

The Surface Reaction of Ozone with Chemically Protected Rubber*

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INTRODUCTION

Much attention has been given to the question of protecting natural rubber from the destructive effects of ozone, most interest having centered on certain chemicals which, when incorporated in the rubber endure it with a greater or lesser degree of ozone resistance. The role of chemical antiozonants has been critically examined by Braden and Gent¹ who showed that the effective materials fall into two categories.

First, there is a small group of chemicals (the *N,N'*-dialkyl-*p*-phenylenediamines) which greatly increase the critical stress required to promote cracking in the presence of ozone. The enhancement of critical stress is very dependent on the ozone concentration (Fig. 1), falling rapidly as the latter increases and vanishing almost completely beyond a certain ozone level. If the quantity of antiozonant in the rubber is raised, the curve in Figure 1 is displaced to the right and vice versa. On the basis of these observations Braden and Gent tentatively inferred that the *p*-phenylenediamines participate in the reaction between the ozone and rubber, reducing the extent of degradation at the surface of interaction. Failure to protect at high ozone concentrations was attributed to the predominance of a competitive effect, namely, the direct reaction of ozone with the antiozonant.

A second and much more diverse class of antiozonants was found to have no effect on the critical stress but simply reduced the rate at which ozone cracks propagated through the rubber. This rate of propagation was otherwise dependent only upon the ozone concentration and not upon the stress applied to the specimen. No mechanism could be advanced to explain protective action of this kind.

A previous paper² (Paper I) described methods of studying the surface interaction of ozone and rubber with the aid of replica electron microscopy. It was decided to use similar methods in investigating the physical aspects of ozone protection.

* The second paper on this subject. The first paper (Ref. 2) is herein referred to as "Paper I."

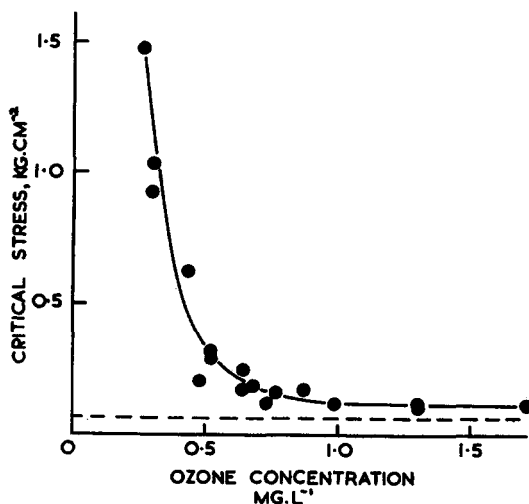


Fig. 1. The dependence of critical stress on ozone concentration in natural rubber protected with a substituted *p*-phenylenediamine. The broken line gives the results for unprotected rubber.

EXPERIMENTAL

Sheets of natural rubber cured with dicumyl peroxide were molded against clean plate glass to give a smooth reference surface. The sheets were extracted for 24 hrs. under nitrogen with hot acetone, to remove soluble impurities, and the acetone was removed under vacuum. Some of the rubber was kept in this condition for a control, and other sheets were treated with one of the two antiozonants, *N,N'*-di-3-(5-methyl heptyl)-*p*-phenylenediamine (DOPPD) and oleic acid. Both reagents were incorporated to the extent of 6% by weight, being swollen into the rubber from solution in ether.

Specimens were exposed to known concentrations of ozone in an apparatus described previously.³ Most of the work was carried out on unstrained specimens exposed for a standard period of 20 min., but some experiments were made with strain as a variable parameter and the exposure time in such cases was 1 min.

The two-stage gelatin-carbon replication procedure⁴ was as described in Paper I except that some specimens, exposed in the unstrained state, were replicated at a strain of 100%. This served to break and thus reveal any inextensible layer formed on the surface.

In view of the marked reduction of critical stress with increasing ozone concentration in rubbers protected with DOPPD (see Fig. 1), specimens of this material were exposed at three different concentrations.

RESULTS

Control Surfaces

The rubber surface before exposure to ozone is quite flat and without significant features.² Exposure results in surface degradation which in its early stages is localized and whose severity is greatly enhanced by applied strain. This is apparent in Figure 2, which shows a specimen exposed unstrained for 20 min., and in Figure 3, which shows the effect of 1 min. exposure at 50% extension. These features have been studied (Paper I) and will not be further discussed here. One interesting difference arises,

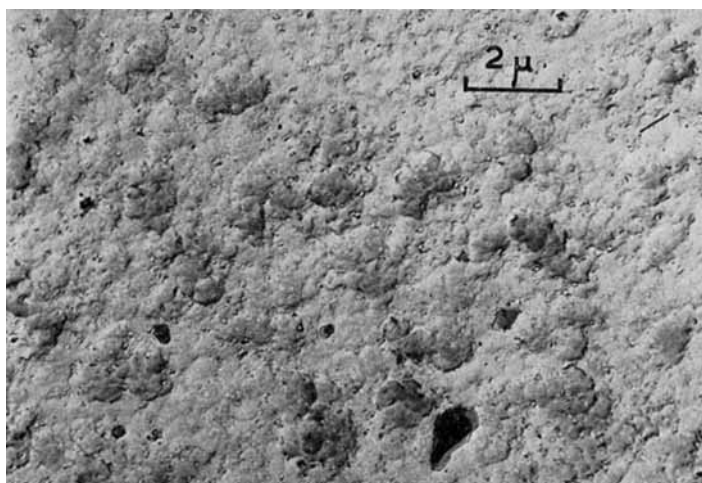


Fig. 2. Replica from the surface of an acetone-extracted natural rubber after 20 min. exposure to ozone, unstrained.

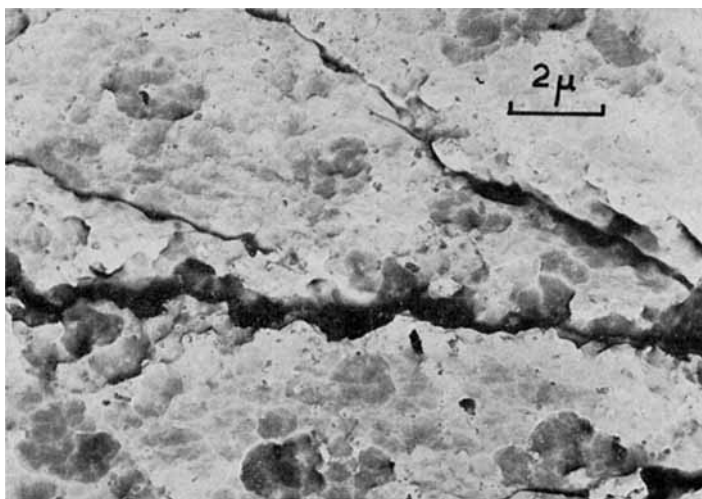


Fig. 3. The same rubber as in Figure 2 after 1 min. exposure at 50% strain.

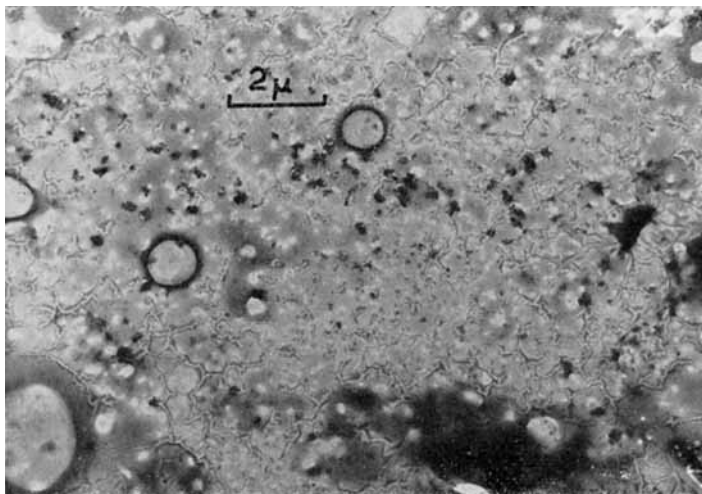


Fig. 4. Replica from the surface of unextracted rubber. 120 min. exposure to ozone, unstrained.

however, between the present specimens, which were acetone-extracted, and those examined in Paper I, which were not. The crumpled surface appearance that was evident in unextracted specimens (Fig. 4) is completely absent in the extracted materials. The significance of this will appear presently. The extracted specimen exposed at 50% extension and shown in Figure 3 contained incipient ozone cracks.

Rubber Containing Oleic Acid

Specimens exposed in the unstrained state for 20 min. showed dark patches associated with a well-developed crumpled appearance (Fig. 5), which appears to be an extreme form of the structure found in unprotected rubbers that have not been extracted (Fig. 4). Specimens exposed in a strained condition for 1 min. showed a certain amount of localization in the crumpled structure and resembled Figure 4, but no orientation was introduced by the strain. Specimens *replicated* in a strained condition also failed to show any directional features, and this suggests that the crumpled structure is an artifact of some kind. This was confirmed by washing the gelatin replica in benzene before depositing the carbon second-stage, which treatment eliminated the effect altogether and showed that the true surface of the exposed specimen was simply etched in a manner similar to unprotected rubber (Fig. 6). Two possible explanations of the "crumpling" are (a) that the structure is formed in the degraded layer during separation of the gelatin replica and (b) that it occurs because the gelatin, carrying a layer of degraded material removed from the specimen surface, is placed in a vacuum for deposition of the evaporated carbon film. The first possibility was ruled out by taking a second replica from the same area and removing any adhering material by washing the gelatin wafer in benzene. No

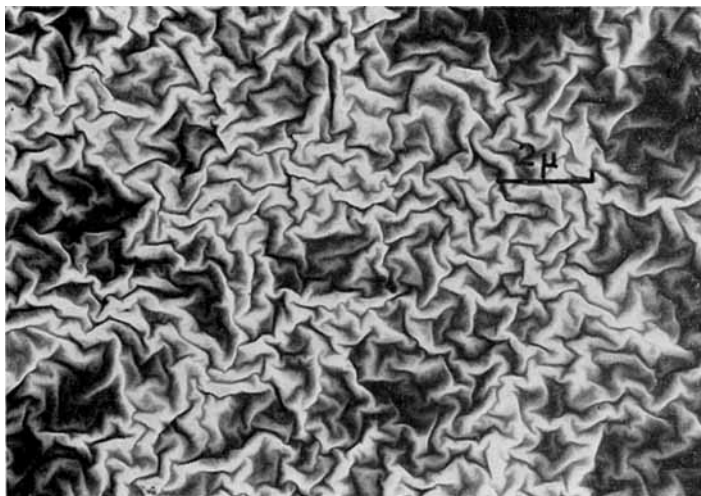


Fig. 5. Replica from extracted rubber containing oleic acid. 20 min. exposure to ozone, unstrained.

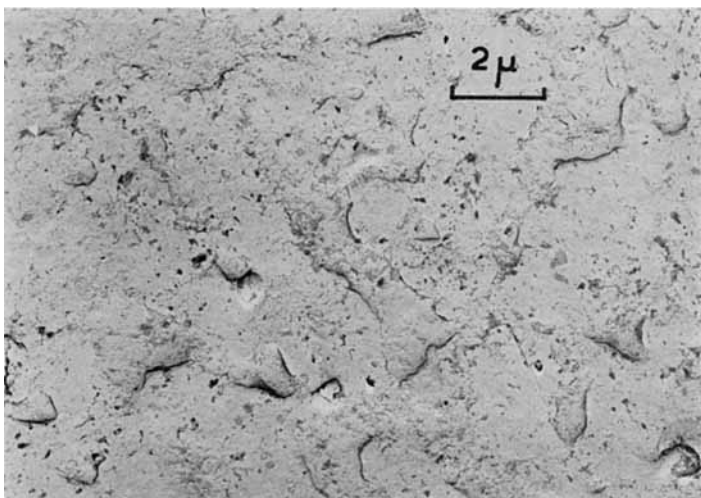


Fig. 6. The same specimen as Figure 5, but the gelatin first-stage replica has been washed in benzene. This reveals the true appearance of the specimen surface.

crumpled structure was found, showing that the surface of the rubber was smooth after separation of the first gelatin replica. The manner in which the structure could arise as a result of evacuation, and the implications of the effect, are discussed below.

Rubber Containing DOPPD

Exposure of this rubber to low concentrations of ozone, at which the protective action of DOPPD is strong, resulted in no apparent degradation of the surface. When, however, specimens exposed in the unstrained state

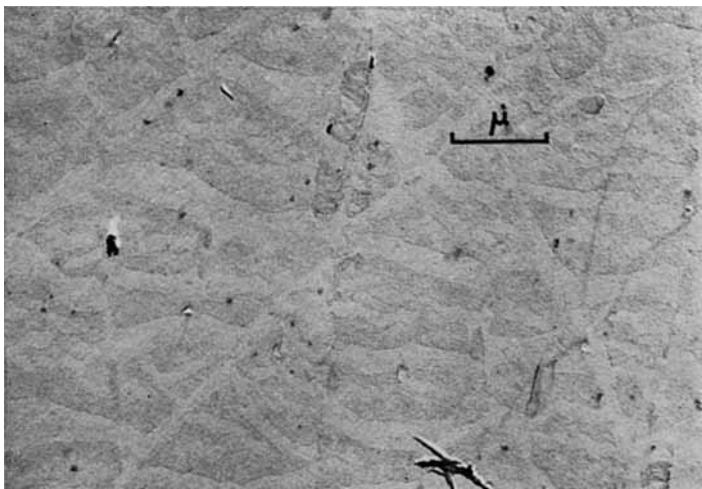


Fig. 7. Brittle layer formation in rubber containing DOPPD. Exposed 20 min., unstrained, but extended 100% for replication. High ozone concentration attained gradually.

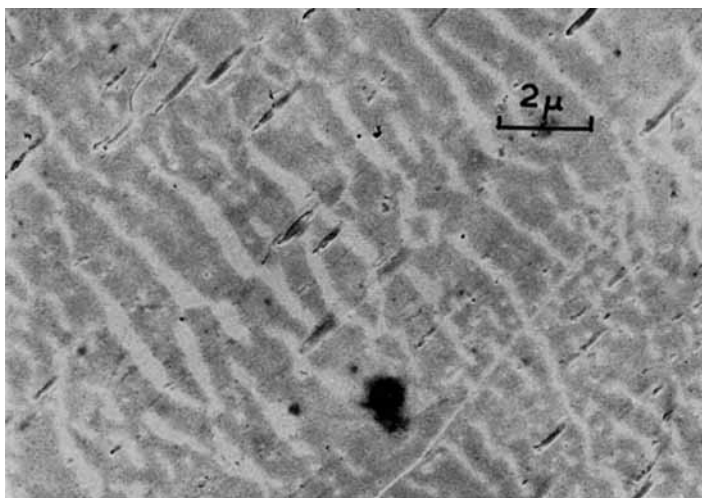


Fig. 8. As in Figure 7; but at steady ozone concentration of 0.15 mg./l.

were extended by 100% and held in this condition during replication, the result shown in Figure 7 was obtained. Extension subsequent to exposure had the effect of breaking down a brittle layer some 100 A. in thickness and having a rather more granular appearance than the background rubber. In Figure 7, where a gradual build-up of ozone concentration occurred unintentionally, the layer appears to have been replicated, but in Figure 8 it has been removed by the replica.

At higher ozone concentrations, when the protective effects of DOPPD are much less striking, brittle layer formation becomes less well defined.

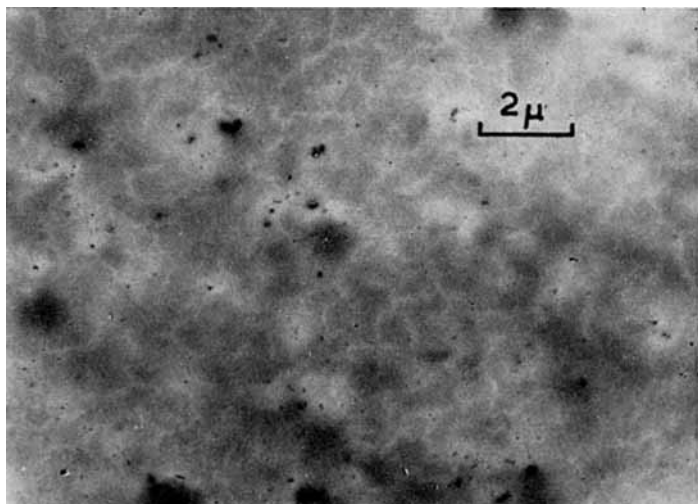


Fig. 9. As in Figure 8; ozone concentration 0.46 mg./l.

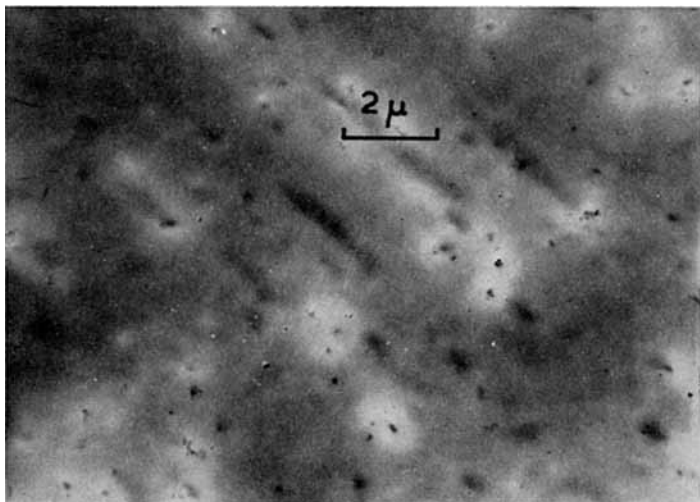


Fig. 10. As in Figure 8; ozone concentration 1.04 mg./l.

Figures 8 to 10 show a series of specimens exposed to increasing concentrations of ozone and indicate a marked reduction in the brittleness of the surface layer with rising ozone level. An estimate could be obtained of the extension at which the layer fractured, by measuring the total gap width produced in the layer by breakdown. Knowing the extension of the rubber substrate and assuming that the brittle layer remains at its maximum strain even after fracture, it is a simple matter to deduce the value of this limiting strain. The results are given below and indicate the effect of ozone concentration on the mechanical properties of the layer. The term "brittle" is of course purely comparative, contrasting the relatively inex-

tensible surface layer with the highly extensible substrate of unreacted rubber.

Ozone concentration (mg./l.)	0.15	0.46	1.04
Breaking extension of brittle layer (% strain)	45	78	>100

Although this concentration dependence is qualitatively obvious, quantitative reproducibility was not obtained, which suggests that some additional factor is at work. If the brittle layer, once formed, is not susceptible to further ozone attack it follows that the rate of *attainment* of ozone concentration at the rubber surface will be as important as its final level; a high concentration built up gradually would produce only the effects expected from the initially much lower value. This was confirmed by experiments in which specimens were (a) plunged into an atmosphere containing ozone and (b) placed in the test chamber in air and the same ozone concentration attained gradually over a period of 10 min. Brittle layer formation was observed in the latter case, but only a liquidlike degradation product in the former. It is probable, therefore, that the failure to obtain quantitative reproducibility stems from the difficulty of ensuring a particular rate of ozone build-up at the surface, even when the final concentration is well defined. Braden and Gent¹ noticed that critical stress in these materials was strongly dependent not only upon the final ozone concentration but also upon the way it was attained, and their observation is clearly paralleled by the present behavior.

DISCUSSION

The two antiozonants studied, representing two classes of materials whose antiozonant actions are quite distinct, have been shown to produce different but characteristic physical effects at the reacting surface. It is now possible, therefore, to discuss their protective properties more precisely, in terms of the mechanism by which they operate.

Oleic Acid

The evidence presented above indicates that the crumpled structure observed in Figure 5 is a result of placing the gelatin replicas in vacuum. Other experience in depositing carbon layers on extended rubber films which were subsequently relaxed leaves little doubt that the crumpling occurred in the *carbon* film after deposition, and this means that between the gelatin replica and the deposited carbon film there must exist a removed layer subject to considerable two-dimensional strain. The fact that replicas of uniaxially stretched specimens do not differ in any way from those taken in the unstrained state suggests that this surface strain on the specimen is not originally present. The most plausible explanation is as follows. The gelatin, bearing a layer of degraded material, is removed from the specimen surface and placed under vacuum. A low molecular weight

fraction volatilizes from the removed layer, but consequent shrinkage is prevented by its attachment to the gelatin. Under such circumstances a flat carbon film would be deposited, but crumpling would occur when the supporting gelatin substrate had dissolved away.

The reaction of ozone with untreated rubber yields a more or less fluid degradation product.² It appears, therefore, that oleic acid enters into the chemical reaction in such a way that the reacted layer, though containing low molecular weight material, remains sufficiently coherent to support considerable strain. An extension of the order of 50% would be necessary to produce the crumpling observed in the carbon film. A further deduction may be made from the observation that replicas washed so as to reveal the true surface of the specimen closely resemble those from unprotected rubbers. This suggests that the coherent layer is only an intermediate product which itself is liable to ozone attack, and would also account for the presence in the layer of a considerable low molecular weight fraction and for the dense patches of liquid-like material found in association with the crumpled structure.

The impermanent nature of the coherent layer would explain why the critical energy for ozone cracking is the same in the presence of oleic acid as in unprotected rubber. On the other hand, the very existence of the layer implies that the material of which it is composed is attacked by ozone less rapidly than is the original rubber, and the overall effect is therefore to reduce the reactivity of the surface. The rate of growth of ozone cracks is known to depend on the rate of chemical reaction, being proportional to the ozone concentration,³ and a reduction in rate is thus to be expected in the presence of oleic acid.

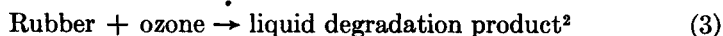
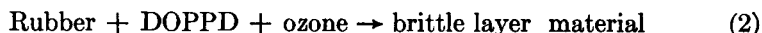
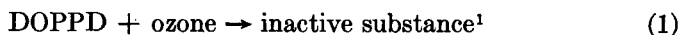
The appearance of crumpled patterns in replicas from peroxide rubbers which have not been extracted with acetone suggests that these rubbers possess a measure of ozone resistance by virtue of naturally occurring protective agents. This is, in fact, the case, the fatty acids appearing to be the most active of the extractable constituents.^{1,3}

DOPPD

The results in the case of DOPPD can readily be related to its known protective behavior. Reference to Figure 1 shows that the enhancement of critical stress (or critical propagation energy for ozone cracking) is strongly dependent on ozone concentration in the same sense as is brittle-layer formation, and there is little doubt that the latter is a causative agent in the protection of rubber by DOPPD. The critical energy for crack propagation (T_c) in an unprotected rubber is in all probability just twice the surface energy of the degraded material at the ozone-rubber interface (Paper I). If the usual degraded layer is now replaced by a relatively inextensible solid the energy required to rupture this coherent layer will include a dissipative term which in solid polymers always greatly exceeds the surface energy. As the brittle layer becomes less coherent, owing to forma-

tion at higher ozone concentrations, T_c will decrease until in the extreme of complete degradation it is no higher than in unprotected rubbers. Such reasoning provides a complete qualitative explanation of Figure 1 and, thus, of the protective action of DOPPD.

The dependence of brittle layer formation upon ozone concentration is clearly a chemical effect. It is most simply explained in terms of competition between the following three reactions, which may be supposed to occur at the surface:



Now, reaction (1) is known to progress rapidly⁵ and, if there is an excess of ozone, reaction (2) may be inhibited through a shortage of unreacted DOPPD, causing more of the rubber to react according to (3). Thus the chemical features of the process also appear to be capable of a consistent explanation. Finally, the apparent absence of any further reaction of the brittle layer with ozone accounts for a number of effects observed by Braden and Gent.¹ These include the ability of a protected rubber to withstand very high ozone levels without cracking if it is first exposed to a low concentration, and the elimination of this "conditioning" effect if the specimen is disturbed, the latter action presumably causing the protective layer to fracture.

It should be emphasized that no direct chemical evidence of reaction (2) exists. However, the very limited range of effective chemical compounds and the fact that some synthetic rubbers derive no protection from these materials suggest that a fairly specific chemical reaction is involved. In a subsidiary experiment, an ozone-resistant polymer (ethylene-propylene copolymer) containing 6% DOPPD was ozonized and examined for brittle layer formation. None was found even under conditions of low ozone concentration and slow build-up, indicating that some such reaction as (2) is responsible for the brittle layer and not the direct reaction (1) of DOPPD with ozone.

CONCLUSION

Both classes of antiozonants, affecting respectively the rate of growth and the critical energy for propagation of ozone cracks, seem to owe their effectiveness to the formation of surface reaction products. The essential difference between the two kinds of protective action lies in the reactivity to ozone of the surface layer formed initially: if this is inert an enhancement of critical stress is to be expected, but if susceptible to further ozone attack a reduction in rate alone will result. Only two representative antiozonants were examined, but it is likely that essentially similar physical mechanisms of ozone protection operate in many other cases.

References

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2. Andrews, E. H., and M. Braden, *J. Polymer Sci.*, **55**, 787 (1961).
3. Braden, M., and A. N. Gent, *J. Appl. Polymer Sci.*, **3**, 90 (1960).
4. Andrews, E. H., and A. Walsh, *Nature*, **179**, 729 (1957).
5. Barnard, D., private communication.

Synopsis

Replica electron microscopy has been used to elucidate the physical mechanisms by which various additives afford ozone resistance to natural rubber. There exist two classes of chemical antiozonants, namely, those that enhance the critical energy required for ozone cracking and those that retard the rate of crack growth; representatives of these two classes were used in the investigation. The process involved in the first of these protective mechanisms was found to be the formation at the exposed surface of an inextensible layer some 100 Å. thick and inert to further ozone attack. That giving rise to rate retardation also involved the formation of a surface layer, but the layer was susceptible to further ozonolysis and, eventually, complete degradation.

Résumé

La microscopie électronique de reproduction a été utilisée pour élucider les mécanismes physiques par lesquels différents additifs confèrent au caoutchouc naturel une résistance à l'ozone. Il existe deux classes d'antiozonisants chimiques, ceux qui élèvent l'énergie critique nécessaire pour le cracking de l'ozone et ceux qui retardent la vitesse de croissance de fente: ces deux classes sont étudiées dans ce travail. Le premier de ces mécanismes de protection pouvait s'expliquer par la formation à la surface exposée d'une couche inextensible d'une épaisseur de 100 Å. et rendue inerte à l'attaque par ozone. Ce qui donne lieu à un retard de vitesse impliquait aussi la formation d'une couche en surface mais dans ce cas la couche était susceptible d'ozonolyser ultérieurement et, éventuellement, de subir une dégradation complète.

Zusammenfassung

Eine elektronenmikroskopische Untersuchung nach dem Replica-Verfahren wurde zur Aufklärung des physikalischen Mechanismus der Entwicklung der Ozonbeständigkeit von Naturkautschuk durch verschiedene Zusätze durchgeführt. Es gibt zwei Klassen chemischer Antiozonkörper, nämlich solche, die die kritische Energie des Ozonangriffes erhöhen und solche die eine Verzögerung der Geschwindigkeit des Risswachstums bewirken; Vertreter beider Klassen kamen zur Untersuchung. Beim erstgenannten Schutzmechanismus war der wirksame Vorgang die Bildung einer nichtdehnbaren, einige 100 Å. dicken und gegen weiteren Ozonangriff beständigen Schichte an der der Ozoneinwirkung ausgesetzten Oberfläche. Der zur Geschwindigkeitsverzögerung führende Vorgang verlief ebenfalls über die Bildung einer Oberflächenschichte, diese war aber einer weiteren Ozonolyse und eventuell einem völligen Abbau zugänglich.

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