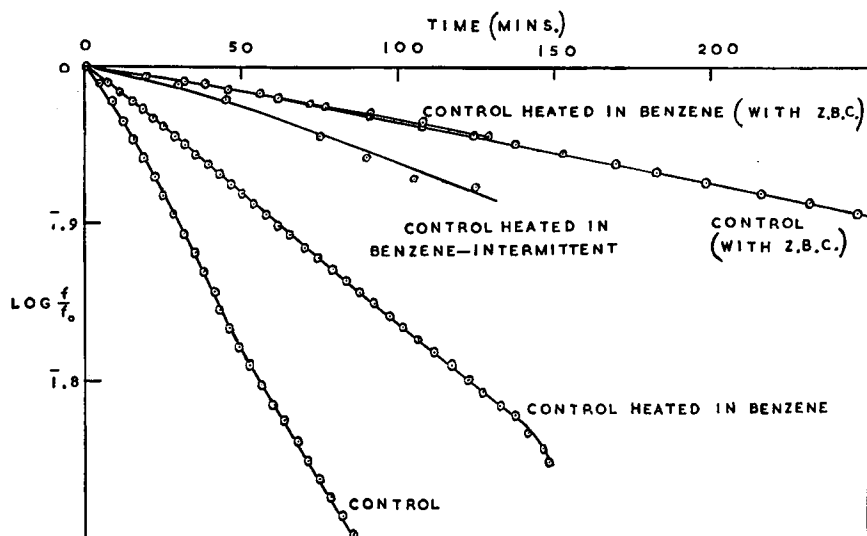


Fig. 3. Stress relaxation at 80°C. of the samples in Figs. 1 and 2 which have been heated for 96 hr. at 80°C. *in vacuo*.

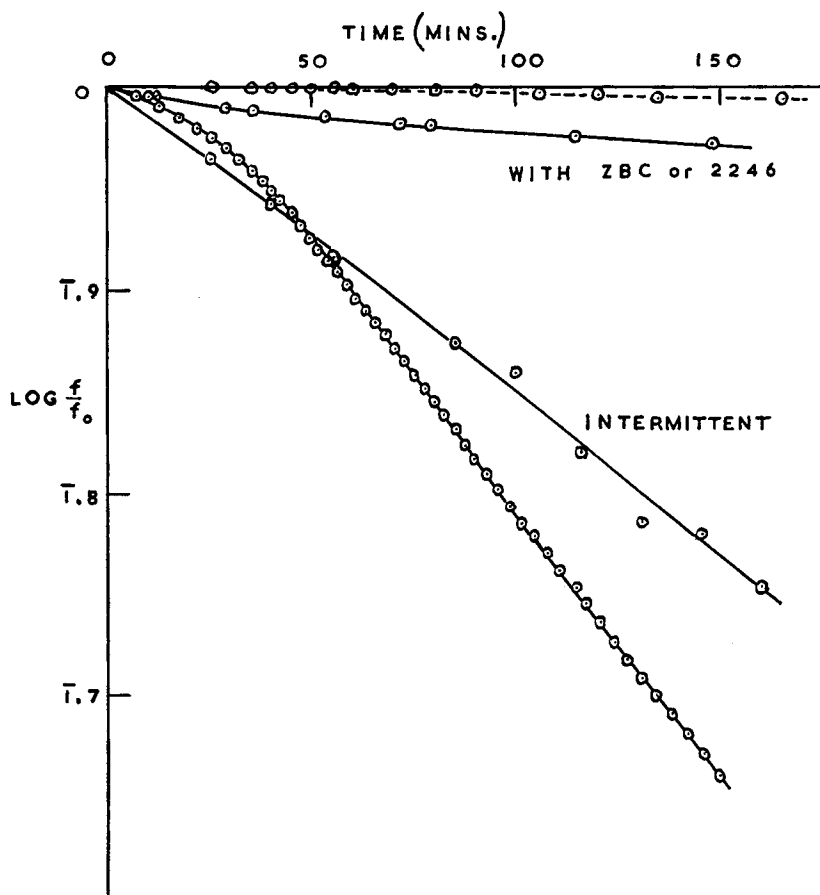


Fig. 4. Stress relaxation at 80°C. of an acetone-extracted unaccelerated sulfur vulcanizate of smoked sheet (cured 4 hr. at 140°C.) treated with triphenylphosphine for 96 hr. at 80°C. in benzene.

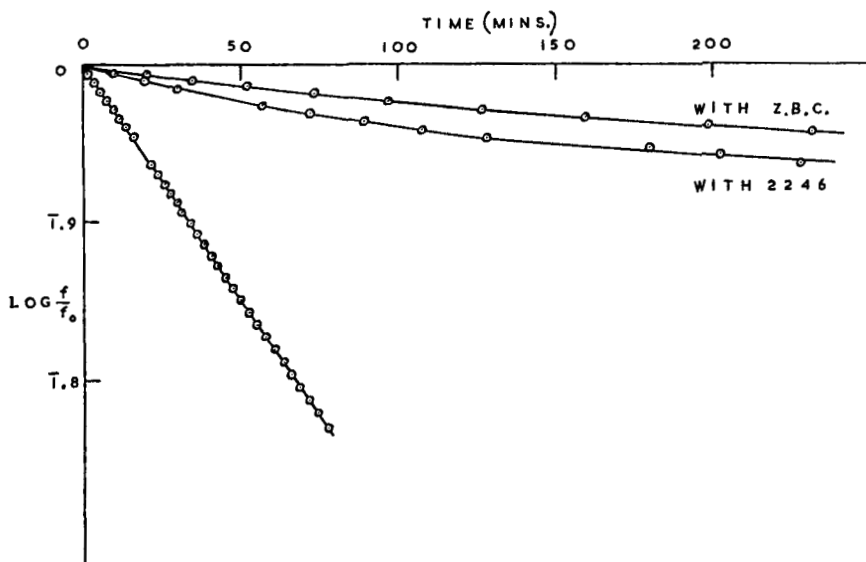


Fig. 5. Stress relaxation at 80°C. of an acetone-extracted sulfur vulcanizate of smoked sheet (cured 4 hr. at 140°C.) treated with triphenylphosphine for 232 hr. at 80°C. in benzene.

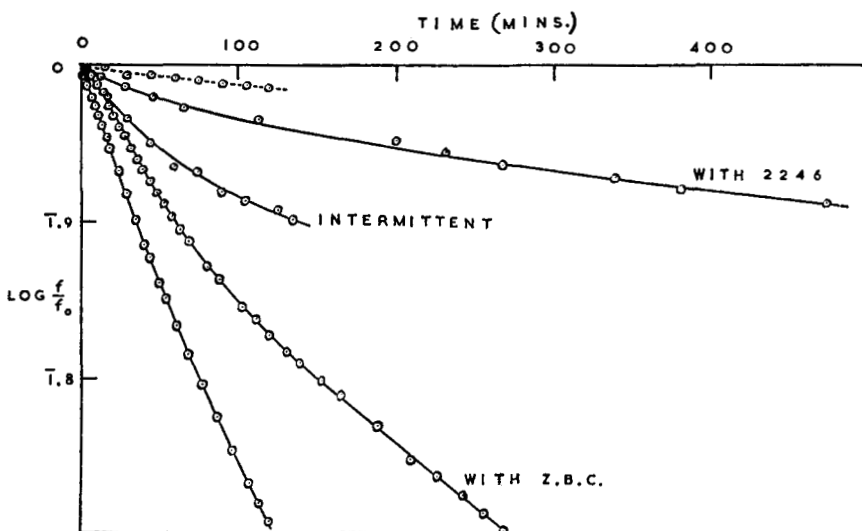


Fig. 6. Stress relaxation at 80°C. of an acetone-extracted unaccelerated sulfur vulcanizate of highly purified natural rubber (cured 6 hr. at 140°C.).

the first 10% of degradation and thereafter the rate is exponential with time (Fig. 7). Intermittent relaxation in air is appreciably slower than continuous. The relaxation *in vacuo* is appreciably slower than that of the untreated sample, and both Antioxidant 2246 and ZBC reduce the rate of aerobic relaxation almost to the *in vacuo* rate (Fig. 7). Reducing the

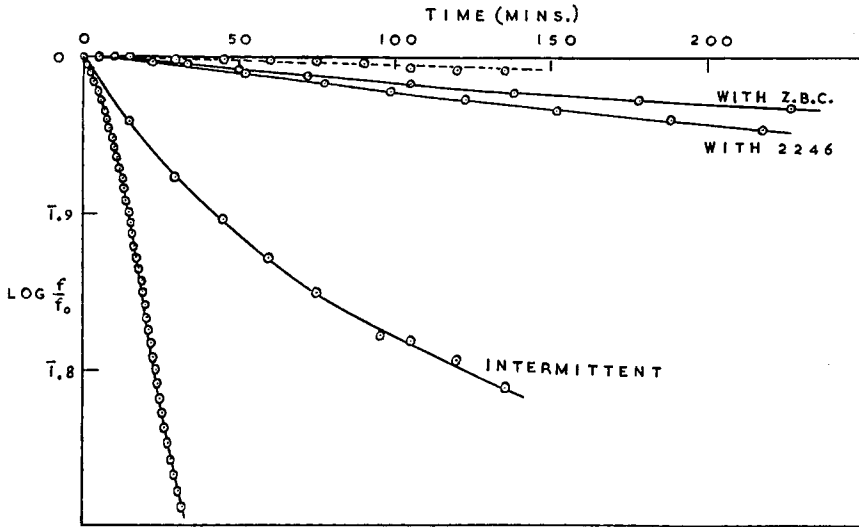


Fig. 7. Stress relaxation at 80°C. of an acetone-extracted unaccelerated sulfur vulcanizate of highly purified natural rubber (cured 6 hr. at 140°C.) treated with triphenylphosphine for 96 hr. at 80°C. in acetone.

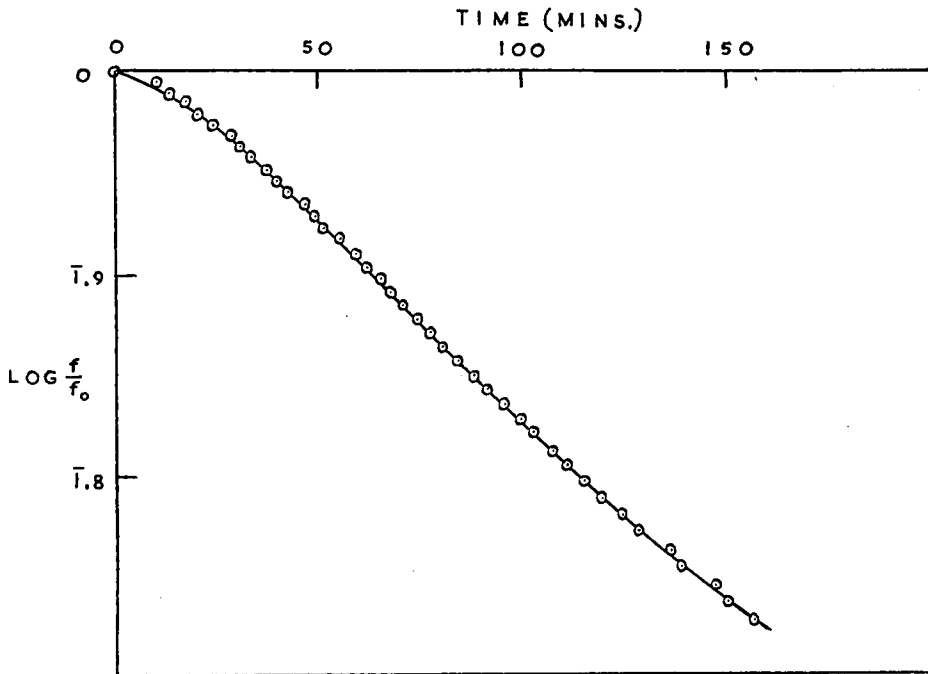
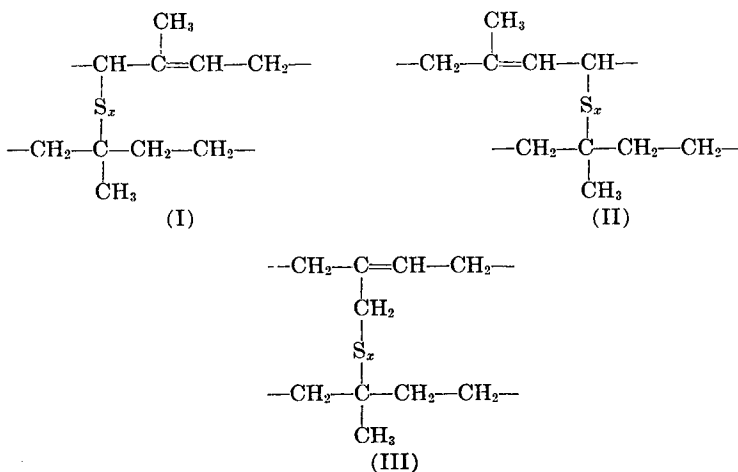


Fig. 8. Stress relaxation at 70°C. of the sample described in Fig. 7.

temperature of relaxation to 70°C. reduces the rate of aerobic relaxation, but again degradation is only autocatalytic during the very early stages of the process (Fig. 8).

IV. DISCUSSION

The structure of an unaccelerated NR-sulfur vulcanizate network is extremely complex; in addition to mono-, di-, and (predominantly) polysulfide crosslinks, much of the sulfur is combined in cyclic monosulfides distributed along the main polyisoprene chains and in addition some of the original 1,5-diene units in the main chains are transformed into conjugated triene units.^{3,4,6} Studies of the unaccelerated sulfuration of 2-methylpent-2-ene (used as a model for NR) suggest that the structures of the cross-linked units in unaccelerated NR-sulfur vulcanizates will be predominantly (I)-(III), i.e., alkenyl-*tert*-alkyl polysulfides (x mainly ≥ 2) in which the alkenyl group is predominantly trialkylethylenic.^{9,10}



In contrast with this, a fully cured vulcanizate network derived from the TMTD-ZnO system contains predominantly monosulfide and to a much lesser extent disulfide crosslinks, in which both of the hydrocarbon units vicinal to the crosslink are alkenyl; the amounts of cyclic monosulfides are insignificant, but there is some slight modification of the main polyisoprene chains due to the combination of fragments from the TMTD molecule.^{11,12}

Treatment of NR-sulfur vulcanizate networks with triphenylphosphine at 80°C. converts polysulfide crosslinks into disulfides, and prolonged treatment slowly converts dialkenyl and alkenyl alkyl disulfides into monosulfides.^{4,5} During these desulfurations a partial or in the case of the disulfides an almost complete allylic rearrangement of an alkenyl group occurs.^{5,13} The conversion of disulfide crosslinks into monosulfides by triphenylphosphine is faster, and therefore, under the present experimental conditions more complete, in acetone than in benzene.¹⁴

The most striking change in the stress-relaxation behavior of unaccelerated NR-sulfur vulcanizates brought about by treating them with triphenylphosphine is in the effect of ZBC under aerobic continuous stress-relaxation conditions. Before treatment, ZBC does not effectively prevent network degradation in air. After treatment, ZBC is as effective in preventing relaxation as Antioxidant 2246. Thus, in unaccelerated NR-sulfur vulcanizates, ZBC is an efficient antidegradant in the presence of mono- and, possibly, disulfide groups but is much less effective in presence of polysulfides, which suggests that its relative inefficacy in the latter case may be due to its destruction by interaction with the polysulfides present in these vulcanizates. It must, however, also be pointed out that the untreated vulcanizate networks after reheating *in vacuo* for 96 hr. at 80°C. are protected to a greater extent by ZBC; independent experiments show that although this heat treatment may cause some thermal interchange of the polysulfide crosslinks it does not cause any appreciable loss or shortening of the polysulfide groups,¹⁴ and thus the reason for the effect described here is still obscure.

Triphenylphosphine treatment markedly reduces the rate of stress relaxation *in vacuo*, a finding which is consistent with the fact that polysulfidic crosslinks are susceptible to purely thermal interchange processes,^{14,15} whereas the disulfide and monosulfide crosslinks which will predominate in the triphenylphosphine-treated network will be thermally much more stable. The slight amount of vacuum relaxation which is still evident after treatment probably arises from the slow thermal rearrangement of disulfide crosslinks still present. The above findings are in keeping with the fact that a fully cured NR-TMTD-ZnO vulcanizate network, in which the crosslinks are mainly monosulfidic, does not undergo any appreciable stress relaxation *in vacuo*.¹

Whereas the continuous aerobic stress relaxation of a fully cured NR-TMTD-ZnO vulcanizate network is autocatalytic down to very low stresses, that of the triphenylphosphine-treated, unaccelerated NR-sulfur vulcanizates, which similarly contain only mono- and disulfide crosslinks, ceases to be autocatalytic after a few per cent of degradation, even when relaxation is conducted at a lower temperature. The last finding suggests that the absence of autocatalysis is not due to the rate of the oxidative stress relaxation being diffusion controlled. The contrasting stress-relaxation behavior of the TMTD network and the triphenylphosphine-treated unaccelerated NR-sulfur network is strongly suggestive of their being structural units in the latter network, but not in the former, which are effective antioxidants or precursors thereof. Complementary studies in these laboratories¹⁶⁻¹⁹ do in fact show that the sulfoxides derived from alkenyl-*tert*-alkyl monosulfides similar in structure to those believed to be present in the triphenylphosphine-treated unaccelerated NR-sulfur vulcanizate networks are potent antioxidants in squalene¹⁶⁻¹⁸ and antidegradants in peroxide-vulcanized NR,¹⁹ whereas dialkenyl mono- and disulfides analogous to the crosslinks in the TMTD-network have markedly inferior

antioxidant activity.^{16,18} Since some of the cyclic monosulfides present in unaccelerated NR-sulfur vulcanizate networks are also alkenyl-*tert*-alkyl in structure,⁶ these also may act as "built-in" antioxidants in such networks and thus be additional structures responsible for the nonautocatalytic nature of the continuous stress relaxation process in air; experimental verification of this must, however, await the determination of the antioxidant activity of relevant model cyclic monosulfides in autoxidizing olefin systems. The observation that the exponential rate of aerobic relaxation is faster after removal of polysulfide groups by triphenylphosphine treatment (cf. Figs. 1 and 4) is significant. It may suggest that polysulfides can give rise to somewhat better antioxidants than mono- and disulfides as has been demonstrated elsewhere,¹⁸ or, alternatively, that the triphenylphosphine treatment has reduced and thus rendered ineffective oxygenated sulfur compounds (e.g., sulfoxides or thioisulfates) present in the original network, such compounds being known to be effective antioxidants for olefin autoxidation.^{16,17}

Finally, when the control NR-sulfur network is heated in benzene *in vacuo* in the stress-relaxation behavior of the resultant deswollen network is very similar to that of its precursor, except that intermittent relaxation in air is much slower, indicating an apparently greater degree of crosslinking occurring concurrently with network degradation (cf. Figs. 1 and 2). This effect is related to the presence of a "supercoiled" network formed as a result of thermal interchange of polysulfide crosslinks in the swollen state.^{14,20} This supercoiled network is less effective than the original network in supporting the stress under the relaxation conditions, but under the thermal conditions prevailing in the intermittent relaxation it gradually reverts by interchange of the polysulfide crosslinks into the original network and thus leads to an actual increase in the elastically effective degree of crosslinking. In keeping with this, if the benzene-treated network is deswollen and subsequently heated unstrained *in vacuo*, which partially returns the network to the state prevailing before it was heated in benzene, then the rate of intermittent relaxation reverts to a value much closer to that found for the control sample (cf. Figs. 1, 2, and 3).

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Résumé

La relaxation sous tension à l'air et en absence d'air de réseaux de caoutchouc naturel et de caoutchouc vulcanisés au soufre a été examiné avant et après traitement à la triphénylphosphine, réactif qui transforme les ponts polysulfurés en liens di- et monosulfurés. Ce traitement réduit la vitesse de relaxation sous tension en absence d'air et rend le réseau plus sensible à l'effet protecteur du dibutyldithiocarbamate de zinc à l'égard de la relaxation sous tension en présence d'air. La relaxation sous tension du réseau à l'air après traitement à la triphénylphosphine reste nonautocatalytique, ce qui indique que le réseau contient encore le précurseur d'un antioxydant et le pontage continue à se faire au cours du vieillissement, ce qui montre que la présence de groupes polysulfurés n'est pas la seule condition pour la formation d'un tel réseau.

Zusammenfassung

Die aerobe und anaerobe Spannungsrelaxation von beschleunigerfreien Naturkautschuk-Schwefelvulkanisaten wurde vor und nach Behandlung mit Triphenylphosphin, einem Reagens, das Polysulfidvernetzungen in Di- und Monosulfidvernetzungen umwandelt, untersucht. Eine solche Behandlung setzt die Geschwindigkeit der anaeroben Spannungsrelaxation herab und macht das Netzwerk dem Schutz gegen aerobe Spannungsrelaxation durch Zinkdibutyldithiocarbamat besser zugänglich. Die aerobe Spannungsrelaxation des Netzwerkes bleibt nach Behandlung mit Triphenylphosphin Autokatalysefrei, was für die Anwesenheit eines Antioxydans-Präcursors spricht; während der Alterung tritt weiterhin Vernetzung auf, ein Beweis, dass die Anwesenheit von Polysulfidgruppen nicht die alleinige Voraussetzung für eine solche Netzwerkbildung ist.

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