Effect of Organic Sulfur Compounds on the Autoxidation and Stress Relaxation of Peroxide Vulcanizates of Natural Rubber

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Synopsis

The effect of various sulfur compounds on the oxidizability and stress relaxation of peroxide vulcanizates of natural rubber has been investigated.   Many of the sulfur compounds reduce the rate of stress relaxation and oxygen absorption, but in general their inhibitory powers are considerably less than those observed when they are added to squalene.

The autoxidation of simple organic sulfur compounds has been previously investigated,[1-4] and more recently the effect of a wide variety of saturated and unsaturated mono- and disulfides and other organic sulfur compounds on the autoxidation of squalene has been reported.[5] These investigations were primarily carried out in order to elucidate the chemistry of the complex problem of the oxidative aging of sulfur vulcanizates of natural rubber (NR).   The compounds used in the earlier investigation represented the sulfidic crosslinks of a vulcanizate and the co-oxidation systems represented "model vulcanizates."   These studies showed that in both types of system autoxidation was very similar to olefin oxidation, in that it was a free radical chain process.   An important difference however was that monosulfide autoxidation was always autoinhibitive.[1] Detailed studies of the co-oxidation system showed that some of the sulfur compounds had a powerful inhibitory action which depended critically upon their structure, the actual inhibitors being the monooxidation products of the sulfides and disulfides.[5,6]

These findings indicated that the oxidizability of sulfur vulcanizates of NR could depend critically upon the structure of the sulfurated groups present, and that certain vulcanizates might contain "built-in" inhibitors.

This paper extends the former work to a model system which more closely resembles a sulfur vulcanizate of NR.   It reports the effect of some sulfur compounds on the autoxidation and stress relaxation characteristics of peroxide vulcanizates.

EXPERIMENTAL

Materials

Highly purified rubber (U.S. Rubber Co.) was extracted with hot ethyl acetate in a Soxhlet apparatus in nitrogen for 24 hr. and dried *in vacuo* before use.

Dicumyl peroxide was purified by precipitation from a chloroform solution by the addition of methanol.

The monosulfides, disulfides, sulfoxides, and thiolsulfinates were synthesized by standard methods previously described and were purified by fractional distillation or crystallization.[1,5] Immediately before use the sulfides were passed through a short column of alumina under nitrogen, after this treatment their purity was not less than 99% by gas–liquid chromatography.

Bis(2-hydroxy-3-tert-butyl-5-methyl phenyl)-methane was a commercial sample (Antioxidant 2246, American Cyanamid Co.).

Methods

Preparation of Vulcanizates. The purified rubber (100 parts) was compounded with dicumyl peroxide (3 parts) on a two-roll mill. Vulcanization in press molds (to give $10 \times 10 \times 0.02$ cm. sheets) was effected by heating at 140°C. for 45 min. The vulcanized sheets were continuously extracted with hot ethyl acetate in nitrogen for 24 hr., dried *in vacuo*, cut into strips (width 0.5 cm.) and stored *in vacuo*.

Incorporation of Additives. Additives were introduced by swelling the vulcanized strips for 20 hr. in ethyl acetate (10 ml.) containing the additive at the following concentrations: sulfide or disulfide, $0.3M$; sulfoxide or thiolsulfinate, $0.03M$; Antioxidant 2246, $0.003M$. The swollen strips were dried *in vacuo* at room temperature, and the amount of additive incorporated was estimated by weighing.

All percentages quoted in the tables or figures are mole per cent, i.e., moles of additive incorporated or combined per 100 isoprene units.

Measurement of Stress Relaxation and Oxygen Absorption. Experiments were carried out in duplicate at 75°C. and 700 mm. oxygen pressure, and the measurements were made with automatic instruments similar to those previously described.[7,8] The stress relaxation results are plotted as f/f_0 against time, where f_0 is the initial stress in the sample and f is the stress at time t. The oxygen absorption results are expressed as retardation ratios, this is the ratio of the times taken for 0.5% (w/w) of oxygen to be absorbed by the vulcanizate plus additive and by the pure vulcanizate respectively. The larger the ratio, the better the performance of the additive as a retarder of oxidation.

RESULTS AND DISCUSSION

Many saturated and unsaturated monosulfides reduce the oxidizability of peroxide vulcanizates (Table I); generally, however, the effects are not
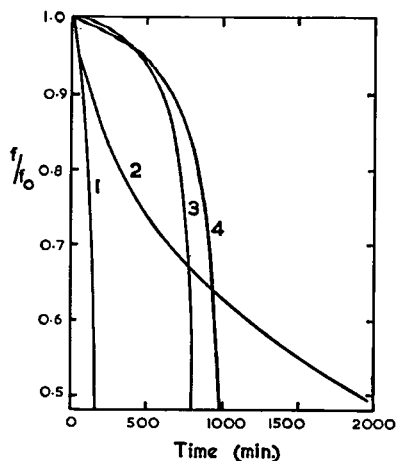
Fig. 1. Stress relaxation of a peroxide vulcanizate of NR containing saturated monosulfides (2.0 mole-%): (*1*) [Me·(CH$_2$)$_2$·CHPr^n]$_2$·S; (*2*) [Me·(CH$_2$)$_2$·CMeEt]$_2$·S; (*3*) Me·(CH$_2$)$_{10}$·S·CHMeEt; (*4*) Me·(CH$_2$)$_{10}$·S·Pr^n.
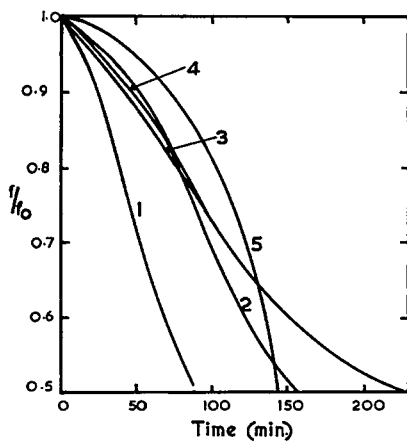

Fig. 2. Stress relaxation of a peroxide vulcanizate of NR containing unsaturated monosulfides (2.0 mole-%): (*1*) CMe$_2$:CH·CHMe·S·CH$_2$·CMe:CHEt; (*2*) (CMe$_2$:CH·CHMe)$_2$·S; (*3*) CMe$_2$:CH·CHMe·S·CMe$_2$Pr^n; (*4*) CMe$_2$:CH·CHMe·S·CHEtPr^i; (*5*) no addition.

so structurally dependent and are much smaller than those produced by these compounds when they are added to squalene.[5,6] Several of the monosulfides also reduce the rate of stress relaxation (Figs. 1 and 2) and di-tert-butyl sulfide, 1,3-dimethylbut-2-enyl 1,1-dimethylbutyl sulfide, and 1,3-dimethyl-but-2-enyl 1-ethyl, 2-methylpropyl sulfide, which are potent inhibitors for the autoxidation of squalene, give autoretardative stress relaxation curves instead of the usual autocatalytic type.

Tertiary disulfides cause larger effects than the monosulfides, since they markedly reduce oxidizability (Table II) and the rate of stress relaxation

TABLE I

Effect of Saturated and Unsaturated Monosulfides on the Autoxidation of a Peroxide Vulcanizate of NR

Sulfide (2.0 mole-%)	Retardation ratio
$[Me \cdot (CH_2)_2 \cdot CHPr^n]_2 \cdot S$	5.4
$[Me \cdot (CH_2)_2 \cdot CMeEt]_2 \cdot S$	13.7
$Me \cdot (CH_2)_{10} \cdot S \cdot CHMeEt$	25.1
$CMe_2 : CH \cdot CHMe \cdot S \cdot CH_2 \cdot CMe : CHEt$	0.4
$(CMe : CH \cdot CHMe)_2 \cdot S$	0.9
$CMe_2 : CH \cdot CHMe \cdot S \cdot CMe_2Pr^n$	8.0
$CMe_2 : CH \cdot CHMe \cdot S \cdot CHEtPr^i$	12.6

(Fig. 3). Primary and secondary disulfides, however, have lesser effect (Table II and Fig. 3). These results differ from those found for the addition of disulfides to squalene where the order of inhibitory activity is
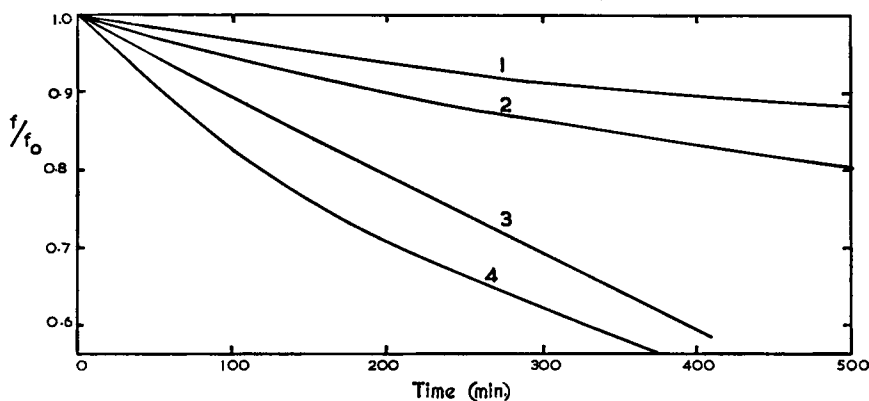

Fig. 3. Stress relaxation of a peroxide vulcanizate of NR containing saturated disulfides (2.0 mole-%): (1) $[Me \cdot (CH_2)_2 \cdot CMe_2S \cdot]_2$; (2) $[Me \cdot (CH_2)_2 \cdot CMeEtS \cdot]_2$; (3) $(Me_2 \cdot CH \cdot CHEtS \cdot)_2$; (4) $[Me \cdot (CH_2)_5 \cdot S \cdot]_2$.

primary > secondary > tertiary.[5] Since the true inhibitors are the corresponding thiolsulfinates and since tert-thiolsulfinates are the most potent,[5] this order depends solely upon the more rapid oxidation of the primary and secondary disulfides by squalene hydroperoxide. Hence, the reversed

TABLE II

Effect of Saturated Disulfides on the Autoxidation of a Peroxide Vulcanizate of NR

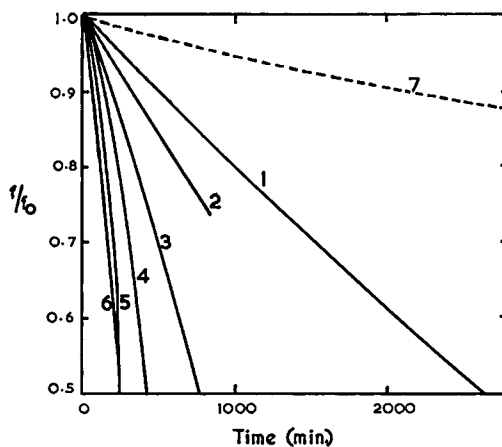| Sulfide (2.0 mole-%)	Retardation ratio
$[Me \cdot (CH_2)_2 \cdot CMe_2S \cdot]_2$	>70
$[Me \cdot (CH_2)_2 \cdot CMeEtS \cdot]_2$	>70
$(Me_2 \cdot CH \cdot CHEtS \cdot)_2$	7.5
$[Me \cdot (CH_2)_5 \cdot S \cdot]_2$	7.6

Fig. 4. Stress relaxation of a peroxide vulcanizate of NR containing sulphinyl compounds (0.2 mole-%): (1) $Bu^t \cdot SO \cdot Bu^t$; (2) $Bu^t \cdot SO \cdot S \cdot Bu^t$; (3) $Bu^t \cdot SO \cdot Pr^i$; (4) $Et \cdot SO \cdot Et$; (5) $Bu^t \cdot SO \cdot Et$; (6) $CMe_2 : CH \cdot CHMe \cdot SO \cdot Pr^i$; (7) Antioxidant 2246 (0.02 mole-%).

order of reactivity found when disulfides are added to peroxide vulcanizates is probably due to *tert*-thiolsulfinate being formed by reaction with hydroperoxide groups present in the vulcanizate (during the incorporation of the disulfide).

The effect of some sulfoxides and a thiolsulfinate is shown in Table III and Figure 4. These compounds had little effect upon oxidizability, although all with the exception of diethyl sulfoxide are potent antioxidants in squalene.[5,6] Di-*tert*-butyl sulfoxide and the thiolsulfinate, which were the most effective antioxidants, caused the greatest reduction in the rate of stress relaxation, but compared to conventional inhibitors their effect was small.

The reduced efficiency of the sulfur compounds as antioxidants and the leveling out of differences between them in the peroxide vulcanizates compared with squalene must be caused by the change from a liquid to a solid system. Apparently, if the sulfur compound is not in the vicinity of

TABLE III
Effect of Sulfoxides and Thiolsulfinates on the Autoxidation of a Peroxide Vulcanizate of NR

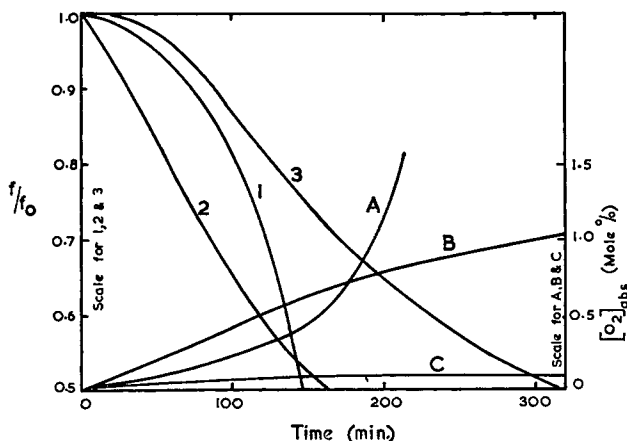| Additive (0.2 mole-%)	Retardation ratio
$Bu^t \cdot SO \cdot Bu^t$	9.2
$Bu^t \cdot SO \cdot S \cdot Bu^t$	10.8
$Bu^t \cdot SO \cdot Pr^i$	2.9
$Et \cdot SO \cdot Et$	2.8
$CMe_2 : CH \cdot CHMe \cdot SO \cdot Pr^i$	1.1
Antioxidant 2246 (0.02 mole %)	35.0

Fig. 5. Stress relaxation and oxygen absorption of a peroxide vulcanizate of NR containing the mono-adduct of 2,6-dimethylocta-2,6-diene and Me·CO·(CH₂)₂·SH (0.56 mole-%), and of the peroxide vulcanizate of a modified NR [0.37 mole-% of combined Me·CO·(CH₂)₂·SH]: (1) and (A) no addition; (2) and (B) modified NR; (3) and (C) adduct from 2,6-dimethylocta-2,6-diene and Me CO·(CH₂)₂·SH.

the hydroperoxide group in the solid system, then it is unlikely to diffuse there before the hydroperoxide has started fresh reaction chains, whereas in the liquid system the hydroperoxide is immediately complexed by the sulfoxide or thiolsulfinate and its free radical activity suppressed.[6] The importance of the mobility factor is demonstrated in Figure 5, which shows that when a ketosulfide is chemically combined with NR its efficiency as an inhibitor of oxidation or stress relaxation is much less than when the keto-sulfide is used as an additive.

The authors wish to thank Dr. B. R. Shephard for the preparation of the adduct of butan-3-one thiol and 2,6-dimethylhepta-2,6-diene, and the modified NR.

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Résumé

On a étudié l'effet de divers composés sulfurés sur l'oxydabilité et la rélaxation à la tension de divers produits vulcanisés au peroxyde de caoutchouc naturel. Beaucoup de composés sulfurés réduisent la vitesse de rélaxation de la tension et de l'absorption de l'oxygène; mais en général, leur pouvoir inhibiteur est beaucoup plus faible que celui observé quand on les ajoute au squalène.

Zusammenfassung

Der Einfluss verschiedener Schwefelverbindungen auf die oxydierbarkeit und Spannungsrelaxation von Naturkautschuk-Peroxydvulkanisaten wurde untersucht. Viele Schwefelverbindungen setzen die Geschwindigkeit der Spannungsrelaxation und Sauerstoffabsorption herab, im allgemeinen ist aber ihre inhibierende Wirkung beträchtlich geringer als bei ihrem Zusatz zu Squalen.