

## The Attack of Ozone on Stretched Rubber Vulcanizates.

### III. Action of Antiozonants

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#### I. INTRODUCTION

In the two previous articles,<sup>1,2</sup> Parts I and II, it was shown that two characteristic parameters govern the ozone cracking of vulcanized rubbers. These are:

(1) An energy requirement, necessary for crack growth to occur at all: the value found was of the order of 100 ergs/cm.<sup>2</sup> of newly formed surface. It was substantially independent of the ozone concentration, and similar in magnitude for a number of different polymers.

(2) A characteristic rate of crack propagation, when an adequate amount of elastically stored energy was made available: the rate was substantially independent of the applied stress, above the critical value, and directly proportional to the concentration of ozone. It was affected by the chemical nature of the polymer, as was to be expected, but it was affected also by the internal viscosity of the material. For example, the low rates of crack growth observed for butyl rubber were attributed, at least to a considerable degree, to this effect. The degree of crosslinking also influenced the rate of crack growth.

These conclusions suggest a number of ways in which protection might be afforded. First, the energy available for crack growth could be reduced to an inadequate level. This might be achieved by altering the vulcanizate stiffness suitably or by adopting an improved surface finish so that severe flaws or other stress raisers were not present. Second, the rate of growth of cracks would be reduced if the chemical resistance, internal viscosity, or degree of crosslinking of the polymer were increased.

In addition to these possible methods of improving the ozone resistance of rubbers, certain additives known as antiozonants are found to be beneficial. The type of protection they afford

and the mechanism of action are, however, little understood. A study was therefore undertaken of the effect of including some representative materials in the mix formulations of a number of polymers.

Two distinct modes of action were found. Many additives, of which 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline is a widely used example, cause the rate of crack growth in the vulcanizate to be considerably reduced. Their effect is described in Section II below. Certain additives, notably dialkyl-*p*-phenylenediamines, show an additional and striking ability to cause large increases in the critical energy required for growth to occur. The behavior of one member of this class, *N,N'*-dioctyl-*p*-phenylenediamine (DOPPD), has been studied extensively; the results are described in Section III.

#### II. ADDITIVES THAT REDUCE RATE OF CRACK GROWTH

##### Experimental

A number of materials have been found to reduce the rate of crack growth in vulcanizates of natural rubber. The experimental measurements were carried out as described in Part I, on thin strips with an initial razor cut 2 mm. long in the center of one edge, to define the location of the crack. The test pieces were subjected to a small tensile load, of about 250 g./cm.<sup>2</sup>, somewhat higher than that necessary for growth to occur at all, and exposed to ozonized oxygen at a concentration of 1.0 or 2.0 mg./l. Subsidiary measurements indicated that the reduced rate is substantially proportional to the ozone concentration; i.e., the additives appeared to cause the same proportionate reduction in rate at all concentrations. Isolated observations at atmospheric concentrations were also in accord with this relation. It appears, therefore, that the high ozone concentrations employed in the experiments described below do not affect the degree of

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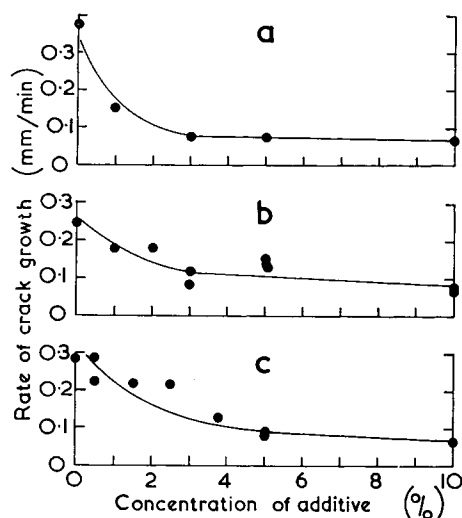


Fig. 1. Effect of additives on rate of crack growth: (a) oleic acid, (b) *N,N'*-dioctyl-*p*-phenylenediamine, (c) 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline.

protection caused by rate-reducing additives.

The additives employed were either included in the mix formulation or added after vulcanization to the acetone-extracted vulcanizate by swelling it with a dilute solution of the additive in diethyl ether or benzene and then pumping off the solvent.

### Carboxylic Acids

In Part I it was reported that oleic acid reduced the rate of crack growth when present in small quantities. Indeed, a material of this kind appeared to be present in smoked sheet rubber in sufficient amount to cause a markedly lower growth rate for peroxide vulcanizates (it was rendered inactive in sulfur vulcanizates, presumably by reaction with vulcanizing ingredients). The active material could be removed from peroxide vulcanizates, or the original rubber, by extraction with hot acetone.

The rate of crack growth is plotted in Figure 1a for peroxide vulcanizates prepared from acetone-extracted rubber having various amounts of oleic acid added after extraction. There is a substantial reduction in rate, large additions reducing it to about one sixth of its original value. Similar effects, although somewhat smaller in magnitude, were obtained with related materials, as the results given in Table I show.

### Dithiocarbamates

Tetramethylthiuram disulfide (TMT) vulcanizates were reported in Part I to exhibit low crack growth rates, and this was attributed to the

TABLE I  
Effect of 1% Addition of Carboxylic Acids on Rate of Crack Growth at 1 Mg. of Ozone/Liter

Additive	Growth rate, mm./min.
None	0.35
Oleic acid	0.10
Linoleic acid	0.21
Stearic acid	0.17
Sebacic acid	0.18

presence of zinc dimethyldithiocarbamate, formed<sup>3</sup> during the vulcanization reaction. The effect of other dithiocarbamates was studied by employing equimolar quantities of the appropriate thiuram disulfide as the vulcanizing agent. The measured crack growth rates are listed in Table II, together with the value obtained on a control (acetone-extracted) vulcanizate C.

Two features of these results are noteworthy: the dithiocarbamates of low molecular weight appear to be more efficient, and the maximum reduction achieved is similar to that obtained with a corresponding amount of oleic acid.

Other metal dithiocarbamates were added to an acetone-extracted TMT vulcanizate by swelling with a dilute solution in diethyl ether, in order to examine their efficiency as rate-reducing agents. The materials employed were nickel dibutyl-dithiocarbamate and copper dialkyldithiocarbamate (Cumate). Although the original zinc dimethyldithiocarbamate seemed somewhat less efficient when added in this manner than when formed in situ, the present additives had no retarding action on crack growth at all. The efficiency of the dithiocarbamate thus seems to be quite sensitive to the nature of the substituents.

### Amines

The efficiencies of a number of amines were determined by measuring the rates of crack growth

TABLE II  
Effect of Zinc Dithiocarbamates on Rate of Crack Growth at 1 Mg. of Ozone/Liter

Thiuram disulfide	Mol. wt.	Wt. employed, %	Crack growth rate, mm./min.
Tetramethyl	240	3.0	0.09
Tetraethyl	296	3.7	0.15
Tetrabutyl	408	5.1	0.17
Tetrabenzyl	544	6.8	0.22
Dimethylphenyl	264	3.3	0.10
Dipentamethylene	330	4.1	0.11
Tetramethyl (C)	240	3.0	0.33

of samples of a peroxide vulcanizate having small amounts added by swelling, after acetone extraction. The results are given in Table III.

TABLE III  
Effect of Amines on Rate of Crack Growth at 1 mg. of Ozone per Liter

Additive	Wt. addn., %	Crack growth rate, mm./min.
None	—	0.35
Phenyl- $\beta$ -naphthylamine	1	0.17
<i>N,N'</i> -Dinaphthyl- <i>p</i> -phenylenediamine	1	0.35
<i>N,N'</i> -Dioctyl- <i>p</i> -phenylenediamine	1	0.21
<i>N</i> -isopropyl- <i>N'</i> -phenyl- <i>p</i> -phenylenediamine	2.3	0.10
<i>N</i> -cyclohexyl- <i>N'</i> -phenyl- <i>p</i> -phenylenediamine	2.0	0.12

With the exception of dinaphthyl-*p*-phenylenediamine, which is particularly insoluble in natural rubber, all the amines examined caused a marked reduction in the rate of crack growth. One of them, DOPPD, was studied at various concentrations by addition to the standard sulfur vulcanizate formulation (Mix A in Part I, without phenyl- $\beta$ -naphthylamine) prior to vulcanization. This particular additive was chosen because it is readily soluble and widely employed as an antiozonant. The experimentally determined crack growth rates are plotted in Figure 1b and are seen to be similar in magnitude and in the form of concentration dependence to those obtained with oleic acid.

### Quinoline Derivatives

Polymerized trimethylquinoline was found to be completely inactive, but 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ETDQ) caused marked reductions in the rate of crack growth. The effect of small quantities in a sulfur vulcanizate are shown in Figure 1c; they are seen to resemble closely the results obtained for oleic acid and DOPPD (Figs. 1a,1b).

### Other Additives

A number of other materials were examined. The radical acceptors hydroquinone, pyrogallol, and thio- $\beta$ -naphthol were found to have little if any effect. Dilauryl diselenide was found to be quite efficient, comparable to the other effective additives.

### Effect of Additives

It is clear that a wide variety of materials can retard the growth process in a similar manner, the most efficient of them causing the rate to be reduced to about one fifth of its original value when about 5% is present. Their action is not easily accounted for, however. It does not seem compatible with a simple scavenging hypothesis, in which the additive undergoes a separate and competitive reaction with ozone, since it is unlikely that the present additives all possess the same high order of reactivity necessary to account for their similar effect at low concentrations. The dependence on additive concentration also appears inconsistent with a simple competitive reaction.

It is interesting to note that a number of these additives are known to impede oxidation reactions. If the crack growth is considered to comprise two parts—molecular scission due to ozone attack and a subsidiary growth step involving oxidative reactions—the effect of such additives is readily accounted for without their direct reaction with ozone being invoked.<sup>4</sup> The carboxylic acids are not generally regarded as oxidation-inhibiting materials, however, and their action presumably is concerned with some other stage in the complex growth process.

### III. ADDITIVES THAT INCREASE THE CRITICAL ENERGY

In Part II, measurements of the critical energy for crack growth were reported for a number of (unprotected) polymers. The values were similar in magnitude and of the order of the surface free energy for simple liquids. The critical condition was therefore attributed to the surface energy requirement in crack growth.

It is somewhat surprising that chemical additives can cause large increases in this property, but certain materials have been found to do so. The action is specific to *N,N'*-dialkyl-*p*-phenylenediamines; neither the *N,N'*-diaryl nor the *N*-alkyl-*N'*-aryl-*p*-phenylenediamines appears to possess it to a comparable degree, if at all. The behavior of *N,N'*-dioctyl-*p*-phenylenediamine (DOPPD) is described below.

#### Measurements at Atmospheric Concentrations

The critical condition was assessed by determining the minimum tensile strain at which cracks formed in the surface of stretched sheets exposed to the outdoor atmosphere. This procedure was

adopted to avoid the difficulty of observing a single razor cut for long periods and maintaining it clean, i.e., free from dust. As described in Part II, the critical extensions are directly related to the critical applied stresses for a model test piece containing a small razor cut, by means of the vulcanizate stiffness and the size of flaw present in the surface. In order to minimize variations in the latter property, the exposed test piece surfaces were obtained by moulding against the same good-quality machined steel plate. The extensions at which cracks appeared were far from reproducible, however, as the ranges listed in Table IV show. The scatter is attributed to variations in flaw severity and ozone concentration.

The results show that a major increase in the critical extension to values higher than those encountered in normal service conditions is brought about by the incorporation of 2.5% of DOPPD. At extensions below the critical amounts no signs of cracking were present after exposure for one year, whereas the test pieces stretched above the critical amounts showed visible cracks after about one week. Thus, cracking either did not occur, or took place at a rate comparable to that for the unprotected vulcanizate; no time-dependent effects of the antiozonant action could be discerned. The protection which can be achieved therefore appears to be considerable, and relatively permanent.

At extensions somewhat above the new critical amount, the number of sites at which a flaw exists

TABLE IV  
Critical Extensions for Surface Cracking on Exposure to an Outdoor Atmosphere

DOPPD concn., %	Crit. extension, %
0	6 to 8
0.5	7 to 15
1.0	7 to 15
1.5	10 to 15
2.0	30 to 80
2.5	>200

of sufficient magnitude to allow crack growth is small, and hence few cracks form. Thus, the very severe condition of one or two deep cracks, which arises in unprotected rubbers at extensions of the order of 10%, may, in inadequately protected vulcanizates, be translated to the extension range encountered in service of, say, 50%. If no protection had been attempted, many small cracks would have formed at this extension—a state that may well be considered preferable. The use of inade-

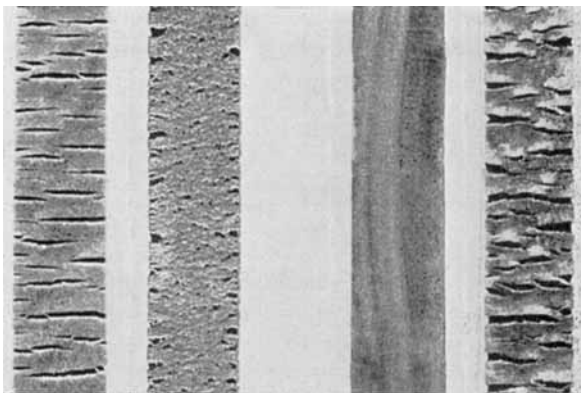


Fig. 2. Cracking in an unprotected vulcanizate (left-hand pair) and one containing 2% DOPPD (right-hand pair). Left-hand test piece of each pair at 10% extension, right-hand test piece of each pair at 40% extension.

quate amounts of antiozonant would therefore be detrimental. This situation is illustrated in Figure 2.

The similarity in Figure 2 of the cracking pattern at 10% extension in the unprotected vulcanizate and 40% in the protected one indicates the amount by which the critical condition has been increased.

#### Effect of Ozone Concentration

The applied stress  $S_c$  necessary to cause a razor cut 2 mm. long to grow as an ozone crack was determined at various ozone concentrations in the range 0.2 to 2.5 mg./l. A standard sulfur vulcanizate of natural rubber was employed, with 6, 7.5, and 10 parts by weight of DOPPD included in the mix formulation. The test pieces were inserted into the test chamber after the test concentration had been achieved so that only the disturbance due to the removal and replacement of the test chamber lid occurred. This procedure was adopted to minimize the period of exposure to ozone concentrations below the desired level. A disconcerting "conditioning" effect was found when prior exposure to low concentrations was permitted; it is described in a later section.

The experimentally determined critical stresses are plotted in Figure 3 against the ozone concentration employed. The constant value obtained for the corresponding unprotected vulcanizate is represented by the horizontal broken line.

Two features are clear. The critical stress is extremely large at low concentrations of ozone, but it falls sharply over a narrow range of concentration to a value only slightly higher than the unprotected level. The ozone concentration at

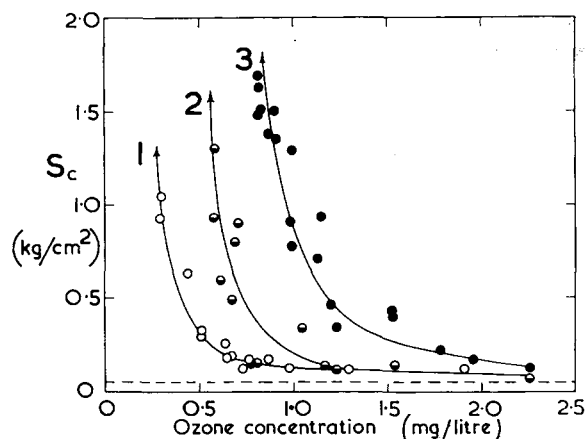


Fig. 3. Dependence of critical applied stress for crack growth upon ozone concentration, for various additions of DOPPD: (1) 6% addition, (2) 7.5%, (3) 10%.

which the critical stress is  $0.5 \text{ kg./cm.}^2$ , i.e., only about ten times the unprotected level, may be considered to represent a limiting value, since protection is virtually absent at concentrations slightly higher than this. The limiting values increase with the amount of DOPPD present, being approximately 0.4, 0.75, and 1.2 mg./l. for 6, 7.5, and 10% by weight of DOPPD. The dependence is clearly not a simple proportionality; as described above, about 2.5% of DOPPD is necessary to confer substantial protection at atmospheric concentrations of the order of  $10^{-4} \text{ mg./l.}$

#### Behavior in Different Polymers.

Hitherto, the effect of DOPPD in natural rubber vulcanizates has been described. Similar behavior was observed in vulcanizates of a butadiene-styrene copolymer (75:25, Polysar S) and polychloroprene (Neoprene W), as shown in Figure 4, where experimental measurements of critical stress are plotted against the concentration of ozone. The limiting ozone concentration seems somewhat lower for the butadiene-styrene copolymer, however.

The action of DOPPD in vulcanizates of two other polymers was found to be extremely small in comparison. In butadiene-acrylonitrile copolymers hardly any protection was obtained for acrylonitrile contents ranging from 27 to 40%. This did not appear to be due to the low molecular mobility of these polymers since the antiozonant action was no greater at a temperature of  $50^\circ\text{C.}$ , or in a plasticized vulcanizate. Furthermore, incorporating the antiozonant by swelling the vul-

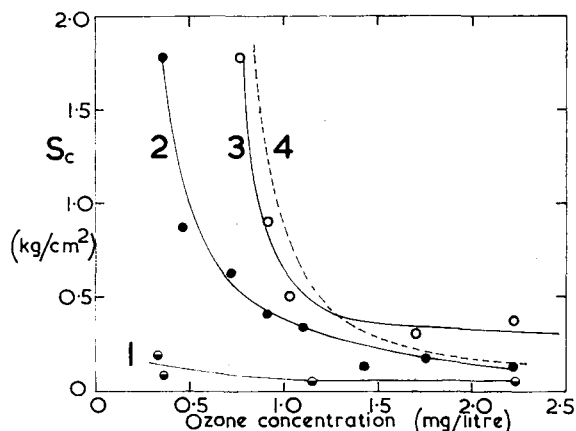


Fig. 4. Dependence of critical applied stress for crack growth upon the ozone concentration for vulcanizates of several polymers containing 10% of DOPPD: (1) butadiene-acrylonitrile copolymer (70/30, Polysar Krynac 802), (2) butadiene-styrene copolymer (75/25, Polysar S), (3) polychloroprene (Neoprene W), (4) natural rubber.

canized polymer with an acetone solution and then removing the solvent did not give improved results, indicating that the low efficiency was not a consequence of interaction between the DOPPD and the vulcanization ingredients. A similar lack of effect was found in a vulcanizate of butyl rubber (Polysar Butyl 400) when the antiozonant was added similarly, from a diethyl ether solution. It is not clear why the antiozonant should have no significant effect in these polymers, under conditions in which considerable effects are observed in natural rubber, polychloroprene and a butadiene-styrene copolymer.

#### Conditioning Effects at Low Ozone Concentrations

The effect of prior exposure to a low concentration of ozone on the critical stress for crack growth at a higher concentration first became apparent when different test procedures were compared. In Figure 5 the critical stress values for crack growth in a natural rubber vulcanizate containing 6% of DOPPD is plotted against the concentration of ozone in the test atmosphere. Three different methods of test were employed.

1. The unstretched test piece was placed in the test chamber and the ozonized gas stream diverted through it. After a sufficient interval, of the order of five minutes, to allow steady conditions to be established, a load was applied to the test piece by a release mechanism. The applied stresses necessary to cause crack growth when applied in this way are represented by crosses in Figure 5.

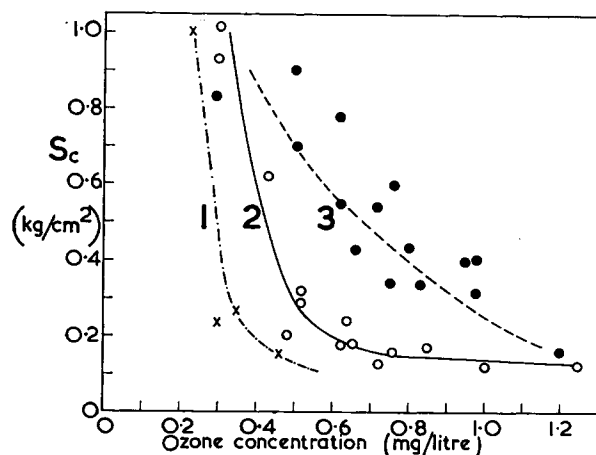


Fig. 5. Dependence of critical applied stress for crack growth upon the ozone concentration, using different test methods: (1) stress applied to test piece in a steady concentration of ozone, (2) stressed test piece placed in ozonized atmosphere, (3) stressed test piece exposed initially to zero concentration of ozone, the steady value being attained in about 3 min.

2. The test piece with the test load attached was rapidly inserted into the test chamber after the steady ozone concentration had been achieved. The process of opening and closing the test chamber lid would, no doubt, lead to a momentary loss of ozone, so that the stretched test piece would be exposed initially to a somewhat lower concentration than intended. The corresponding critical stress values are represented by open circles in Figure 5; they are seen to be similar in form to the previous results, but are displaced toward somewhat higher concentrations of ozone.

3. The test piece under load was inserted into the ozone-free test chamber, and the gas stream then diverted through it. Due to the size of test chamber and the rate of gas flow, a period of about three minutes was required before the appropriate steady ozone concentration was achieved in the entire chamber. The critical stress values obtained in this way are represented by filled-in circles in Figure 5; they are seen to lie at markedly higher ozone concentrations than corresponding values obtained by methods 1 and 2.

It thus appears that in the stretched state a short period of exposure to low ozone concentrations confers protection at higher ones, where no appreciable protection would be found if the same concentrations were developed abruptly. A comparison of results from methods 1 and 2 suggests that this conditioning effect is only significant if the test pieces are exposed in the stressed state, no

protection being obtained by prior exposure to low ozone concentrations in the unstressed state.

The following additional experiments were carried out, to examine these conclusions. A test piece subjected to an applied stress of approximately 1 kg./cm.<sup>2</sup> was exposed to an ozone concentration of 0.2 mg./l. for a period of about five minutes. No crack growth was observed, as expected, because the critical stress at this concentration is appreciably higher than the imposed stress (Figs. 3 and 5). The concentration was then increased to 2 mg./l., without disturbing the test piece. No crack growth occurred in consequence, although the applied stress was now some six times larger than the small critical value normally measured at this concentration, about 0.15 kg./cm.<sup>2</sup>.

Growth could, however, be brought about by a substantial disturbance of the test piece, imposing higher stresses momentarily. Also, exposure under small applied stresses at the low concentration of ozone, followed by the imposition of additional loads at the high concentration, resulted in crack growth.

These observations suggest that an ozone-resistant layer is created at the crack tip when protection occurs, and this layer prevents ozone attack subsequently, even at high concentrations. The layer seems to be rather weak; it does not survive a substantial deformation of the crack tip.

In a separate experiment, the reaction products of DOPPD with ozone were swollen into an unprotected vulcanizate. The critical stress values were not significantly increased. Thus, the conditioning phenomenon can not be attributed to the direct reaction of ozone with the antiozonant. A possible mechanism is advanced below.

### Mechanism of Action of DOPPD

It is known that DOPPD reacts readily with ozone, and presumably for this reason it has been suggested that DOPPD acts by competitive ozonolysis, thus "scavenging" ozone. This seems improbable for the following reasons.

1. The nature of the protection is not in accord with a simple scavenging mechanism, in which a reduction in *rate* might well be expected, but not an increase in critical energy. The latter effect is, however, the important action of DOPPD.

2. A material which is still more reactive toward ozone, dilauryl selenide,<sup>5</sup> was found to have no protective action.

A simple mechanism accounting for the action of DOPPD as described in preceding sections, is advanced below.

Three reactions are proposed as occurring at the crack tip. The first is the direct reaction of ozone with the rubber, resulting in molecular scission and the formation of ozonized rubber. The second is a direct reaction of ozone with the antiozonant, yielding an inactive product, as the experiments with ozonized DOPPD indicate; this reaction is thus a wasteful one. The third reaction proposed is a combination of the antiozonant with the ozonized rubber, yielding a stable coherent material. It is noteworthy in this connection that the effective antiozonants are bifunctional in character.

This mechanism accounts qualitatively for the observed dependence of protection upon the concentration of ozone. At high concentrations the loss of antiozonant by the second reaction is increased, and ozonolysis of the rubber is also increased, so that the stabilization of a significant fraction of the product is unlikely. Failure to protect at high concentrations would therefore be expected.

Moreover, the formation of a stable layer under suitable conditions would confer protection subsequently, provided the protective layer was not disrupted. The conditioning phenomenon which has been described would therefore be anticipated. Also, the concept of a protective layer accounts satisfactorily for the long life shown by protected test pieces.

Thus, the varied experimental results are in accord with the proposed hypothetical mechanism, and the postulated reactions do not seem improbable although there is as yet no chemical evidence that the third reaction occurs.

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### Synopsis

The character and extent of protection by certain additives (antiozonants) have been investigated for a number of vulcanized rubbers over a wide range of ozone concentrations. Two distinct modes of action are found: a reduction in the rate of crack growth and an increase in the critical energy necessary for attack to occur. Neither seems explicable on a simple hypothesis of scavenging. Several materials which act in the first manner have been examined. They were found to be similar in effect, reducing the growth rate to about one fifth of its original value when a sufficient amount of the additive was present. The mechanism is obscure. Certain additives, notably *N,N'*-dioctyl-*p*-phenylenediamine, also cause a striking and important increase in the critical energy condition. The circumstances under which this occurs have been studied, and a tentative hypothesis for the mode of action is advanced.

### Résumé

On étudie le genre et la portée d'une protection de caoutchoucs vulcanisés par adjonction de certains produits (antiozonisants), dans un large domaine de concentrations d'ozone. On a trouvé schémas différents de réaction: une réduction de la vitesse de croissance des craquelures et une augmentation de l'énergie critique pour que la réaction se fasse. Un certain nombre de composés qui agissent de la première façon ont été examinés. On a trouvé que leur effet est fort similaire, c.à.d. entraîne une réduction de la vitesse de croissance au cinquième de sa valeur originale, dès qu'une quantité suffisante du produit y est ajoutée. Le mécanisme reste toutefois obscur. Certains additifs, notamment la *N,N'*-dioctyl-*p*-phénylène diamine, provoquent une augmentation marquée et assez étrange de l'énergie critique. Les conditions dans lesquelles ceci se passe ont été étudiées, et une hypothèse provisoire concernant ce mode d'action a été suggérée.

### Zusammenfassung

Der Charakter und die Schutzwirkung bestimmter Additivs (Antiozonate) wurden an einigen vulkanisierten Kautschukarten über einen grossen Konzentrationsbereich an Ozon untersucht. Es wurden zwei bestimmte Einwirkungsarten gefunden: Eine Verminderung der Geschwindigkeit des Risswachstums und eine Erhöhung der für einen Angriff notwendigen kritischen Energie. Keine der beiden scheint durch eine einfache Abfängerhypothese erklärbar zu sein. Es wurden einige Stoffe untersucht, die in der beschriebenen Art wirksam sind. Es wurde gefunden, dass sie in ihrer Wirkung ähnlich sind: Sie setzen bei Anwesenheit einer genügend grossen Additivmenge die Wachstumsgeschwindigkeit auf ungefähr  $\frac{1}{5}$  des ursprünglichen Wertes herab. Der Mechanismus ist undurchsichtig. Bestimmte Additivs, besonders *N,N'*-Dioctyl-*p*-phenylenediamin, verursachen ebenfalls ein auffallendes und starkes Anstigen der kritischen Energie. Die Bedingungen für das Auftreten dieser Erscheinungen wurden untersucht und eine Hypothese für den Wirkungsmechanismus wird versuchsweise vorgeschlagen.

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