Oxidative Aging of Natural Rubber Vulcanizates. Part II. Effect of Vulcanizate Structure

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Synopsis

The oxidation characteristics of protected and unprotected vulcanizates from natural rubber have been examined. With unpurified rubber (RSS1) in the presence or absence of added antioxidants the rate of oxidation of the vulcanizates is: unaccelerated sulfur > accelerated sulfur > TMTD sulfurless or EV > peroxide. This order is obtained because the sulfur compounds present in the sulfurated vulcanizates are antagonistic towards both natural and added antioxidants. The antagonism is greatest with polysulfides, and when they are present they dominate the aging behavior of vulcanizates.

INTRODUCTION

Oxidative aging is important because the absorption of a small amount of oxygen (ca. 1%) by natural or synthetic rubber vulcanizates causes considerable changes in their physical properties,[1] e.g., with natural rubber, tensile strength falls by about 50%.

Rubber technologists have known for a long time that the aging behavior of sulfur vulcanizates differs considerably from that of peroxide vulcanizates and the base polymer and depends markedly on the type and degree of cure. Clearly, the combination of sulfur within the network or the formation of sulfur compounds which although not combined remain in the vulcanizate has a marked effect upon aging properties. These properties are also influenced by the natural inhibitors present in rubber made from field latex, by added conventional antioxidants, and by carbon black. As will be apparent later, these four entities do not necessarily act independently; in some cases specific effects are exerted by one type of ingredient upon the action of another, and it is complications like these which have made the overall character of vulcanizate oxidation so difficult to understand.

It is the purpose of this paper to elucidate the present confused state of knowledge, to account for the oxidation characteristics of both protected and unprotected vulcanizates, and to reveal the reasons for the poor response of accelerated sulfur vulcanizates to conventional antioxidants. The last problem is particularly important, because this type of vulcanizate, when compounded with carbon black, is of great industrial significance.

RESULTS AND DISCUSSION

Structure of Vulcanizates

Recent studies by Moore and co-workers have revealed many features of the chemical structure of gum vulcanizates made from RSS1.[2] Their data [3a,4] concerning the vulcanizates used in this investigation are summarized in Table I. Briefly, the structural features of the various networks are as follows. Unaccelerated sulfur networks are the most complex; the crosslinks are mainly alkenyl *tert*-alkyl polysulfides with some di- and monosulfides. Much of the combined sulfur is present as cyclic monosulfides since about 40–50 sulfur atoms are combined per crosslink; another modification of the main polyisoprene chains which occurs is the formation of conjugated dienes and trienes. Tetramethylthiuram disulfide (TMTD) sulfurless and efficient vulcanization (EV) networks are very similar and structurally much more simple; more than 90% of the crosslinks are monosulfide, and no polysulfides are present. Relative to the unaccelerated sulfur vulcanizate, much less sulfur is combined in the main chains as cyclic sulfides, and only small amounts of conjugated dienes and trienes are present. N-Cyclohexylbenzthiazole-2-sulfenamide (CBS)-accelerated sulfur networks are intermediate in complexity between those of the EV and the unaccelerated sulphur networks. At optimum crosslinking about 70% of the crosslinks are polysulfide and the remainder are mono- and disulfide in equal amounts; more cyclic monosulfides, conjugated dienes, and trienes are present than in the EV network. All the crosslinks in TMTD sulfurless, in EV, and in CBS-accelerated sulfur networks are dialkenyl mono-, di-, and polysulfides based on the structures A_1S-, A_2S-, B_1S-, and B_2S-, where
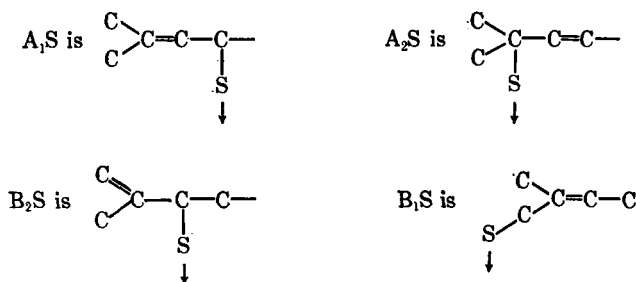
Dicumyl peroxide (peroxide) vulcanizates which are also used in the present investigation are structurally the most simple type of vulcanizate. Vulcanization with di-*tert*-butyl peroxide or dicumyl peroxide gives a network consisting of dialkenyl carbon carbon crosslinks, and some cyclic structures in the immediate vicinity of the crosslinks. Modification of the main chain at points distant from the crosslink is negligible.[2]

TABLE I
Structural Features of Sulfurated Networks

Type of vulcanizate	Combined sulfur in network, %	Chemical crosslinks, g.-mole/g. of rubber network × 10⁵			Sulfur not combined in the form of crosslinks, g.-mole/ g. of rubber, network × 10⁵
		Monosulfide crosslinks	Disulfide crosslinks	Polysulfide crosslinks	
TMTD sulfurless	0.35	3.3	—	—	8.6
EV	0.70	4.2	0.35	—	12.4
CBS-accelerated sulfur	2.08	0.85	0.82	3.6	21.7
High-modulus CBS-accelerated sulfur	3.01	1.27	1.23	5.4	32.5
ZDMC-accelerated high sulfur	2.27	—	—	6.05	—
Unaccelerated sulfur	5.57	1.0	1.0	3.44	146
Triphenylphosphine-treated CBS-accelerated sulfur	1.25	5.3	—	—	21.7

Effect of Sulfur Compounds and Other Additives on the Oxidation of Polyisoprenes

The co-oxidation of the hexaisoprene, squalene, and simple sulfur compounds (this mixture simulates a sulfurated vulcanizate) has been previously studied.[5-7] Compounds closely resembling the crosslinks present in sulfurated vulcanizates had an inhibitory effect on the autoxidation of squalene, and of these compounds the polysulfides were the most potent.[7] Cyclic monosulfides also have an inhibitory effect,[8] but conjugated dienes and trienes resembling other main-chain modifications present in sulfurated networks and the oxidation products of these dienes and trienes have a catalytic effect on the oxidation of squalene and peroxide vulcanizates.[8,9] It is important to note that the cyclic sulfides and the polysulfides are inhibitors, since these compounds have been said by other authors to catalyze the oxidation of peroxide vulcanizates.[10,11]

Aging Characteristics of Vulcanizates

Oxygen absorption measurements were carried out on unprotected and protected gum stocks from highly purified rubber and from RSS1, and also from the latter rubber in the presence of carbon black, all vulcanizates being extracted after cure.

All the networks made from purified natural rubber and which contained no added antioxidants oxidized rapidly, 1% of oxygen being absorbed in less than 100 min. (Fig. 1). The uptake-time curve for the peroxide network was autocatalytic, as found for simple 1,5-dienes and other nonconjugated olefins.[3b] The CBS-accelerated sulfur and the TMTD sulfurless networks initially oxidized more rapidly than the peroxide compound; this is presumably due to the catalytic effect of the conjugated
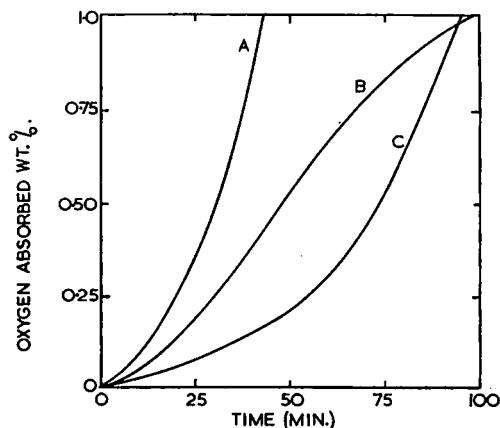

Fig. 1. Autoxidation of vulcanizates from purified natural rubber at 100°C. and 760 mm. oxygen pressure: (A) TMTD sulfurless; (B) CBS-accelerated sulfur; (C) peroxide.
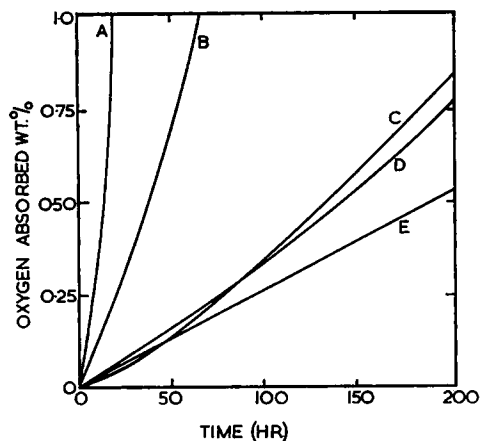
Fig. 2. Autoxidation of vulcanizates from RSS1 contaning N-isopropyl-N'-phenyl-p-phenylenediamine (1%) at 100°C. and 760 mm. oxygen pressure: (A) unaccelerated sulfur; (B) CBS-accelerated sulfur; (C) TMTD sulfurless; (D) EV; (E) peroxide.

dienes or trienes or their oxidation products which are present only in the sulfurated networks. After the absorption of about 0.5% of oxygen the autoxidation of the CBS-accelerated sulfur network was no longer autocatalytic and became slower than that of the peroxide network (Fig.1). This is due to the sulfurated structures, primarily the polysulfides exerting an inhibitory action when the catalytic effect of the conjugated dienes and trienes has been expended. The TMTD sulfurless network contains less conjugated dienes and trienes than the accelerated sulfur network, but since the sulfurated structures in the former have much weaker inhibitory properties (no polysulfides are present) its autoxidation continued to follow an autocatalytic course and was still faster than that of the peroxide network even after the absorption of 1% of oxygen (Fig. 1).

The results with the vulcanizates made from RSS1 (with and without added antioxidants) show that the rate of oxidation follows the order unaccelerated sulfur > accelerated sulfur > TMTD sulfurless or EV > peroxide (Figs. 2 and 3).

Other workers[1] have carried out oxygen absorption measurements on natural rubber vulcanizates made from pale crepe. The results differed from those given above only in that the unprotected TMTD sulfurless compound oxidized more slowly than the unprotected peroxide vulcanizate. This difference is not, however, in conflict with our results, because their vulcanizates were not extracted after cure, and unless the TMTD compound is extracted after cure it cannot be regarded as an unprotected vulcanizate, as it contains the antioxidant zinc dimethyldithiocarbamate produced *in situ* during vulcanization.[12,13]

The order of oxidizability of the unprotected RSS1 vulcanizates differs from that obtained with similar compounds from purified rubber, and,
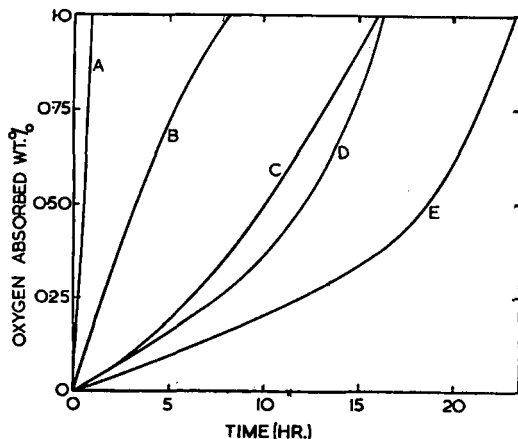
Fig. 3. Autoxidation of vulcanizates from RSS1 at 100°C. and 760 mm. oxygen pressure: (A) unaccelerated sulfur; (B) CBS-accelerated sulfur; (C) TMTD sulfurless; (D) EV; (E) peroxide.
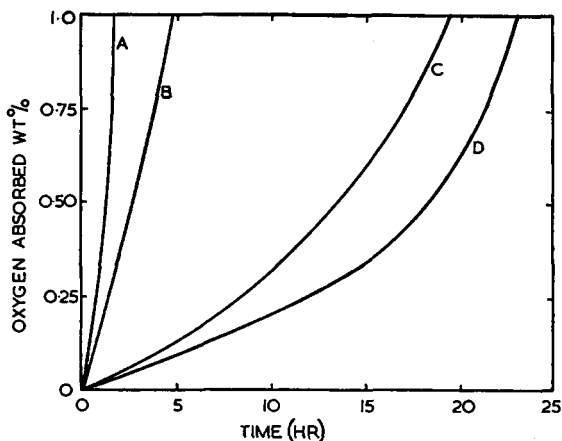

Fig. 4. Effect of $A_1S_2A_1$ (0.25 M) on the autoxidation of peroxide vulcanizates from purified natural rubber and RSS1 at 100°C. and 760 mm. oxygen pressure: (A) purified natural rubber, no addition; (B) purified natural rubber, $A_1S_3A_1$ added; (C) RSS1, $A_1S_3A_1$ added; (D) RSS1, no addition.

furthermore, the former vulcanizates differ much more from each other than do those made from purified rubber (cf. Figs. 1 and 3).

Obviously factors other than the simple competitive catalytic-inhibitory effects of the conjugated dienes, trienes, and sulfurated groups, respectively, are needed to explain these observations. An informative result was obtained when a trisulfide ($A_1S_3A_1$) was added to peroxide vulcanizates from purified rubber and from RSS1, respectively (Fig. 4). The large difference in the rates of oxidation of the two peroxide compounds (in the absence of $A_1S_3A_1$) is due to natural inhibitors present in the RSS1 vulcan-
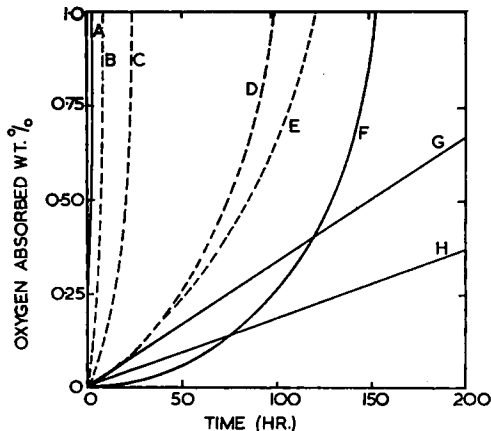
Fig. 5. Effect of $A_1S_2A_1$ (0.25M) and conventional antioxidants (1%) on the autoxidation of peroxide vulcanizates from purified natural rubber at 100°C. and 760 mm. oxygen pressure: (A) no addition; (B) $A_1S_3A_1$ added; (C) cadmium dithiocarbamate and $A_1S_3A_1$ added; (D) 2,2'-methylenebis-4-methyl-6-*tert*-butylphenol and $A_1S_3A_1$ added; (E) N-isopropyl-N'-phenyl-p-phenylenediamine and $A_1S_3A_1$ added; (F) cadmium dithiocarbamate added; (G) N-isopropyl-N'-phenyl-p-phenylenediamine added; (H) 2,2'-methylenebis-4-methyl-6-*tert*-butylphenol added.
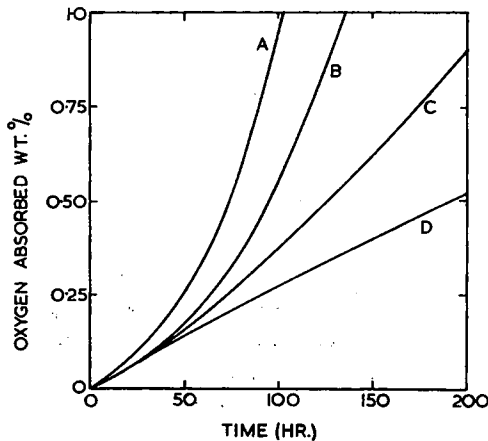

Fig. 6. Effect of sulfur compounds (at the same sulfur concentration) on the autoxidation of peroxide vulcanizates from RSS1 containing N-isopropyl-N'-phenyl-p-phenylenediamine (1%) at 100°C. and 760 mm. oxygen pressure: (A) $B_1S_3B_1$ (0.25M) added; (B) $A_1S_3A_1$ (0.25M) added; (C) A_1SA_1 (0.75M) added; (D) no addition or di-n-hexyltrisulfide (0.25M) added.

izate, even though it has been extracted after cure. In the purified rubber network the trisulfide acted as an antioxidant just as it does in squalene,[7] but in the RSS1 vulcanizate it caused an acceleration of the oxidation. Furthermore in peroxide vulcanizates made from purified rubber or RSS1 containing conventional antioxidants it caused a marked acceleration of the oxidation (Figs. 5 and 6). Clearly the trisulfide reduces the effi-
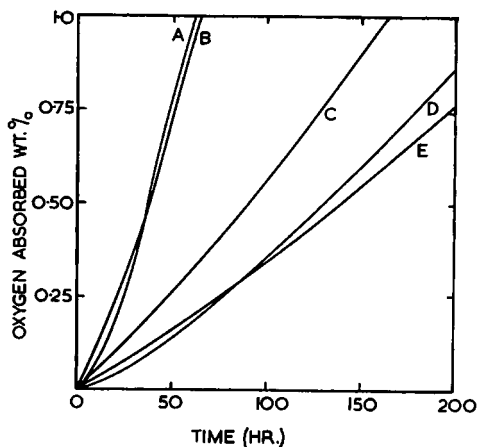
Fig. 7. Effect of triphenylphosphine on the autoxidation of a CBS-accelerated sulfur vulcanizate from RSS1 containing N-isopropyl-N'-phenyl-p-phenylene-diamine (1%) at 100°C. and 760 mm. oxygen pressure: (A) CBS-accelerated sulfur vulcanizate, triphenyl phosphine-treated, and A₁S₃A₁ (0.16M) added; (B) CBS-accelerated sulfur vulcanizate; (C) CBS-accelerated sulfur vulcanizate, triphenylphosphine-treated; (D) EV vulcanizate; (E) TMTD sulfurless vulcanizate.

ciency of both conventional and natural antioxidants, even though it is itself an antioxidant. This effect occurred with all the conventional antioxidants which were examined and with both A and B types of trisulfides, but a saturated trisulfide was inert (Figs. 5 and 6). Antagonism towards conventional antioxidants also occurs but to a much lesser extent with the A₁ monosulfide (Fig. 6); presumably unsaturated cyclic sulphides also show this activity, although these compounds have not yet been examined.

Further evidence of the importance of polysulfides in reducing the efficiency of conventional antioxidants was forthcoming when a CBS-accelerated sulfur vulcanizate from RSS1 was treated with triphenyl phosphine. The function of this reagent is to convert all the di- and polysulfides into monosulfides without affecting the cyclic monosulfides and conjugated dienes and trienes also present in the vulcanizate.[14] After such treatment the oxidation of the CBS-accelerated sulfur vulcanizate was similar to that of the TMTD sulfurless and EV compounds (Fig. 7). Its somewhat higher rate of oxidation is no doubt due to its greater conjugated diene and triene content and to its higher concentration of cyclic sulfides, which probably exert a weak antagonistic effect towards the conventional antioxidant. Addition of the A₁ trisulfide to the triphenyl-phosphine-treated compound increased its rate of oxidation so that it was now very similar to that of the original CBS-accelerated sulfur vulcanizate. Vulcanizates containing higher concentrations of polysulfides than the normal CBS-accelerated sulphur vulcanizate, such as the high-modulus CBS-accelerated sulfur and the high-sulfur zinc dimethyldi-
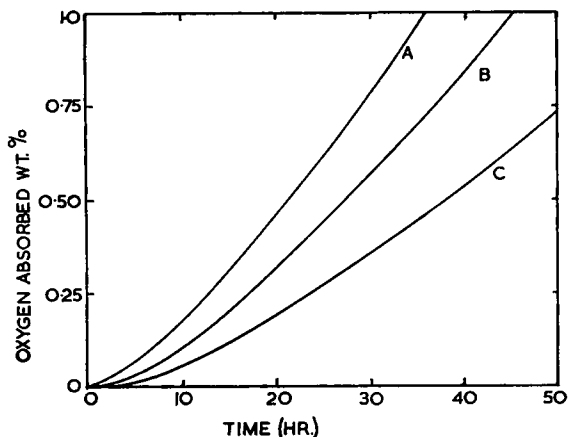
Fig. 8. Effect of polysulfide concentration on the autoxidation of vulcanizates from RSS1 containing N-isopropyl-N'-phenyl-p-phenylene-diamine (1%) at 100°C. and 760 mm. oxygen pressure: (A) ZDMC-accelerated high sulfur, (B) high-modulus CBS-accelerated sulfur; (C) CBS-accelerated sulfur.

thiocarbamate (ZDMC) compounds (Table I) oxidized even faster (Fig. 8), the last compound being the fastest even though it had a lower sulfur content than that of the high-modulus CBS-accelerated sulphur compound. This shows in agreement with the relative effects of $A_1S_3A_1$ and A_1SA_1 on peroxide vulcanizates (Fig. 6) that polysulfides have a much greater effect on the rate of oxidation of protected vulcanizates than do the other forms of combined sulfur.

The difference between TMTD sulfurless or EV compounds and peroxide vulcanizates from RSS1 (in the presence or absence of conventional antioxidants) can be explained as follows. The faster rate of oxidation

TABLE II

Effect of Carbon Black on the Time for RSS1 Vulcanizates
to Absorb 0.5% of Oxygen at 100°C. and 760 mm. Oxygen Pressure

	Time, hr.			
	Pure gum		Black-filled	
Type of vulcanizate	No addition	N-Isopropyl-N'-phenyl-p-phenylene-diamine (1%) added	No addition	N-Isopropyl-N'-phenyl-p-phenylene-diamine (1%) added
Peroxide	18	190	28	116
EV	12.5	130	23	53
CBS-accelerated sulfur	3.2	37	3.5	27
Unaccelerated sulfur	0.4	11	0.5	10.5

of the sulfurated vulcanizates is due to catalysis by the conjugated dienes and trienes and also to a weak antagonism exerted by the unsaturated monosulfide structures towards the conventional and natural antioxidants.

Effect of Carbon Black

With vulcanizates from RSS1 which were extracted after cure and which contained no added antioxidant, carbon black acted as a weak inhibitor, reducing the rate of oxidation of peroxide and EV compounds about twofold and having less effect upon unaccelerated and accelerated sulfur compounds (Table II). In the presence of N-isopropyl-N'-phenyl-p-phenylenediamine, carbon black accelerated the rate of oxidation, the extent of the acceleration decreasing through the series peroxide, EV, CBS-accelerated sulfur, and unaccelerated sulfur vulcanizates (Table II).

In general the effect of carbon black on oxidation is small compared to that of antioxidants, and the above results agree with those of other workers.[15-17] Further studies are required however before an explanation can be given for the complex behavior of carbon black.

EXPERIMENTAL

Preparation of Vulcanizates

All vulcanizates were made from either a single bale of Yellow Circle ribbed smoked sheet, grade 1 (RSS1), or from highly purified natural rubber (U.S. Rubber Co.) according to the recipes given in Table III. The black-filled stocks were prepared from a master batch mixed in a 1-lb. laboratory size Banbury. The vulcanizates were prepared in a chromium-plated mold to give sheets $10 \times 10 \times 0.03$ cm. and extracted in a Soxhlet apparatus, first with cold chloroform–acetone–methanol azeotrope for 24 hr. followed by a further 24 hr. with hot azeotrope. The sheets were dried overnight *in vacuo* (<0.1 mm.) and stored at $-20°$C.

Preparation of Additives

N - Isopropyl - N' - phenyl - p - phenylenediamine, 2,2' - methylenebis-4-methyl-6-*tert*-butylphenol and phenyl-β-naphthylamine were purified by crystallization from methanol. Cadmium dibutyldithiocarbamate was prepared by Dr. B. Saville from cadmium chloride and sodium dibutyldithiocarbamate. The A_1 and B_1 trisulfides and A_1SA_1 were prepared by Mr. M. E. Cain by methods previously described.[18-21]

Incorporation of Additives

The vulcanizates were immersed in ethyl acetate solutions of the additives and allowed to stand for 16 hr. under nitrogen; the solvent was removed *in vacuo*. The concentration of N-isopropyl-N'-phenyl-p-phenylenediamine in the vulcanizates was determined by extraction in the dark with an excess of chloroform, followed by estimation of its concen-

TABLE III
Vulcanization Recipes

Ingredient	CBS-accelerated sulfur	High-modulus CBS-accelerated sulfur	Unaccelerated sulfur	EV	TMTD sulfurless	ZDMC-accelerated high sulfur	Peroxide
Natural rubber[a]	100	100	100	100	100	100	100
ZnO	5.0	5.0	5	5.0	5.0	4.0	—
Lauric acid	0.7	1.0	—	1.0	1.5	—	—
Sulfur	2.5	3.7	10	0.4	—	6.0	—
CBS	0.6	0.9	—	6.0	—	—	—
TMTD	—	—	—	—	4.0	—	—
ZDMC	—	—	—	—	—	4.0	—
Dicumyl peroxide	—	—	—	—	—	—	2.2 or 2.6[b]
Cure time at 140°C.	40 min.	40 min.	7 hr.	2 hr.	7 hr.	15 min. at 100°C.	10 min. at 100°C. then 50 min. at 150°C.
Black stock[b]	30 min.	—	7 hr.	2 hr.	—	—	as above

[a] RSS1 or highly purified natural rubber (U.S. Rubber Co.) was used as appropriate.
[b] Also contains 50 parts of Philblack O, an HAF black.

tration in the chloroform solution from its absorption at 290 mμ. By suitable adjustment of the concentration of the antioxidant in the ethyl acetate a concentration of 1% in the vulcanizate could be achieved. The amounts of the sulfur compounds added were calculated from the increase found in the total sulfur contents of the vulcanizates. The antioxidants described in Figure 5 were swollen into the vulcanizates from 1% solutions in ethyl acetate. Where two compounds were added they were swollen in together.

Treatment with Triphenyl Phosphine

After preswelling in sodium-dried benzene, the vulcanized sheets were immersed in a solution of triphenylphosphine (ca. 3 g. in 60 ml. of sodium-dried benzene) for 16 hr. The benzene was then removed *in vacuo* at room temperature, and the dry vulcanizates heated *in vacuo* for 72 hr. at 80°C. The treated vulcanizates were freed from triphenylphosphine and its sulfide by continuous extraction with cold benzene for 24 hr. under nitrogen.[14]

Oxygen Absorption

The apparatus used for measurement of oxygen absorption was similar to that described by Shelton and McDonel.[22] To avoid contamination of the apparatus the vulcanized sheets were laid on aluminum foil and were oxidized in 4 × 1 in. specimen tubes. The aluminum foil had no effect on the oxidation of the vulcanizates.

CONCLUSION

Parkes and Lorenz[10] have previously studied the effect of network structure on aging.   Their data for diphenylguanidine-accelerated sulfur, efficient mercaptobenzothiazole sulfur, and peroxide vulcanizates, protected by phenyl-β-naphthylamine, are respectively almost identical with that obtained by us for CBS-accelerated sulfur, EV and peroxide vulcanizates protected by N-isopropyl-N'-phenyl-p-phenylenediamine (Fig. 2). Their interpretation of their results was that polysulfides and cyclic sulfides were responsible for the faster rate of oxidation of sulfurated vulcanizates, because the polysulfides underwent homolytic cleavage giving perthiyl radicals which acted as oxidation initiators, and that the cyclic sulfides provided activated hydrogen atoms which were susceptible to oxidation.

Our results however lead to the following different conclusions. In unprotected systems, polysulfides and cyclic sulfides inhibit oxidation and in protected systems they accelerate oxidation; this indicates that the acceleration is due to antagonism between the sulfur compounds and the other antioxidants.   Furthermore, when unsaturated polysulfides are present, they are the dominating factor in determining the oxidation characteristics of the vulcanizate, since their antagonistic effect is much

greater than that of other sulfur compounds. The lack of antagonism between saturated polysulfides and conventional antioxidants, suggests that a vulcanizate in which the polysulfide crosslinks are saturated, would have good aging properties comparable to those of a peroxide vulcanizate.

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Résumé

Les caractéristiques d'oxydation de vulcanisats protégés et non-protégés provenant du caoutchouc naturel ont été examinées. Pour le caoutchouc non purifié (RSS1) en présence ou en absence d'antioxydants, la vitesse d'oxydation des vulcanisats est: soufre non accéléré > soufre accéléré > TMTD sans soufre ou E.V. > peroxyde. Cet ordre provient du fait que les composés du soufre, présents dans les vulcanisats sulfurés ont une réaction antagoniste à l'égard des antioxydants naturels et ajoutés. L'antagonisme est le plus grand dans le cas des polysulfures, et lorsque ceuxci sont présents ils déterminent le comportement au vieillissement des vulcanisats.

Zusammenfassung

Das Oxydationsverhalten geschützter und ungeschützter Naturkautschukvulkanisate wurde untersucht. Bei ungereinigtem Kautschuk besteht in Gegenwart oder Abwesenheit zugesetzter Antioxydantien folgende Reihenfolge der Oxydationsgeschwindigkeit der Vulkanisate: Schwefel ohne Beschleuniger > Schwefel mit Beschleuniger > TMTD schwefelfrei oder E.V. > Peroxyd. Diese Reihenfolge wird deshalb erhalten, weil die in schwefelhältigen Vulkanisaten vorhandenen Schwefelverbindungen sich gegen natürliche und zugesetzte Antioxydantien antagonistisch verhalten. Der Antagonismus ist bei Polysulfiden am stärksten; falls sie vorhanden sind, spielen sie eine dominierende Rolle für das Alterungsverhalten der Vulkanisate.