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Aging of SBR. II*

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Synopsis

Comparison of aging of a sulfur vulcanizate with a control having stable crosslinks, shows that oxygen affects reactions of the crosslink as well as of the hydrocarbon. Crosslink scission is inhibited. Results are in agreement with an earlier suggestion that new crosslinking is enhanced by oxygen, although less than observed for natural rubber. This may be an effect of carbon black and amine antioxidants present in the vulcanizates.

In a recent review[2] is was suggested that effects of oxygen on crosslinks in sulfur vulcanizates could be detected by analysis of changes in stress–strain properties during aging. This report illustrates application of the analysis to an SBR vulcanizate.

Although vulcanized rubber contains a complex mixture of structural features, each of which may contribute to aging,[3,4] to a good approximation reactions which occur during thermal aging of sulfur vulcanizates may be divided conveniently into those involving the hydrocarbon chain and those involving crosslinks. There will be both purely thermal reactions and those involving oxygen. The relative importance of each depends on polymer, nature of the vulcanizing system, and external conditions, but in ordinary vulcanizates both will occur at moderate temperatures. Division in this way leads to the summary in Table I,[2] in which occurrence of each kind of reaction is illustrated, so far as it has been reported for SBR.

ANALYSIS

If modulus M and stress S at constant strain are determined as a function of extent of oxidation during aging, then $[1 - (S/S_0)]$ is a direct measure of scission and $[(M/M_0) - (S/S_0)]$ of crosslinking.

These can be analyzed into contributions from the sources indicated in Table I by Greek letters in the following way.

Oxidative reactions *in vacuo* are negligible, or, $\gamma = \delta = \sigma = \rho = 0$.

Therefore

$$1 - (S/S_0) = \alpha$$

* For part I see Reference 1. Presented at a meeting of the Division of Rubber Chemistry, American Chemical Society, San Francisco, California, May 3-6, 1966.

TABLE I
Reactions During Aging on SBR Accelerated Sulfur Vulcanizate[a]

Affected portion	Thermal		Oxidative	
	Scission	Crosslinking	Scission	Crosslinking
Hydrocarbon	Negligible[b]	Negligible[b]	Occurs (σ)	Occurs (ρ)
Crosslinks	Occurs (α)	Occurs (β)	[c] (γ)	? (δ)

[a] Greek letters represent the extent to which each reaction occurs as a fraction of the original network chain density in the vulcanizate.
[b] At temperatures below 200°C.
[c] Molecular oxygen has been reported to inhibit crosslink scission in natural rubber,[5,6] SBR,[1] and EPT[2] under certain conditions.

and (1)

$$(M/M_0) - (S/S_0) = \beta$$

In an atmosphere containing oxygen, for a control vulcanizate which has thermally stable crosslinks, $\alpha = \beta = \gamma = \delta = 0$ and

$$1 - (S/S_0) = \sigma$$

(2)

$$(M/M_0) - (S/S_0) = \rho$$

For the sulfur vulcanizate in oxygen

$$\gamma = 1 - (S/S_0) - (\alpha + \sigma)$$

and (3)

$$\delta = (M/M_0) - (S/S_0) - (\beta + \rho)$$

Values of σ and ρ must be correlated with extent of oxidation, values of α and β with time. Values of α and β used in eqs. (3), therefore, will be chosen at the times required to obtain values of σ and ρ used there.

Evidence that hydrocarbon oxidation in natural rubber proceeds by a mechanism independent of the presence or absence of crosslinks, as assumed here, has been reviewed.[2,7] Direct evidence is not available for any other polymer, but it is a reasonable assumption for SBR. Scission and crosslinking of the polymer chain occur at approximately the same rate during oxidation of unvulcanized rubber.[8]

EXPERIMENTAL

General

Commercial polymers were compounded and cured by standard laboratory procedures. Masterbatches were mixed in a Banbury B mixer in 8-min. cycles, dumping at 150°C. Vulcanizing ingredients were added on a mill at 65–75°C. Samples used for oxidation measurements alone were vulcanized in sheets 0.008–0.010 in. thick.[7] Samples used for stress relaxation and modulus increase measurements were vulcanized 0.04 in. thick.

For continuous stress relaxation T-50 test pieces were died from cured slabs. Extensions during relaxation were in the range 20–30%. Within experimental error the rate of relaxation is independent of extension up to the capacity of the apparatus used. Samples were extended, relaxed two hours at room temperature, then placed in the aging block. Stress was measured with Dynisco strain gages and recorded with a Daystrom multiple-point recorder. A slow stream of gas was passed through the apparatus during aging. Oxygen, air, or argon was used to provide the atmosphere desired.

Intermittent stress–strain measurements were made on samples used for oxygen absorption measurements or samples aged *in vacuo*. Pieces 2 in. × 6 in. were cut from slabs and aged in oxygen, in air, or sealed *in vacuo;* oxygen consumed was measured in those samples exposed to oxygen or air. Ring test pieces were died from the aged samples for autographic stress–strain measurements as described by Brooks et al.[9] Stress at 100% elongation was used as a measure of relative crosslinking.

Samples were aged up to 24 hr. at 130°C., but it was necessary to estimate oxygen absorbed at times longer than 9 hr. because of the high rate of oxidation of B720 samples.

Vulcanizate

Composition of the experimental sulfur vulcanizate, B720, whose aging behavior was to be examined, is given in Table II along with those of three possible controls which are expected to have stable crosslinks. The crosslinks in the peroxide vulcanizate, B721, are carbon-to-carbon bonds, in the TMTD vulcanizate, B722, short, stable sulfur links. The last composition, B723, is the same as the first except for the time of cure. Prolonged cure

TABLE II
Composition of Vulcanizates

	B720	B721	B722	B723
Masterbatch[a]	135	135	135	135
Stearic acid	1	—	—	—
CBS[b]	0.8	—	—	0.8
Sulfur	2.5	—	—	2.5
TMTD[c]	—	—	5.0	—
Cumyl peroxide[d]	—	0.8	—	—
Vulcanization				
Time, hr.	1.25	2.5	2	17
Temp., °C.	145	150	145	145

[a] Masterbatch: SBR 1500, 100 parts; FEF, 30 parts; zinc oxide, 5 parts.
[b] *N*-Cyclohexyl-2-benzothiazolesulfenamide.
[c] Bis(dimethylthiocarbamoyl) disulfide.
[d] As 40% dispersion on calcium carbonate.

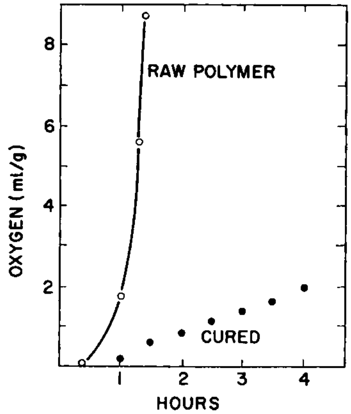

Fig. 1. Effect of vulcanization with cumyl peroxide on rate of oxidation of SBR 1500 after extraction: (O) raw polymer; (●) vulcanized with peroxide before extraction. Oxidized in oxygen at 130°C.

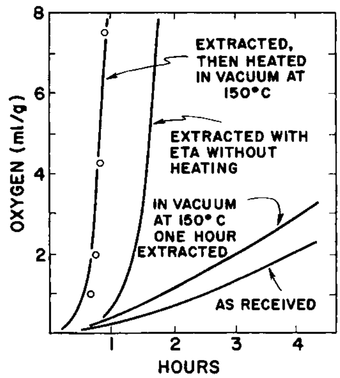

Fig. 2. Effect of various treatments on initial rate of oxidation of SBR 1500 in oxygen at 130°C.: (——) raw polymer treated as indicated; (O) sample vulcanized at −80°C. by irradiation, but not heated before extraction.

shortens crosslinks and gives stability approaching that of the other two vulcanizates.[1]

Carbon black was added to increase tear strength of the vulcanizates so that intermittent measurements could be made on aged samples. Maisey and Scanlan[10] have shown this should not obscure interpretation of chemical stress relaxation. Physical relaxation involving the filler is negligible compared with effects to be measured.

Use of SBR 1500 and of carbon black in this experiment make it difficult to assess effects of antioxidant. Antioxidants present during vulcanization may become extremely difficult to remove by extraction afterward; there is some suggestion that they may affect the nature of changes involving crosslinks during aging. We have had erratic results with SBR containing amine antioxidants. One set of experiments is illustrated in Figures 1 and

2. In Figure 1 the rate of oxidation of SBR 1500 vulcanized with cumyl peroxide, then extracted with acetone, is compared with that of extracted raw polymer. There is no obvious reason why the vulcanizate should absorb oxygen so much more slowly than raw polymer unless it contains inhibitor. The experiment illustrated in Figure 2 suggests that the inhibition comes from some reaction occurring during heating of the polymer, not necessarily related to vulcanization.[11,12] This effect may have occurred in the samples used in this work. This, or the antioxidant effect of carbon black itself, may account for the small effect of extraction of vulcanizates on net crosslinking reported here, compared with that reported by Maisey and Scanlan[13] for natural rubber.

RESULTS

Oxidation Rate

The rate of oxygen absorption of the sulfur vulcanizate of Table III is compared with that of the potential "controls" in Figures 3 and 4. Only the stabilized vulcanizate, B723, absorbed oxygen at a rate near enough to that of the experimental vulcanizate, B720, to permit comparisons at the same extent of oxidation, from measurements made over short experimental periods. Even with it some extrapolation is required. However, it has the advantage as a control that noncrosslinking modifications of the polymer are nearly the same as those of the experimental vulcanizate, B720.

Scission

Stress relaxation of the sulfur vulcanizate, B720, and of the control, B723, vulcanized 17 hr. at 140°C. are compared in Figure 5. Relative net

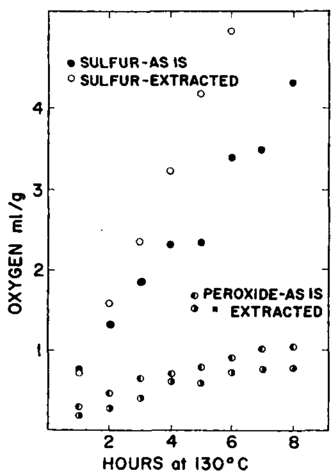

Fig. 3. Oxidation of sulfur and peroxide vulcanizates of Table II as cured and after 48 hr. extraction with cold benzene.

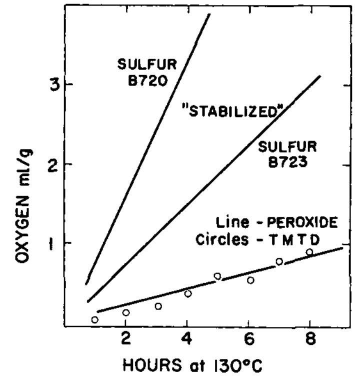

Fig. 4. Oxidation of vulcanizates of Table II, all extracted with cold benzene 48 hr. before oxidation.

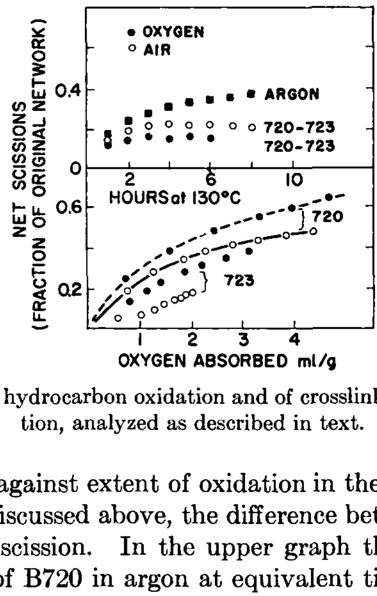

Fig. 5. Contributions of hydrocarbon oxidation and of crosslink scission to stress relaxation, analyzed as described in text.

scissions are plotted against extent of oxidation in the bottom graph. For oxidation alone, as discussed above, the difference between B720 and B723 represents crosslink scission. In the upper graph this difference is compared with scission of B720 in argon at equivalent times. The difference indicates inhibition of crosslink scission by oxygen, as has been reported at lower temperatures for natural rubber[5,6] and SBR.[1,2]

Crosslinking

In Figure 6 net crosslinking of B720 in air is compared with crosslinking in vacuum and with crosslinking of the same vulcanizate after extraction with benzene. These results, like those of Maisey and Scanlan[13] for natural rubber, show that oxygen contributes to crosslinking, but more detailed analysis is required to distinguish in SBR between crosslinking involving hydrocarbon oxidation and that involving existing crosslinks.

In Figure 7 net crosslinking of sulfur vulcanizate and of control are plotted against extent of oxidation. Differences between the two represent

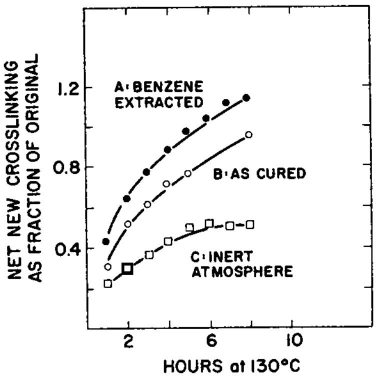

Fig. 6. Net new crosslinking of sulfur vulcanizate B720 after aging, showing contribution of oxygen to crosslinking. A and B aged in air.

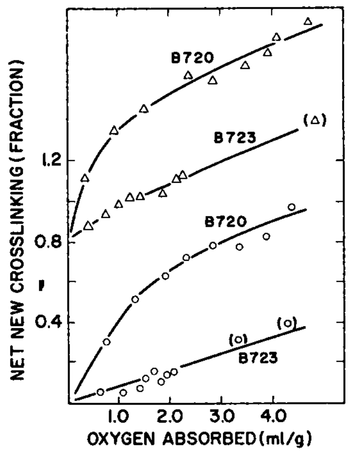

Fig. 7. Derivation of net new crosslinking arising from existing crosslinks: (lower pair) as vulcanized; (upper pair) after extraction and reinfusion of antioxidant. B720: short cure; B723: stabilized by long cure.

new crosslinks derived from existing crosslinks. The reproducibility is indicated by comparison of the upper and lower sets of curves, which apply to the original vulcanizates as cured (lower) and the same vulcanizates aged after extraction with benzene and readdition of antioxidant (*N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine) by infusion. Comparison of oxidation in air and in oxygen indicates that new crosslinking derived from existing crosslinks is relatively insensitive to the rate of oxidation, as was suggested earlier.[1,2] Figure 8, however, supports the suggestion[1,13] that oxygen has an effect on new crosslinking. In this figure the same analysis is applied to crosslinking as was applied in Figure 5 to scission. Solid lines are smoothed curves of net crosslinking in an inert atmosphere. Experimental points are the excess of crosslinking in air of sulfur vulcaniz-

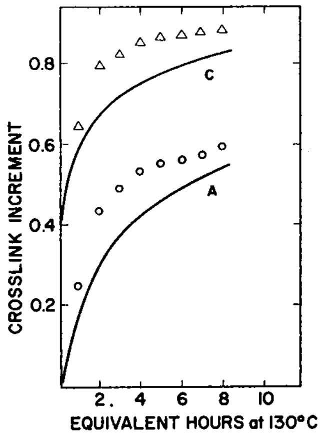

Fig. 8. Apparent increment in new crosslinking from existing crosslinks caused by the presence of oxygen in the atmosphere. A (lower) and C (upper) as in Figure 7.

ate B720 over that of the "control" B723. The difference represents the contribution of oxygen to new crosslinking formed from existing crosslinks.

These results demonstrate the applicability of the analysis outlined,[2] but certain precautions are required in their interpretation. Because of approximations discussed earlier, only qualitative significance can be attributed to the data reported although they are in full agreement with inferences from earlier work.

For this analysis it has been assumed that new crosslinks are derived from existing crosslinks. There is no direct evidence on this point; the work of Parks and Lorenz[14] has been shown to lead to the inference that other, noncrosslinking, sulfur moieties formed during vulcanization are involved in oxidative crosslinking of natural rubber. The same may be true in SBR, but the choice of control could obscure this in the present work.

The effects described here occur during the "recovery" observed by Bueche[15] in his studies of the Mullins effect, and may fully account for them. All measurements made in this work were without initial prestressing, which produces no detectable changes in network density as determined by swelling.[16]

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Résumé

La comparaison du veillissement de vulcanisats au soufre avec un échantillon contrôle contenant des ponts stables montre que l'oxygène affecte les réactions de pontage aussi bien que l'hydrocarbure lui-même. La cassure du pont est inhibée. Les résultats sont en accord avec une suggestion antérieure suivant laquelle la formation de ponts nouveaux est facilitée par la présence d'oxygène bien que d'une façon moindre que dans le cas du caoutchouc naturel. Ceci peut être un effet du noir de carbone et des anti-oxydants aminés présents au sein des vulcanisats.

Zusammenfassung

Ein Vergleich der Alterung eines Schwefelvulkanisats mit einer Kontrollprobe mit stabilen Vernetzungen zeigt, dass Sauerstoff sowohl die Reaktionen der Vernetzung als auch die des Kohlenwasserstoffs beeinflusst. Die Spaltung der Vernetzungsstellen wird inhibiert. Die Ergebnisse stimmen mit einer früher gemachten Annahme überein, dass Sauerstoff die Vernetzung fördert, obleich in geringerem Ausmass als es bei Naturkautschuk beobachtet wurde. Dies kann auf den Einfluss von in den Vulkanisaten vorhandenem Russ und Aminantioxydantien zurückzuführen sein.

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