

The Ozone Attack on Swollen Elastomeric Networks

R. L. ZAPP and J. H. PEERY,* *Enjay Polymer Laboratories,
Linden, New Jersey*

INTRODUCTION

In recent years, a part of the research on the ozone attack of elastomers has been directed toward explaining the differences in vulnerability between elastomer systems. This interest has been kindled by the increasing variety of low-functionality elastomers which embody only the necessary minimum of reactive sites for crosslinking. Butyl rubber, one of the early low-functionality rubbers has been studied extensively by Buckley and Robison.¹ They characterized ozone attack on extended specimens as a work change manifested by a decrease in stress and increase in length as ozone cracking occurred. This work change was related to the generation of new surfaces as cracks. Rate of ozone attack was related to the original unsaturation as well as to the state of cure or degree of crosslinking. For a given unsaturation level the more reactive sites that were tied up in crosslinks, the lower would be the cracking rate. This was attributed to a steric shielding of the double bond area as well as an immobilization of that area by crosslinking.

Braden and Gent,²⁻⁵ in their studies of the propagation rate of a single crack, suggested that the mechanism was controlled by the rate at which severed molecular ends moved apart to expose new surfaces. Thus it was suggested that the ozone resistance of butyl was due to its higher hysteresis. Tucker⁶ also suggested breaking or separating of the ozonized surface layer as a necessary function for crack growth. In the unstretched state the ozonized layer would act in the same way as a protective oxide film in metal technology.

To further study the attack of ozone on vulcanized rubbers, use was made of networks swollen in a solvent. In a network whose volume may be expanded several hundred per cent by the swelling solvent, the individual molecular chains are under an internal extension. Ozone cleavage at a vulnerable site should remove the strained segment as a soluble fragment, immediately revealing a new surface segment for attack. Swollen networks are almost perfectly elastic,⁷ so hysteretic effects would have no influence on the results.

The technique utilizing swollen networks was devised to emphasize the attack by ozone at the individual reactive site and to observe what effect the type of crosslink had upon the rate of attack. Further, the protection

* Present address: Esso Production Research, Houston, Texas.

or alteration of the reactive site by various methods of crosslinking should be readily observed. For elastomers of low functionality this would be a unique way (when compared to highly unsaturated rubbers) to improve ozone resistance. With elastomers of low functionality all the reactive sites could be protected or "saturated" without radically changing the nature of the network. This technique would be impossible with highly unsaturated rubbers.

EXPERIMENTAL

Ozone was produced by passing dry air through a Welsbach ozonator. This machine produces a constant concentration of ozone at a given flow rate, pressure, voltage, and cooling-water temperature.

The reactor system consisted of a closed 250-ml glass container equipped with a fritted glass gas inlet extending below the surface of the liquid, an outlet above the liquid surface, and a wire hook on which to suspend the rubber sample. A swollen vulcanizate sample was suspended in the solvent and the ozonized air was bubbled through the solvent in such a way that the

TABLE I
Operating Conditions

Ozone concentration	5400 ppm
Gas flow rate	200 cc/min
Pressure	2 psi
Voltage	45 V
Solvent	200 ml of CCl ₄
Temperature	25°C

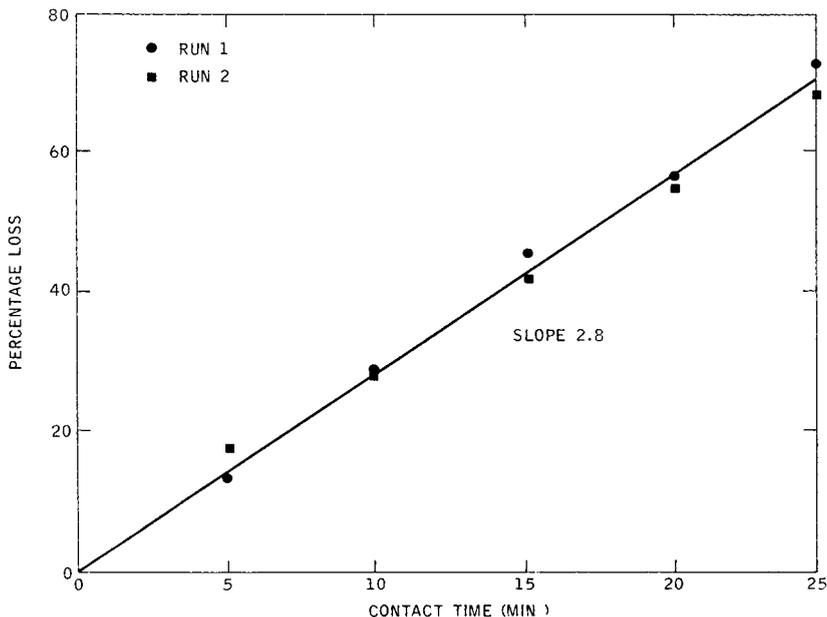


Fig. 1. Ozone attack on a swollen butyl network: degree of reproducibility.

TABLE II
Elastomers Studied

Isoprene butyl (regular)	98-99%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{C} \end{array} \right)$	1-2%	$\left(\text{---C---C=C---} \right)$
Piperylene butyl	98-99%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{C} \end{array} \right)$	1-2%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C=C---} \end{array} \right)$
Isoprene butyl with small amounts of divinyl benzene and cyclopentadiene (butyl IDC)	97%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{C} \end{array} \right)$	2%	$\left(\text{---C---C=C---} \right)$
			0.5%	$\left(\begin{array}{c} \text{---C---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{---C---} \end{array} \right)$
			0.5%	$\left(\begin{array}{c} \text{---C---} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{---C---} \end{array} \right)$
Methyl cyclopentadiene butyl	96%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{C} \end{array} \right)$	4%	$\left(\begin{array}{c} \text{---C---} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ \backslash \quad / \\ \text{C} \quad \text{C} \\ \\ \text{---CH}_3 \end{array} \right)$
Chlorobutyl	98%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{C} \end{array} \right)$	2%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{Cl} \end{array} \right)$
Bromobutyl	98%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{C} \end{array} \right)$	2%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{Br} \end{array} \right)$
Conjugated butyl	98%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{C} \end{array} \right)$	1%	$\left(\text{---C---C=C---} \right)$
			1%	$\left(\begin{array}{c} \text{C} \\ \\ \text{---C---C---} \\ \\ \text{Br} \end{array} \right)$ (from partial dehydrohalogenation of brominated butyl)

bubbles were not allowed to impinge on the rubber sample. Therefore, the ozone in equilibrium solution in the swelling agent, carbon tetrachloride, attacked the swollen network. No attempt was made to measure the actual solubility of ozone in carbon tetrachloride, but estimates from a table in the Welsbach manual⁸ would indicate a concentration of 15,000 parts O₃ pphm of solvent at 25°C. For the comparative purposes of these experiments it was sufficient to control the ozone concentration in the air, the flow rate, and the bubble size through the swelling solvent. The ozone attacked the sample at the surface producing soluble fragments.* Specimen discs

* Early in this study the possibility of diffusion of dissolved ozone into the interior of the swollen network was considered. If this did occur, ozone attack in the interior should affect the network chain density, resulting in an increase in swelling volume. Some experiments were conducted in a special cell wherein a change in swelling could be observed optically, in two dimensions, by the technique of D. J. Buckley, M. Berger, and D. Poller, *J. Polym. Sci.*, **56**, 163 (1962). No change in swelling was observed, and it was concluded that the oxone attack was at the surface.

$\frac{5}{16}$ in. in diameter and 0.035 in. thick were cut from vulcanized sheets to provide an essentially constant area of exposure. Each sample was weighed dry, allowed to swell to equilibrium, inserted in the reactor for a measured contact time, and then removed, dried, and reweighed. By exposing a series of samples to different contact times, a curve of percentage weight loss versus time was constructed which characterized the rate of attack of a given rubber vulcanizate.

All experiments were conducted under the conditions given in Table I.

Representative data are shown in Figure 1 for two check runs on samples from the same cured butyl sheet. The thin disc minimizes a surface shape factor and the loss in weight due to attrition by ozone appears as a linear function of time up to about the point of 60% weight loss. Thus, during the course of the experiment, an approximately constant concentration of vulnerable sites (double bonds) at the surface is maintained.

TABLE III
Vulcanization Formulations

	Parts by wt
Sulfur Cure	
Butyl rubber	100
Zinc oxide	5
Sulfur	2
Tetramethyl thiuram disulfide	2
Zinc Oxide Cure (Chloro-Butyl)	
Chlorobutyl	100
Zinc oxide	5
Tetramethyl thiuram disulfide	1
Resin Cure I	
Regular butyl	100
Phenol-methylol resin	12
SnCl ₂	2
Resin Cure II	
Chlorobutyl	100
Phenol-methylol resin	12
Zinc oxide	5
Dioxime Cure	
Regular butyl	100
<p><i>p</i>-Quinone dioxime</p>	2
PbO ₂	4
Quinone Cure I	
Conjugated butyl	100
<p><i>p</i>-Benzoquinone</p>	2
Quinone Cure II	
Conjugated butyl	100
<p><i>p</i>-Benzoquinone</p>	2
Zinc oxide	5
MPBM Cure	
Conjugated butyl	100
<p><i>m</i>-phenylene bis-maleimide</p>	1

Elastomers Studied

Except for a brief investigation of natural rubber, butyl rubber and its variations provided the basic swollen network for study in these experiments. The characteristic low unsaturation level of butyl elastomers can be varied significantly without greatly changing the overall structure of the elastomer, making it ideal for this purpose. The composition of the polymers studied is shown schematically in Table II.

Vulcanization Formulations

The formulations used to produce crosslinked networks were selected to give a wide variety of crosslink types and are listed in Table III.

The vulcanizates were prepared by press molding at 153°C and sulfur-cured regular butyl vulcanizates having different unsaturation levels were first investigated. The difference in unsaturation was characterized by the average molecular weight between points of unsaturation, \bar{M}_u , calculated from determinations of unsaturation by the iodine-mercuric acetate method. Each vulcanizate was also varied by curing a series of samples to different concentration of crosslinks. This was done with piperylene butyl as well as regular isoprene butyl. The extent of cure was characterized by the average molecular weight between crosslinks, \bar{M}_c , calculated from volume swelling data in cyclohexane using the Flory-Rehner⁹ relationship and an interaction coefficient, μ , between cyclohexane and butyl of $0.44 + 0.17V$, as refined by Kraus.¹⁰

RESULTS AND DISCUSSION

Before studying the effect of crosslink type on the rate of ozone attack of swollen networks, the effects of extent of vulcanization with butyl rubbers of various unsaturation levels was examined. The purpose was to observe if the presence of a sulfur crosslink bridge close to a double bond site restricted ozone attack. In this part of the study butyl rubbers were used wherein the major portion of the unsaturation was along the main polymer chain.

Effect of Original Unsaturation and Degree of Crosslinking

In Figure 2, results are shown for a series of isoprene butyls of varying unsaturation vulcanized to a constant degree of crosslinking represented by an M_c (molecular weight between crosslinks) of 44,000. These lightly crosslinked networks possessed considerable residual unsaturation not involved in sulfur crosslinking. The rates of attack as indicated by the slopes of the lines bear a relationship to the original unsaturation. Thus a fragment the size of M_u is removed and not a unit tetrahedron of the crosslinked network.

When the same series of isoprene butyl was vulcanized to a higher degree of crosslinking, as shown in Figure 3, the rate of ozone attrition was little changed from the rates of Figure 2 in spite of the increased concentration

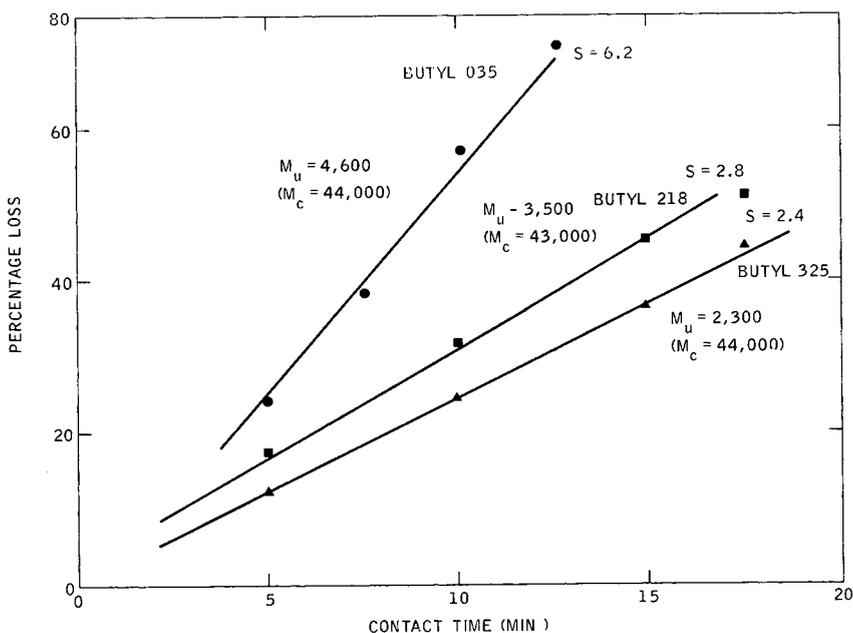


Fig. 2. Ozone attack on swollen networks of various isoprene butyls vulcanized to the same degree of crosslinking (constant M_c):— M_u , original average molecular weight between points of unsaturation calculated from iodine adsorption; M_c , molecular weight between crosslinks from volume swell.

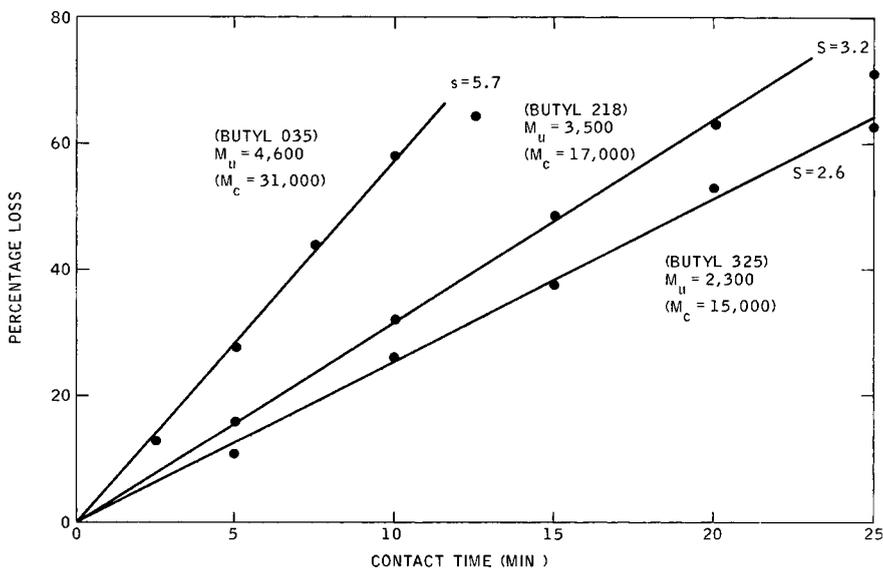


Fig. 3. Ozone attack on swollen networks of isoprene butyls vulcanized to high degrees of crosslinking (regular isoprene butyl of varying unsaturation): M_u , original average molecular weight between points of unsaturation calculated from iodine adsorption; M_c , molecular weight between crosslinks from volume swell.

TABLE IV
Molecular Weight of Fragments from
Ozonized Swollen Networks

Network	M_u^a	Viscosity-average mol wt of fragments
Butyl 035	4,600	7,400
Butyl 325	2,300	1,300

^a Molecular weight between points of unsaturation calculated from unsaturation values measured by the iodine-mercuric acetate method.

of crosslinks. This would indicate that the crosslink itself has no chemically protecting effect at the double bond site as suggested by Buckley and Robison¹ for a partial explanation of the "cure state" effect. The effect of state of cure that they reported when studying the ozone attack on unswollen systems must therefore be explained on a physical basis whereby the crosslink restricts chain motion in the solid state and this immobilization increases the ozone resistance.

Contrary to what has been observed in unswollen rubber compositions, these rate relationships state that the vulcanizate with the largest M_u or the lowest percentage unsaturation experiences the most rapid rate of attrition, as represented by the slopes in Figure 2. The conclusion reached from these results is that the ozone cleavage at the double bond extracts the largest fragments from the swollen network which contains the largest M_u . This statement is further verified by an analysis of the average molecular weight of the soluble fragments. Sample vulcanizates were swollen and

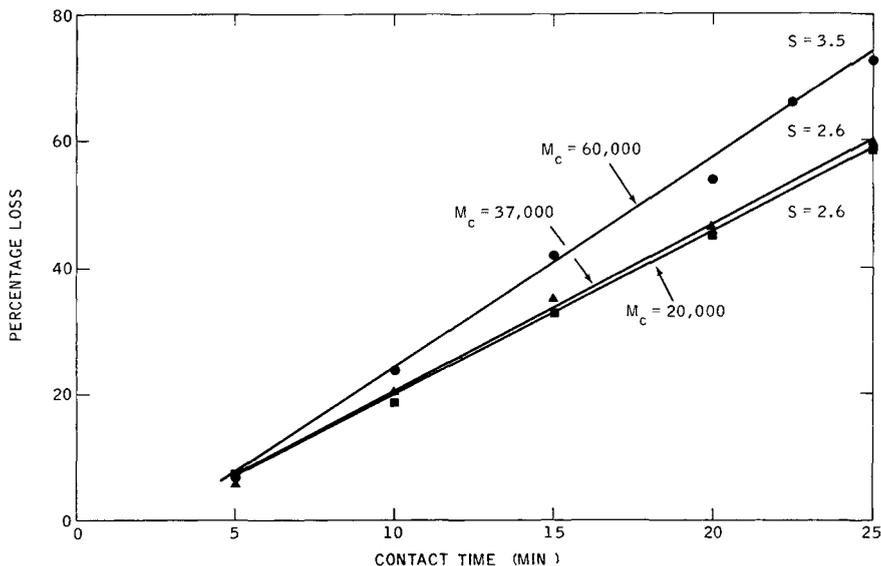


Fig. 4. Ozone attack on a piperylene butyl vulcanized to increasing degrees of crosslinking: M_c , molecular weight between crosslinks.

completely decomposed by the action of ozone. The soluble fragments were collected and molecular weight based upon an intrinsic viscosity was determined. These results are shown in Table IV, where the molecular weights of the fragments determined by viscosity are compared with the original molecular weights between points of unsaturation in the original butyl polymer, and the trend of the fragment size is certainly in the right direction. Differences in absolute values can be attributed to the fact that one set of molecular weight measurements is determined from iodine adsorption while the other is determined by viscosity measurements. Furthermore, the accuracy of the viscosity measurements is interfered with by unremoved colloidal zinc oxide particles necessary for the vulcanization process. Also the fragments may not all correspond to the linear habit of the segments between points of unsaturation.

A further experiment showing that the state of cure or degree of cross-linking has little effect on the ozone attack of swollen butyls is shown in Figure 4 using a piperylene butyl system. The slopes of the attrition reaction curves are identical for M_c values of 37,000 and 20,000 and only slightly increased when a very low state of cure represented by the largest M_c is subjected to ozone attack. This figure, compared with Figure 3, also shows that there is no difference between the intrinsic ozone resistance of a piperylene butyl and an isoprene butyl.

The experiments described thus far have indicated a relationship between the rate of attrition in the swollen state and the molecular weight distance between points of unsaturation. An extension of this analysis was directed toward the investigation of the ozone attack on a swollen natural rubber vulcanizate. In this system the distance between points of unsaturation on a molecular weight scale would be 68 rather than values in the thousands as represented by butyl. Natural rubber in the solid state exhibits a low resistance to ozone attack because of the high concentration of double bonds, but in the swollen state the rate of attrition by ozone when compared to butyl is just the reverse. This seeming paradox is shown in Figure 5 and must be explained on the basis that, for natural rubber, very small fragments are attrited from the vulcanized surface resulting in the much lower slope. In other words, we have an ozone sponge that soaks up a considerable quantity of ozone per unit weight loss. When a swollen natural rubber sample was completely disintegrated, it was not possible to collect fragments for any sort of viscosity measurement by evaporation of the swelling solvent. The implication is that the fragments were small enough to be volatile.

In the attack of ozone on solid rubber specimens, the immediate surface of butyl is certainly rapidly attacked but it is not removed immediately to form a new surface. The ozonized layer then must be a barrier, and subsequently ozone molecules must find a point where another double bond site is exposed. Since there are so few of these in butyl as compared to natural rubber, the result in solid state exposure is a reduction in crack formation for butyl.

Effect of the Type of Crosslink

If a crosslinking system could be found that saturates the double bond as crosslinking occurs, then a low-functionality elastomer, which has excellent ozone resistance, could be made essentially impervious to attack without radically changing its nature. With butyl, other crosslinking systems are possible in addition to sulfur vulcanization, and these have been schematically listed in Table V. No attempt has been made to show the mechanisms of these reactions; the representations are merely indications of the possible types of crosslinking. If any of these curing systems would result in a drastic lowering of the slope or rate of ozone attrition in swollen networks, one could assume that saturation or bridging of the double bond produces a protective action.

The vulcanizates for this study were again prepared by press molding at 153°C; the formulations for the various types are shown in Table III. Regular isoprene butyl was used in a comparison of the resin cure and dioxime cure with a conventional sulfur vulcanization, and results for adequately cured systems are shown in Figure 6.

The resin cure of regular butyl has not markedly decreased the ozone resistance of the swollen network, but there is a definite indication that the crosslinking with quinone dioxime has resulted in a small intrinsic protection of the reaction site. The fact that the resin cure has made little change in ozone resistance suggests that the methylene quinone mechanism is predominant. All suggested mechanisms for the dioxime cure of butyl leave a residual double bond, and thus it is not quite clear why any im-

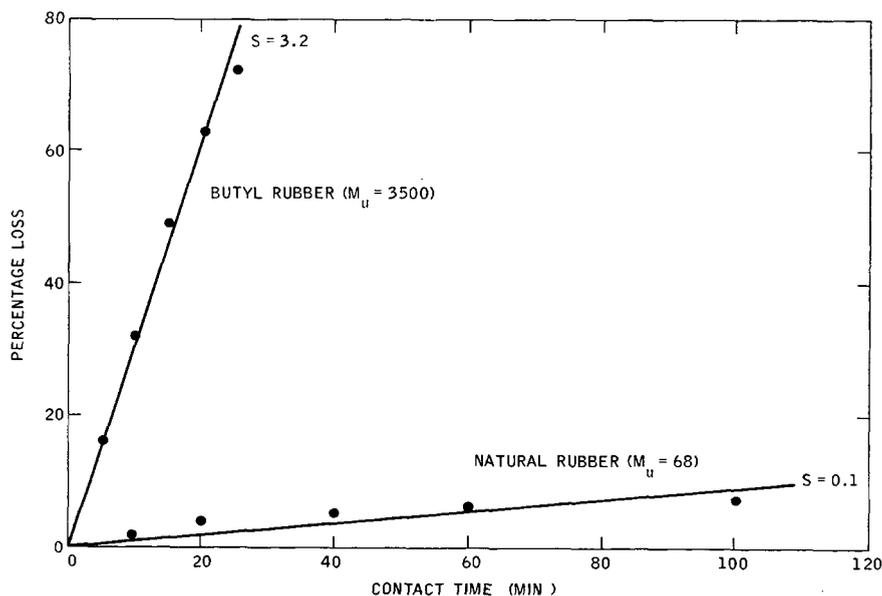


Fig. 5. The paradox of butyl and natural rubber in the swollen state.

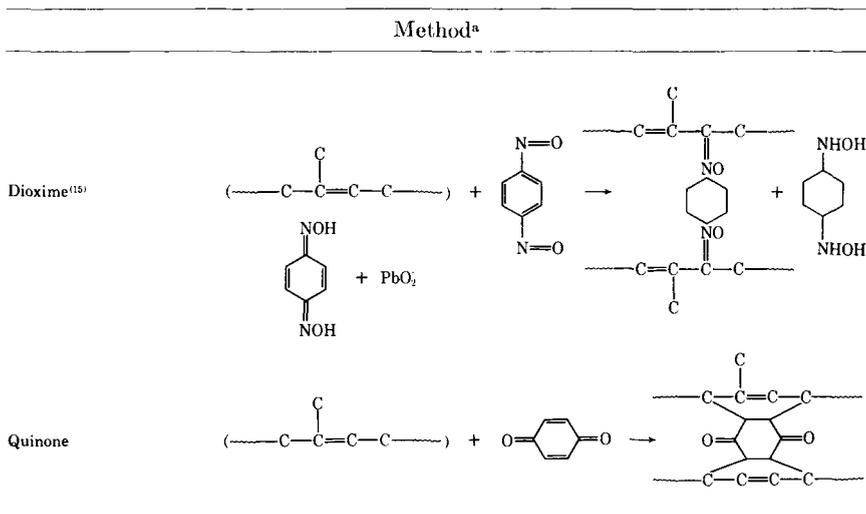
provement should exist if one discounts an explanation on the basis of a bulky crosslink bridge.

Resin cure of chlorobutyl produces a markedly improved ozone resistance

TABLE V
Curing Reactions

Method ^a	
Sulfur ⁽¹¹⁾	$\left(\text{---C} \begin{array}{c} \text{C} \\ \\ \text{C}=\text{C} \end{array} \text{---C---} \right) + \text{S}_x \xrightarrow{\text{ZnO}} \begin{array}{c} \text{C} \\ \\ \text{---C} \text{---} \text{C}=\text{C} \text{---} \text{C---} \\ \\ \text{S}_{2-4} \\ \\ \text{---C} \text{---} \text{C}=\text{C} \text{---} \text{C---} \\ \\ \text{C} \end{array} + \text{ZnS}$
Zinc oxide ⁽¹²⁾	$\left(\text{---C} \begin{array}{c} \text{C} \\ \\ \text{C}=\text{C} \end{array} \text{---C---} \begin{array}{c} \text{C} \\ \\ \text{X} \end{array} \right) + \text{ZnO} \rightarrow \begin{array}{c} \text{C} \\ \\ \text{---C} \text{---} \text{C}=\text{C} \text{---} \text{C---} \\ \\ \text{---C} \text{---} \text{C}=\text{C} \text{---} \text{C---} \\ \\ \text{C} \end{array} + \text{ZnCl}_2$
Resin (chroman mechanism) ⁽¹³⁾	$\left(\text{---C} \begin{array}{c} \text{C} \\ \\ \text{C}=\text{C} \end{array} \text{---C---} \right) + \text{HOCH}_2 \text{---} \text{C}_6\text{H}_3(\text{OH}) \text{---} \text{CH}_2\text{OH} \rightarrow$ $\begin{array}{c} \text{C} \\ \\ \text{---C} \text{---} \text{C} \text{---} \text{C} \text{---} \text{C---} \\ \quad \\ \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_3(\text{OH}) \\ \\ \text{CH}_2 \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{C}_6\text{H}_3(\text{OH}) \\ \quad \\ \text{O} \quad \text{O} \\ \quad \\ \text{---C} \text{---} \text{C} \text{---} \text{C} \text{---} \text{C---} \\ \\ \text{C} \end{array} + \text{H}_2\text{O}$
Resin (methylene quinone mechanism) ⁽¹⁴⁾	$\left(\text{---C} \begin{array}{c} \text{C} \\ \\ \text{C}=\text{C} \end{array} \text{---C---} \right) + \text{HOCH}_2 \text{---} \text{C}_6\text{H}_3(\text{OH}) \text{---} \text{CH}_2\text{OH} \rightarrow$ $\begin{array}{c} \text{C} \\ \\ \text{---C} \text{---} \text{C}=\text{C} \text{---} \text{C---} \\ \\ \text{CH}_2 \\ \\ \text{C}_6\text{H}_3(\text{OH}) \\ \\ \text{CH}_2 \\ \\ \text{---C} \text{---} \text{C} \text{---} \text{C} \text{---} \text{C---} \\ \\ \text{C} \end{array}$

TABLE V (continued)



^a Superior numbers are reference numbers.

in the swollen state. This is shown in Figure 7 where a comparison is made with a zinc oxide cure of the halogenated butyl. The vulcanization system with the highest slope is the zinc oxide vulcanization activated with a thiuram; the rate of attack is similar to that found with sulfur vulcanization of regular butyl, indicating that the double bond site is still vulnerable. The resin cure of chlorobutyl appears intrinsically much more resistant than the resin cure of regular butyl shown in Figure 6. This suggests that with chlorobutyl a chroman formation, as indicated in Table V, could be operative for at least part of the crosslinking mechanism. The chroman mechanism postulates a ring formation at the double bond site. As indicated in the next paragraph, ZnO and halogenated butyl offer the possibility of conjugated double bond formation. This may in part explain the different response of chlorobutyl to crosslinking by resin systems.

Recent work in these laboratories has shown that conjugated unsaturation can be induced along a butyl molecular chain through dehydrohalogenation of a halogenated butyl. Such a modified butyl shows marked reactivity with *p*-benzoquinone in a crosslinking reaction that can be explained by a Diels-Alder mechanism. As indicated in Table V, this reaction would provide a point of ozone attack which would not result in the severance of a long polymer chain. It was therefore of interest to know whether such a vulcanized system would produce an intrinsically ozone-resistant network in the swollen state. Figure 8 shows some results with special crosslinking systems involving the conjugated unsaturated butyl. When quinone is used as the sole vulcanizing ingredient, only a modest decrease in ozone attrition of the swollen network is noted even after a prolonged vulcanization of 80 min at 153°C. However, when quinone is used

in conjunction with zinc oxide, a network results that has a marked improvement in intrinsic ozone resistance, as shown by the bottom line with a slope of only 0.1. This highly ozone resistant network is only obtained, however, after the prolonged cure of 80 min and suggests that in the presence of zinc oxide further dehydrohalogenation occurs which is subsequently

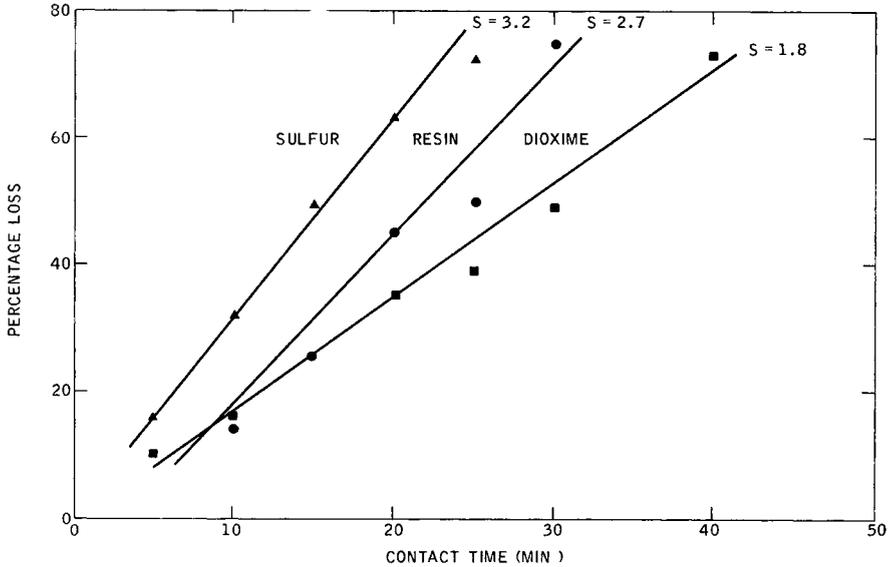


Fig. 6. Ozone attack on swollen networks of isoprene butyl vulcanized by various methods.

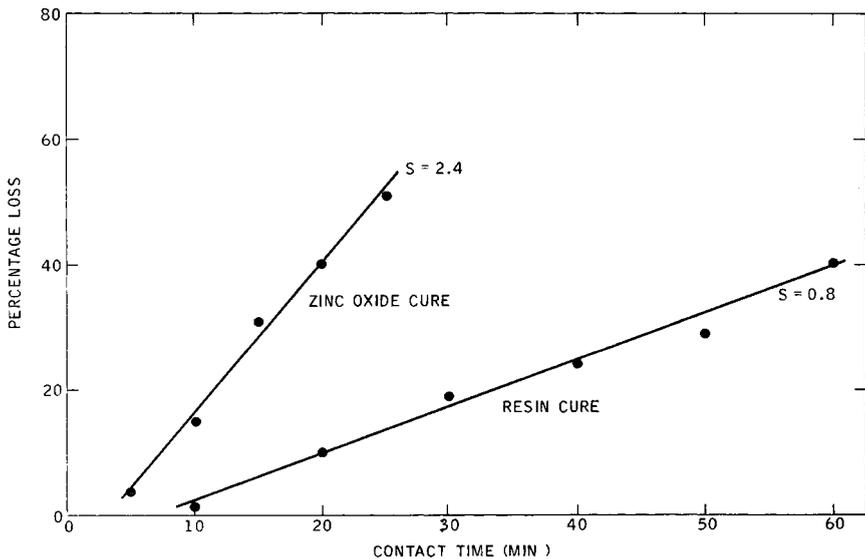


Fig. 7. Ozone attack on swollen network of chlorobutyl.

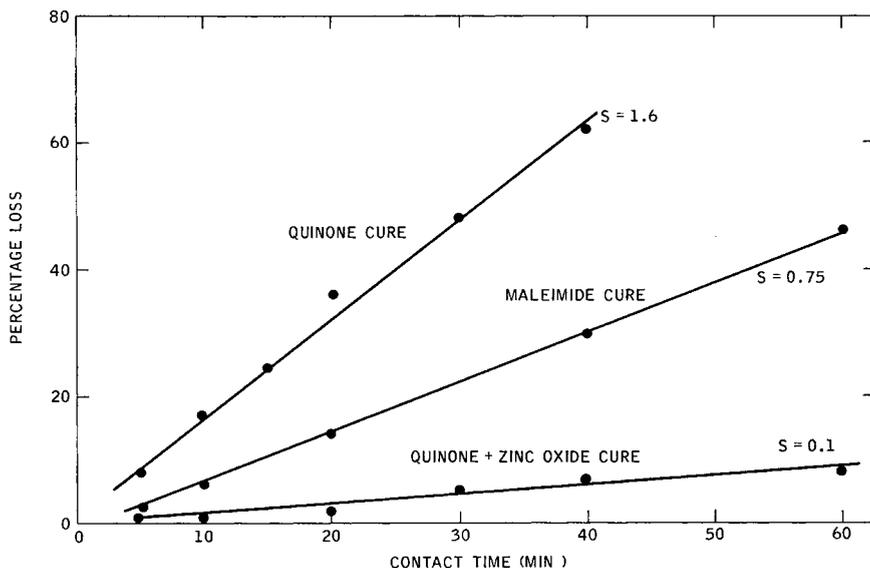
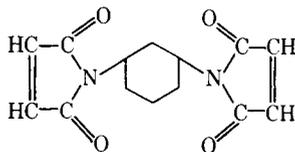


Fig. 8. Ozone attack on swollen networks of special crosslinked systems involving possible Diels-Alder addition to conjugated unsaturation.

linked in a Diels-Alder type of crosslink. Only the results with methyl cyclopentadiene butyl have resulted in lower rates of ozone attack. If this system could be made practical, these experiments point the way toward a method for improving the ozone resistance of low-functionality elastomers. The middle line with an intermediate slope represents an alternate vulcanization mechanism for the conjugated butyl. This involves the use of phenylene bis-maleimide shown below:



The crosslinking rate of this system, in a preliminary experiment, was not improved by the addition of a metallic oxide, but the use of only one part of this bulky molecule per 100 parts of polymer is stoichiometrically insufficient to react with all the conjugation that might be formed through further dehydrohalogenation. Increased quantities of this reactant should result in decreased rate of attrition by ozone.

Cyclic Diolefin Butyls

The butyl systems that have been studied so far have incorporated the double bond site along the main polymer chain. A classical method of increasing ozone resistance is to place the reactive site for vulcanization in a side chain. Experimental butyl polymers have been prepared which

utilize cyclic diolefins as the sole or as part of the unsaturated functionality in an isobutylene molecule. Figure 9 dramatically shows how cyclic diolefins decrease the rate of attrition during ozone attack on swollen networks. Isoprene butyl 325 is used as a reference point and is to be compared with the IDC and the methyl cyclopentadiene butyl. The IDC butyl polymer, containing small quantities of cyclopentadiene as well as isoprene, has an attrition rate roughly one third that of regular butyl 325.

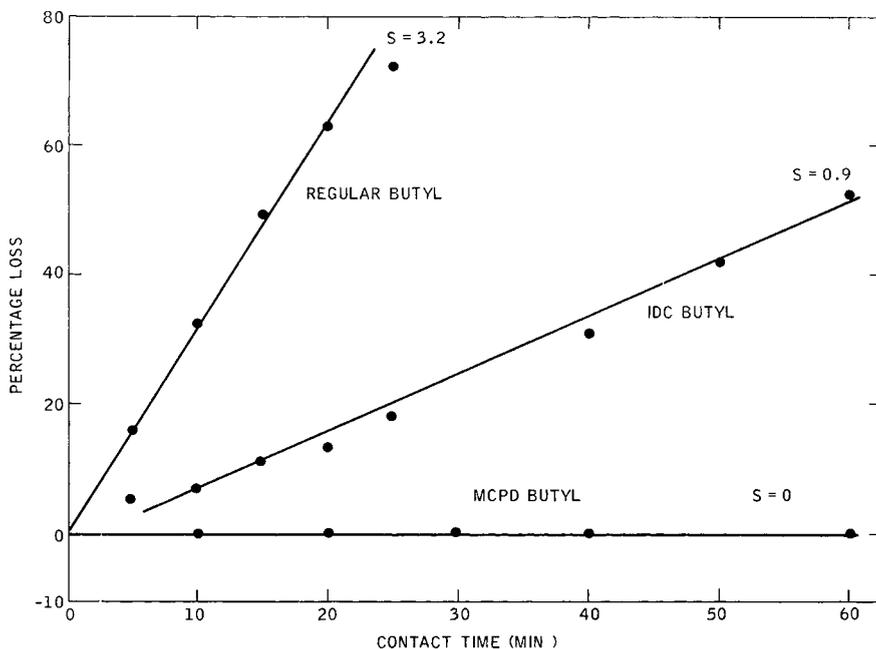


Fig. 9. Ozone attack on swollen networks of cyclic diolefin butyls.

The action of the cyclopentadiene in this case must be that of an ozone adsorbent at reactive sites which do not result in chain severance. When the reactive unsaturation is all in a side chain, as would be the case with methyl cyclopentadiene butyl, the rate of ozone attrition on a swollen network is virtually zero. This elastomer is intrinsically ozone resistant as shown by this technique, for any cleavage at the double bond would not effect the overall structure of the network.

SUMMARY

Ozone attack on vulcanized rubbers was studied when these networks were swollen in a solvent, carbon tetrachloride. In this highly swollen state where hysteresis effects are at a minimum and where the molecular segments are under internal strain, the basic vulnerability of the reactive sites was exposed.

Ozonized air was bubbled through the solvent containing the swollen network and the ozone in solution attacked the surface of the specimen. Soluble fragments were rapidly removed as a linear function of exposure time. This rate of attrition was directly related to the segmental molecular weight between points of unsaturation in systems containing internal double bonds (i.e., double bonds along the main polymer chain). Thus one observes, in contrast to studies in the unswollen state, that isoprene butyls with the lowest degree of unsaturation (largest segmental molecular weight) had the greatest rate of attrition. Actual viscosity-average molecular weights of the fragments supported this observation. In sulfur-vulcanized systems, the state of cure or degree of crosslinking had little or no effect on the attrition rate, thus contributing no real chemical protection for the double bond site. No difference in the rate of attack could be noted between isoprene and piperylene butyls.

The presence of cyclic diolefins in a butyl molecular chain markedly reduces ozone attack. Methyl cyclopentadiene butyl in this very sensitive swollen state appears invulnerable; the slope of the attrition loss-time relation was essentially zero.

Some alternate crosslinking systems for butyl resulted in markedly reduced rates of ozone attack in the swollen state. This suggested that actual protection (or saturation) of the double bond site had occurred. Notable was the quinone-zinc oxide crosslinking of a conjugated unsaturated butyl prepared from a halogenated butyl. Here, rates of attrition in the swollen state were reduced 30-fold over regular sulfur vulcanization, supporting a Diels-Alder addition at this conjugated site. Another large-scale reduction in ozone attrition was observed when chlorobutyl was cured with phenol-methylol resins, suggesting that some of the crosslinking groups were of the chroman structure or a mechanism that bridges the double bond.

Finally, it is proposed that experiments of this type could be utilized for studying the protecting of reactive sites during vulcanization. This protection during cure is one basic way to improve the ozone resistance of low-functionality elastomers since complete alteration of the double bond sites would not radically change the elastomeric properties of the network.

References

1. D. J. Buckley and S. B. Robison, *J. Polym. Sci.*, **19**, 145 (1956).
2. M. Braden and A. N. Gent, *J. Appl. Polym. Sci.*, **3**, 90 (1960).
3. M. Braden and A. N. Gent, *J. Appl. Polym. Sci.*, **3**, 100 (1960).
4. M. Braden and A. N. Gent, *J. Appl. Polym. Sci.*, **6**, 449 (1962).
5. M. Braden and A. N. Gent, *Rubber Chem. Tech.*, **35**, 200 (1962).
6. H. Tucker, *Rubber Chem. Tech.*, **32**, 269 (1959).
7. G. Gee, *Trans. Faraday Soc.*, **42**, 585 (1946).
8. Int. Crit. Tab. 3-263.
9. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).
10. G. Kraus, *Rubber Chem. Tech.*, **30**, 928 (1957).
11. R. L. Zapp, et al., *J. Polym. Sci.*, **6**, 331 (1951).
12. F. P. Baldwin et al., *Rubber Plastic Age (London)*, **42**, 500 (1961).

13. A. Greth, *Kunststoffe*, **31**, 345 (1941).
14. S. Van der Meer, *Rec. Trav. Chem.*, **63**, 149 (1944).
15. P. J. Flory and J. Rehner, *Ind. Eng. Chem.*, **38**, 500 (1946).
16. W. J. Sparks and R. M. Thomas, U. S. Pat. 2,577,822 (Dec. 11, 1951).

Received March 26, 1969

Revised May 22, 1969