

The Attack of Ozone on Stretched Rubber Vulcanizates.

I. The Rate of Cut Growth

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(With an Appendix by E. D. FARLIE)

INTRODUCTION

The growth of cracks in the surface of stretched components of vulcanized rubber on exposure to the atmosphere is a serious deficiency. It detracts from the appearance, serviceability, and strength, and may lead to early failure. A comprehensive review of the process and the evidence for attributing it to the action of ozone in the atmosphere has been given by Newton,¹ the following features being established.

(1) The action of ozone on unstretched rubber is slight, no cracks being formed.

(2) At small extensions, of the order of 10%, cracks appear and grow to form large incisions in the exposed surface.

(3) At higher extensions, the number of cracks is larger, but their final size is smaller due to mutual interference. The deterioration of the rubber may be considered less serious, therefore, since the component possesses a finely etched surface rather than one containing a few large cuts.

The basic process appears to consist of the initiation and propagation of a single incision in a deformed rubber under the action of an atmosphere containing ozone. However, the experimental studies that have been reported previously have been concerned with the gross deterioration of an exposed surface when many cracks form simultaneously. It is difficult to deduce from such observations the behavior of a growing incision for the following reasons.

Firstly, the presence of a crack will alter the surface deformations in its neighborhood, and hence may seriously affect the growth of nearby cracks.² Secondly, cracks formed on the surface grow simultaneously in length and in depth, the deformation in the region of the growing edges presumably varying with the crack shape as well as with its size. Thirdly, the cracks may propagate by ozone attack

at the growing tips and also by attack at points on the surface in close proximity to them. Finally, it is likely that surface irregularities will affect the local deformation, while foreign materials such as dust, decomposition products, or "bloomed" ingredients of the rubber compound may affect the access of ozone.

Although these effects may be of importance in determining the gross deterioration of the surface, it seems reasonable to consider them separately from the basic process. An attempt has therefore been made to examine the latter. In the present part, an experimental study is described of the factors that determine the rate of propagation of a single incision in a thin sheet of rubber. In a subsequent part³ an examination of the conditions which determine whether a crack will form or, being present, will grow is reported.

EXPERIMENTAL METHOD

Conditions of Exposure

The experimental arrangement for producing a steady flow of ozonized oxygen through the test chamber was constructed by E. D. Farlie of these laboratories. It is described in the Appendix, together with the method used for estimating the ozone concentration employed, which ranged from 0.2 to 2.5 mg./l. The rate of flow of gas through the test chamber was held constant at about 25 l/hr. The volume of the test chamber was about 1 l. The gas pressure in the apparatus was only about 1 cm. head of water in excess of atmospheric pressure.

In order to carry out measurements at temperatures other than ambient, the test chamber was placed either in a heated water bath or in a bath containing a mixture of ice and water. The incoming gas stream was warmed or cooled before

entering the test chamber by passing through a long glass tube immersed in the bath.

Measurement of Rate of Growth of an Incision

The test pieces consisted of rubber strips 1.5 cm wide and 7 cm. long. They were cut from vulcanized rubber sheets, for which the mix formulations and vulcanization conditions are given in Table I.

TABLE I
Mix Formulations and Vulcanization Conditions^a

	Composition, parts by weight				
	Mix A	Mix B	Mix C	Mix D	Mix E
Natural rubber (smoked sheet)	100	—	—	—	—
Butadiene-styrene copolymer (75/25) (Polysar S)	—	100	—	—	—
Butadiene-acrylonitrile copolymer (60/40) (Polysar Krynac 801)	—	—	100	—	—
Butyl rubber (Polysar Butyl 400)	—	—	—	100	—
Polychloroprene (Neoprene GN)	—	—	—	—	100
Zinc oxide	5	5	3	5	5
Stearic acid	1	1	0.5	1	2
Sulfur	2.5	2	1.5	—	—
<i>N</i> -Cyclohexylbenzthiazolesulfenamide	0.6	0.8	—	—	—
Dibenzthiazyl disulfide	—	—	1.0	—	—
Tetramethyl thiuram disulfide	—	—	—	4	—
Light calcined magnesia	—	—	—	—	5
Phenyl- β -naphthylamine	1	1	—	—	1
Vulcanization time at 140°C., min.	40	40	50	50	50

^a Mix formulations A' to E' were as A to E, respectively, but contained, in addition, 25 parts of diethylhexyl adipate and 50 parts of whiting.

The test pieces were secured by two light aluminum clamps so that the free length between the clamps was 5 cm. The upper clamp was suspended from a hook in the test chamber roof, and weights were added to the lower clamp to place the central region of the test piece in a state of simple extension. In order to produce a single incision at a convenient position, a small razor cut was made in the center of one edge of the test piece, the surfaces and edges elsewhere being liberally coated with

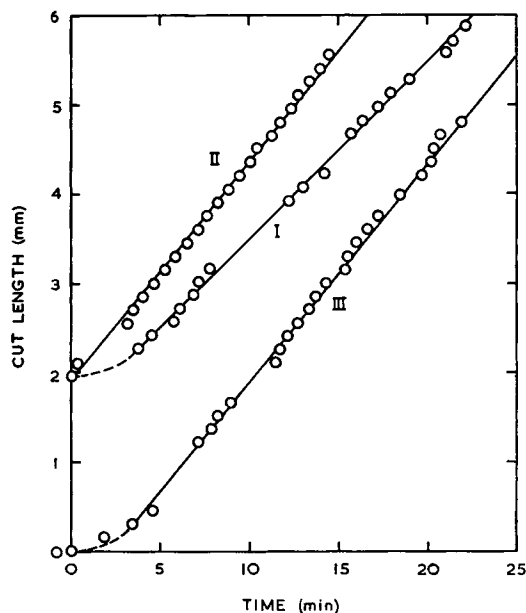


Fig. 1. Cut growth in an atmosphere containing ozone: (I) initial cut 2 mm. long, time measured from the entry of ozone into the test chamber containing the stretched test piece; (II) initial cut 2 mm. long, time measured from the application of a tensile stress in a steady atmosphere containing ozone; (III) no initial cut, time measured as in (I).

a silicone stopcock grease to prevent ozone attack. A low-power microscope was used to observe the tip of the razor cut and its growth across the test piece under the action of an atmosphere containing ozone.

It was found that, unless a characteristic well-defined value of the tensile load was exceeded, no growth took place. This feature is discussed in a subsequent part.³ When the applied tensile stress was adequately large, however, the cut grew linearly across the test piece, finally severing it into two equal pieces. For the major part of its course, the cut grew at a fairly uniform rate, as is shown in Figure 1 (curve I), where the measured cut length is plotted against time for a natural rubber vulcanizate A.

The apparent induction period seen in curve I is attributed to the interval required for the ozone concentration to reach a steady level in the neighborhood of the test piece, after the gas stream is diverted into the test chamber. To verify this, a similar test piece was subjected to the tensile load after the gas stream had been passing for about ten minutes. The resulting progress of the cut is shown in Figure 1 (curve II). It is clear that growth starts immediately at a steady rate.

In order to confirm that the use of a small razor cut to locate the crack did not affect the subsequent growth, a test piece was prepared without a razor cut. A small region in the center of one edge was left ungreased, and, when a considerably larger tensile load than before was imposed, a cut formed at this site and grew across the test piece under the action of the ozonized atmosphere. The cut length is plotted in Figure I (curve III), against time from the entry of the gas stream. The rate of growth is seen to be similar to the previous values.

A series of measurements were made of the rates of cut growth when various loads were applied to the test piece containing a small razor cut about 0.2 cm. long. As the imposed stress increased the region around the cut tip subject to attack became increasingly large, and the growing cut changed from a sharp incision to the coarse erosion of a relatively wide strip. However, the rate of propagation was found to be substantially constant for a wide range of imposed stresses, extending from that necessary for the initial cut to grow at all, about 70 g./cm.², up to a value about ten times as large.

When very large values of tensile stress were imposed, of the order of 2000 g./cm.², the rate of cut growth was appreciably larger and less well-defined, as might be expected when the imposed stress approaches that required to make the razor cut propagate by simple tearing in the absence of ozone.

For all the vulcanized rubbers examined the rate of cut growth was found to be substantially constant over a considerable range of applied stress, above the minimum value necessary for cut growth to occur. It was also found to be largely independent of the test-piece thickness over the range 0.02–0.2 cm., and hence may be considered appropriate to growth through the bulk rubber. A standard test-piece thickness of about 0.08 cm. was chosen for the experiments described subsequently.

In a large number of similar determinations of the rate of cut growth, the measured values were found to vary within the range of $\pm 20\%$ of the mean. This was not considered unacceptable, since relatively large differences in the observed rates were being examined. The scatter is attributed partly to variations in the efficacy of the greasing procedure and partly to fluctuations in the concentration of ozone.

It appears, therefore, that the action of ozone on a stretched rubber vulcanizate can be described

by a single parameter, the rate of linear growth of an incision. The effect of the conditions of exposure and the chemical composition of the vulcanizate on this quantity are described below.

Test Conditions

The characteristic rates of cut growth were determined at the normal ozone concentration (1.15 mg./l.) and at ambient temperature for test pieces of a number of vulcanized rubbers. The test pieces were about 0.08 cm. thick and thoroughly greased on their major surfaces in an attempt to obtain rates characteristic of growth through the bulk. The applied stresses were sufficiently small that the measured rates may be considered typical of the rubbers under light stresses, i.e., where the rate is independent of the applied stress.

EFFECT OF TEST-PIECE COMPOSITION

Effect of Naturally-Occurring Impurities

The measured rate for a dicumyl peroxide vulcanizate of natural rubber (0.08 mm./min.) was found to be markedly lower than that for a conventional sulfur vulcanizate A (0.22 mm./min.) at an equivalent degree of crosslinking. After extraction with hot acetone for 24 hr. in an atmosphere of nitrogen, however, the rates were closely similar, 0.31 and 0.29 mm./min., respectively. The rates were also found to be of this order for both materials when extracted rubber was used in the mix formulations. It appears, therefore, that some acetone-soluble impurity is present in smoked sheet rubber and is capable of surviving the vulcanization reaction when a peroxide system is employed to retard cut growth in the vulcanizate. A conventional sulfur vulcanizing system appears to destroy its efficacy to a large extent, since subsequent extraction has a much smaller effect on a sulfur vulcanizate than on a peroxide vulcanizate.

A peroxide vulcanizate prepared from extracted raw rubber (rate of cut growth of 0.33 mm./min.) was swollen in a benzene solution of the extract, after which the benzene was pumped off, to leave the raw rubber extract in the vulcanizate. The rate of cut growth was then found to be 0.07 mm./min.; this confirms that the extract contained a potent impurity.

In order to ascertain what natural impurities may act as rate-reducing agents, small amounts of various substances which have been identified in the acetone extract of smoked sheet rubber⁴ were

added on an open mill to samples of extracted rubber. Peroxide vulcanizates were then prepared and the rates of cut growth determined. It was found that oleic acid effectively retarded cut growth in the vulcanizate, linoleic, and stearic acids, although significantly active, being considerably less efficient. When, for example, 1% of oleic acid was added to the extracted rubber prior to vulcanization with a peroxide system, the measured rate of cut growth for the vulcanizate was found to be 0.105 mm./min., which is near the value obtained when unextracted rubber was used.

Oleic acid (1%) was also added to a test piece of a conventional sulfur vulcanizate A by swelling in from a benzene solution. The measured rate (0.09 mm./min.) was comparable to that observed for peroxide vulcanizates.

It seems clear, therefore, that certain impurities present in smoked sheet rubber, notably oleic acid, are capable of reducing the rate of cut growth by a factor of about three. In conventional vulcanizates their action is largely suppressed, presumably because they react with the compounding ingredients.

The rate of cut growth for a peroxide vulcanizate of a butadiene-styrene copolymer (75/25 Polysar S) was also found to be much lower than the value for a sulfur vulcanizate B crosslinked to an equivalent degree. The values obtained after acetone extraction of the vulcanizates were closely similar, however. It seems probable that the cause is similar to that deduced for the natural rubber, namely, the presence in the raw polymer of a rate-reducing impurity.

Effect of Vulcanization with TMT

The rate of cut growth for extracted natural rubber vulcanized with tetramethylthiuram disulfide (TMT), zinc oxide, and stearic acid was also found to be small, i.e., 0.08 mm./min. After extracting the vulcanizate the measured rate was 0.32 mm./min., which is closely comparable with that found for conventional sulfur vulcanizates of a similar degree of crosslinking.

It is known that zinc dimethyldithiocarbamate is formed during the TMT vulcanization reaction. A small quantity (about 3%) of this material was therefore added to the extracted vulcanizate by swelling in from a chloroform solution. The rate of cut growth was then found to be reduced to 0.16 mm./min. It appears, therefore, that an acetone-soluble reaction product of TMT, probably

zinc dimethyldithiocarbamate, can be effective in reducing the rate of cut growth.

TMT vulcanizates have been reported⁵ to show greater resistance to ozone than conventional ones in exposure tests. This is probably due to the lower rate of crack propagation reported above.

The mode of action of such dissimilar materials as zinc dimethyldithiocarbamate and oleic acid is obscure. However, the maximum effect obtained, a reduction in rate by a factor of about three, is small in comparison with the large effects considered in later sections.

Effect of Crosslinking

A number of peroxide and accelerated-sulfur vulcanizates of natural rubber and Polysar S, a butadiene-styrene copolymer (75/25), were extracted with acetone and the rates of cut growth measured. The corresponding degree of crosslinking of each test piece was characterized by a measurement of stiffness, the tensile stress necessary to extend the test piece by 25% being determined.

In Figure 2 the rate of cut growth is plotted against the stress at 25% elongation for the vulcanizates of natural rubber and the butadiene-styrene copolymer. It is seen that the rates of cut growth for the two polymers are virtually identical at equivalent degrees of crosslinking. Also, a direct relationship between the rate of cut growth and the degree of crosslinking appears to obtain, the rate decreasing by a factor of about six as the degree of crosslinking increases from an impractically low level to a relatively high one. Only a relatively small variation of the rate of cut growth (a factor of two or three) would be ex-

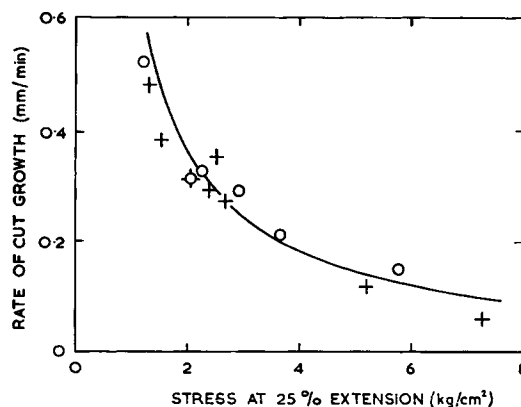


Fig. 2. Experimental relation between the rate of cut growth and the vulcanizate stiffness (stress at 25% extension) for acetone-extracted vulcanizates of (O) natural rubber and (+) butadiene-styrene copolymer.

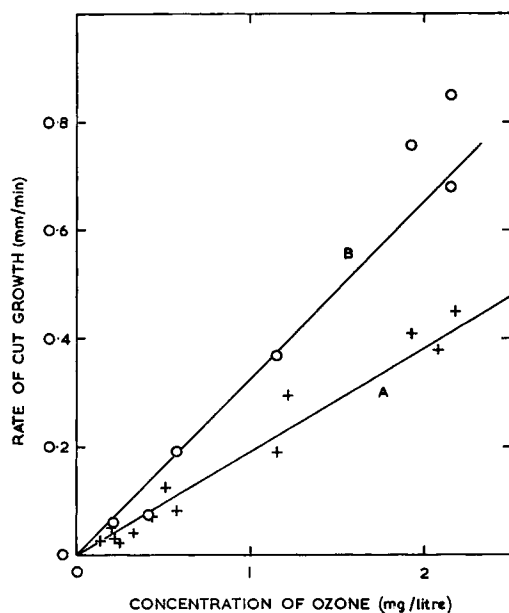


Fig. 3. Experimental relations between the rate of cut growth and the concentration of ozone for vulcanizates of (+) natural rubber A and (O) butadiene-styrene copolymer B.

pected due to changes in the degree of crosslinking within the conventional range.

The rate of cut growth was found to be inversely proportional to the stress at 25% elongation, i.e., to the number of network chains in unit volume, to a first approximation (Fig. 2). It is therefore inversely proportional to the number of chains crossing a randomly positioned plane, as, for example, the plane of propagation of the cut. It seems reasonable that the rate of progress of an ozone cut should vary inversely with the number of chains which have to be severed.

Effect of Filler

Test pieces were prepared from natural rubber mix formulations similar to A but containing, in addition, 45 parts by weight of carbon black (Philblack 0) and 50 parts by weight of whiting, per hundred parts of rubber. It was found necessary to impose markedly higher tensile stresses in order to make a cut grow at all in the ozone atmosphere, and this feature is discussed in a subsequent paper.³ However, the measured rates of cut growth, 0.30 and 0.28 mm./min., respectively, are similar to the value obtained for the unfilled vulcanizate A (0.23 mm./min.), and it appears, therefore, that large quantities of these fillers do not materially affect the characteristic rate of cut growth.

Effect of Polymer

The rates of cut growth were determined on standard test pieces cut from vulcanized sheets of a number of different polymers. The measured rates are listed in Table II.

TABLE II
Rates of Cut Growth for Vulcanizates of Various Polymers

Polymer	Mix reference	Rate of cut growth, mm./min. at 1.15 mg. ozone/l.
Vulcanizates Containing No Plasticizer		
Butadiene-styrene copolymer (95/5)	—	0.22
Butadiene-styrene copolymer (75/25) (Polysar S)	B	0.37
Natural rubber	A	0.22
Synthetic polyisoprene	—	0.245
Butadiene-acrylonitrile copolymer (82/18)	—	0.22
Butadiene-acrylonitrile copolymer (70/30)	—	0.055
Butadiene-acrylonitrile copolymer (60/40) (Polysar Krynac 801)	C	0.04
Butyl rubber (Polysar Butyl 400)	D	0.02
Polychloroprene (Neoprene GN)	E	ca. 0.01
Gutta-percha	—	0
Chlorosulfonated polyethylene (Hypalon)	—	0
Vulcanizates Containing 25 Parts of Diethylhexyl Adipate		
Butadiene-styrene copolymer (75/25) (Polysar S)	B'	0.40
Natural rubber	A'	0.26
Butadiene-acrylonitrile copolymer (60/40) (Polysar Krynac 801)	C'	0.20
Butyl rubber (Polysar Butyl 400)	D'	0.24
Polychloroprene (Neoprene GN)	E'	0.05

It appears that the relative resistance to ozone of these rubbers can be associated, at least in part, with the relative rates of cut propagation. Butyl rubber and neoprene, for example, are commonly considered to be ozone-resistant, and the rates are seen to be an order of magnitude lower than for natural rubber and the butadiene-styrene copolymers.

For the butadiene-acrylonitrile copolymers the rate is seen to decrease markedly as the proportion of acrylonitrile increases. It is well known that the molecular mobility decreases also, as is evidenced by a corresponding rise in the rubber-to-glass transition temperature. It seems possible that the observed changes in rate arise from changes in the internal viscosity of the polymer. To examine this, the effect of increasing the molecular mobility by plasticization was studied.

Effect of Plasticization

Vulcanized test pieces were prepared similar to those described above but containing, in addition, 25 parts by weight of an ester plasticizer, diethylhexyl adipate, per hundred parts of polymer. Also, 50 parts by weight of an inert filler, whiting, were added to assist the incorporation of the plasticizer; it has been noted earlier that this ingredient appears to have virtually no effect on the cut growth rate.

The measured rates of cut growth for the plasticized materials are given in Table II for comparison with the original values. Natural rubber and the 75/25 butadiene-styrene copolymer which were originally subject to rapid cut growth are seen to be little affected by plasticization. However, the relatively viscous polymers, butyl rubber and the 60/40 butadiene-acrylonitrile copolymer, exhibited cut growth rates many times larger than before, and similar to that for the first two materials. It appears, therefore, that the low rates observed for the unplasticized materials are primarily due to their high internal viscosity.

The plasticized polychloroprene is seen to show more rapid cut growth than the unplasticized sample, but the value is still very low.

EFFECT OF TEST TEMPERATURE AND OZONE CONCENTRATION

Effect of Temperature of Test

Measurements were made of the characteristic rates of crack growth for a number of the vulcanized rubbers described in the previous section, at several temperatures in the range 0–80°C. The ozone concentration employed was 1.15 mg./l.

The results obtained for four of the materials at temperatures of 2, 20, and 50°C. are given in Table III. Erratic cut growth was found at 80°C. for all the materials except the natural rubber vulcanizate, probably due to incipient tearing. The results obtained were generally similar to those

at 50°C. Similar difficulties were experienced with the plasticized materials at elevated temperatures, probably due to the same cause, but the measurements again indicated that substantially the same rates of cut growth obtained over the temperature range 20–80°C.

TABLE III
Rates of Cut Growth for Four Polymers at 2, 20, and 50°C.

Mix reference	Cut growth, mm./min.		
	2°C.	20°C.	50°C.
A	0.15	0.22	0.19
B	0.13	0.37	0.34
C	0.004	0.04	0.23
D	—	0.02	0.16

It is seen in Table III that the rates of cut growth for the relatively viscous materials C and D are strongly dependent on temperature. This is in accord with the conclusion of the previous section, that the internal viscosity determines the rate of cut growth for these materials.

It also appears that, provided a minimum degree of segmental mobility is present, further increases in mobility do not act to increase the rate of cut growth. Natural rubber A and the 75/25 butadiene-styrene copolymer B appear to possess adequate molecular mobility, even at 2°C., although the cut growth is somewhat retarded at this temperature, particularly for the latter material. In consequence, raising the test temperature and incorporating plasticizer have only minor effects on the rate of cut growth. In butyl rubber D and the 60/40 butadiene-acrylonitrile copolymer C, on the other hand, the motion of molecular segments appears to be so slow under normal conditions that it restricts the rate at which a cut can advance. Hence it is only at elevated temperatures or when plasticizer is incorporated, that the molecular mobility becomes sufficiently great to cause no impediment to the progress of the cut. Thereafter, further increases in molecular mobility have no effect.

It might be concluded that the four polymers have similar reactivities to ozone, since the maximum rates attained are not dissimilar, namely 0.2–0.4 mm./min. It seems probable, however, that the reactivities are sufficiently high for the maximum rates to be governed largely by the rate of incidence of ozone, the reaction of each incident molecule being completed before the arrival of the next.

The rates of cut growth for the neoprene test pieces were found to be somewhat increased by raising the temperature, although at 80°C. the rate was still relatively low (of the order of 0.05 mm./min.). The markedly lower rates, which are retained at elevated temperatures and after plasticization, indicate that the intrinsic reactivity of this material is considerably smaller, as its chemical composition might suggest.

It is interesting to note that no growth could be induced in crosslinked gutta-percha at room temperature when the material is highly crystalline. At 80°C., however, when it is amorphous and rubberlike, cut growth took place at a rate comparable to that for the natural rubber vulcanizates. This behavior also suggests that no cut growth can occur if the polymer chains are immobile.

Effect of Ozone Concentration

The characteristic rates of cut growth were determined over a range of ozone concentrations at ambient temperature. The concentrations employed ranged from about 0.1 to 2.5 mg. of ozone/l.

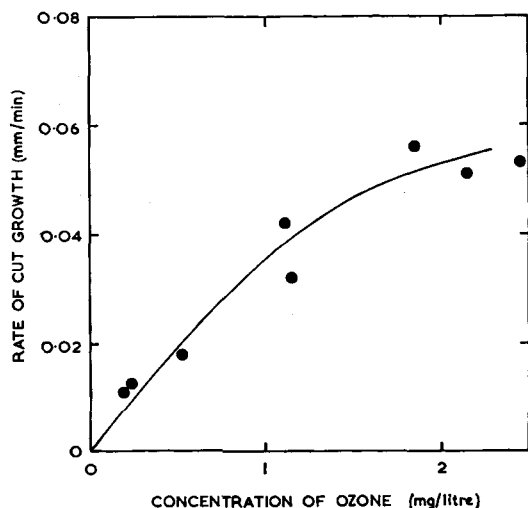


Fig. 4. Experimental relation between the rate of cut growth and the concentration of ozone for a butadiene-acrylonitrile copolymer C.

In Figure 3 the rate of cut growth is plotted against the ozone concentration for natural rubber A and the 75/25 butadiene-styrene copolymer B, representative of relatively rapidly-attacked materials. Substantially linear relations are seen to obtain within the limited experimental accuracy, the rate of cut growth being directly proportional to the concentration of ozone. A similar depend-

ence was found to obtain for the plasticized polymers. The rates for the more slowly attacked polymers were found to increase with increasing concentration also, but the measurements were, in general, insufficiently accurate to establish the form of dependence. The measurements for the 60/40 butadiene-acrylonitrile copolymer C are plotted in Figure 4, and are seen to suggest a departure from linearity at high concentrations, the rates being lower than a linear relation would predict.

The direct proportionality found for the vulcanized natural rubber A, for example, may be used to obtain a rough estimate of the effects of exposure to a normal outdoor atmosphere, where the concentration of ozone is about 7×10^{-5} mg./l.¹ The corresponding rate of cut growth is predicted to be about 1.3×10^{-5} mm./min., by means of the linear relation shown in Figure 3. Hence, the first signs of deterioration, which might be taken as the presence of surface cracks 0.2 mm. long, would be noticed after 7.5×10^3 min. (about 5 days). This figure is in good agreement with observations of the time necessary for visible deterioration to occur in outdoor exposure tests.

It has been noted in the preceding section that the rates of cut growth in natural rubber, the butadiene polymers, and butyl rubber are similar when the restricting effect of hindered molecular motion is overcome by plasticization or raising the temperature. It now appears that the rate depends directly on the concentration of ozone, so that for the four polymers the rate is given approximately by (0.2 mm./min.)/mg. of ozone/l.

CUT GROWTH IN THIN TEST PIECES

The study of cut growth in various materials and under various exposure conditions was carried out with specimens greased on their major surfaces to restrict the attack of ozone to the tip of the growing cut. A subsidiary series of measurements was made using test pieces of the natural rubber vulcanizate A, with a narrow central strip across the test piece (the region through which the cut advanced) left *ungreased*, since this is more representative of conventional test methods.

It was found in preliminary experiments that cracks tended to form ahead of the growing incision, particularly in the thinner test pieces, yielding high, irregular rates of growth. This difficulty was overcome by the use of test pieces cut from sheets molded between clean glass plates

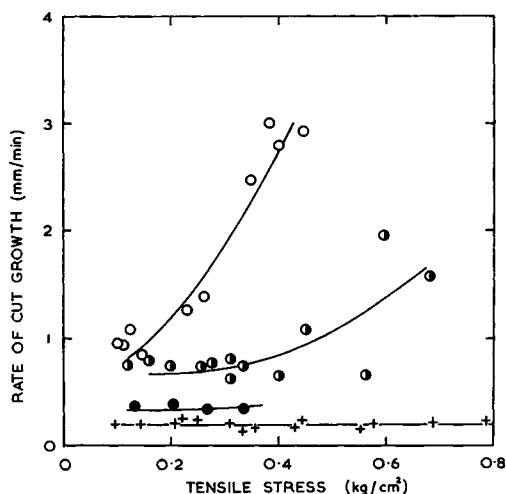


Fig. 5. Experimental relations between the rate of cut growth and applied tensile stress for various test-piece thicknesses: (○) 0.25 mm.; (●) 0.65 mm.; (●) 2.0 mm.; (+) 0.6-2.0 mm. (greased on major surfaces).

and having smoother major surfaces. The experimental irreproducibility was, unfortunately, still large, as is evident in Figure 5, where the experimental results are portrayed. However, major differences are shown in Figure 5, the thinner test pieces exhibiting more rapid cut growth at any given value of the imposed tensile stress and a greater dependence of the rate of growth on the imposed stress. The increased rate in the thin test pieces is ascribed to the following mechanism.

It is assumed that, for a short distance d ahead of the growing cut, the local tensile stress exceeds that necessary for ozone attack to occur, and a cut may therefore be propagated by attack from the major surfaces immediately ahead of the tip. For sufficiently thin test pieces, i.e., when d is much greater than the thickness, this process may take place rapidly in comparison with the normal growth, leading to rapid crack propagation. Moreover, since the distance d will clearly increase as the applied tensile stress is increased, the rate of cut growth for the thinner test pieces would be expected to increase similarly, as is observed experimentally. It has been found possible to predict approximately the relative rates of cut growth by such a treatment, but the experimental scatter renders the agreement obtained of doubtful significance. However, the mechanism proposed, namely attack in advance of the crack tip, provides a satisfactory qualitative explanation of the observations.

When the surfaces between which the cut grew were protected from ozone attack by a thick

coating of silicone grease, the observed rates of growth were small and largely independent of the test-piece thickness or the applied tensile stress over the range employed (100-1000 g./cm.²). There was still some tendency for the thinner test pieces to show more rapid growth, presumably due to failure or disturbance of the grease film caused by the propagation of the crack. A standard test-piece thickness of about 0.08 cm. was chosen for the experiments described in the previous sections, and all test pieces had their major surfaces covered with grease. The measured rates of cut growth should therefore be appropriate to growth through the bulk, to a first approximation.

It has frequently been reported that cracks form (i.e., grow to a visible size) more rapidly in the surface of highly stretched rubber.^{1,2} The present observations suggest that this is due to attack in advance of the growing crack tip. The rate of growth of a surface crack may therefore not be representative of the rate of attack.

GENERAL CONCLUSIONS

(1) It has been found that a cut in the edge of a stretched sheet of rubber grows across it at a constant rate in an atmosphere containing ozone. In thin sheets the rate is increased, apparently by attack of ozone in advance of the growing cut. This effect may be greatly reduced by coating the major surfaces of the test piece with silicone grease, when the measured rate is assumed to be characteristic of growth through the bulk.

(2) Provided the applied tensile stress exceeds a well-defined critical value, the cut advances at a rate substantially independent of the applied stress until the stress approaches the much larger value sufficient to cause tearing in the absence of ozone.

(3) The characteristic rates of cut growth for natural rubber (smoked sheet) and a butadiene-styrene copolymer (75/25 Polysar S) depend on the vulcanization system employed, being appreciably lower for peroxide and tetramethylthiuram disulfide (TMT) vulcanizates. In peroxide vulcanizates, the effect is attributed to small quantities of impurities, notably oleic acid in natural rubber. In TMT vulcanizates the effect is attributed to a product of the vulcanization reaction, probably zinc dimethyldithiocarbamate.

(4) The rates of cut growth for clean vulcanizates, i.e., acetone-extracted ones, are very similar for natural rubber and the butadiene-styrene

copolymer at equivalent degrees of crosslinking. The rates are decreased by increased crosslinking, but the effect is relatively small over the conventional range, the measured rates varying by a factor of two or three.

(5) The inclusion of large quantities of whiting or carbon black in the mix formulation appears to have little effect on the characteristic rate of cut growth.

(6) The more viscous polymers, a butadiene-acrylonitrile copolymer C and butyl rubber D, exhibit slower cut growth than the relatively mobile ones, A and B, at room temperature. On raising the temperature or on plasticization, however, the observed rates were increased markedly to approach those observed for materials (A and B) which are virtually unaffected by these changes. It is concluded therefore, that the rate of cut growth is limited in relatively viscous polymers by the restricted mobility of polymer chains.

(7) Specific effects are suggested in the case of polychloroprene E, which exhibited much slower cut growth under all conditions, and chlorosulfonated polyethylene, which appeared to be completely resistant to ozone.

(8) The similar rates of cut growth observed for the relatively mobile polymers A and B and the plasticized polymers A' - D' were found to be directly proportional to the concentration of ozone to a first approximation, the rates being of the order of (0.2 mm./min.)/mg. of ozone/l.

Appendix: Laboratory Preparation of Ozonized Oxygen

E. D. FARLIE

Ozone was produced by the ultraviolet irradiation of oxygen,⁶ which was passed through a glass vessel enclosing a quartz low-pressure mercury discharge lamp (Mercury Vapour Burner, Type T/M5/369, the Thermal Syndicate, Ltd., London). A reducing valve, a constant-head leak, and a flowmeter were incorporated before the generator to control and measure the rate of flow of oxygen. A cooling coil immersed in an ice-water mixture was also included at the inlet to the ozone generator, as this provision was found to reduce fluctuations in the ozone concentration.

The output concentration of ozone was found to be largely independent of the rate of flow of oxygen over the range 2-25 l./hr. To provide lower

concentrations at a constant rate of flow of 25 l./hr., a separately controlled stream of oxygen was used to dilute the output from the generator.

The combined gas stream was led either through the test chamber to an estimation column or to a destroyer vessel containing soda lime, which was found, in contrast to other experience,⁷ to remove ozone efficiently from a gas stream passing through it.

For estimation, the gas stream was passed up a vertical glass column, 2.5 cm. in diameter and 45 cm. long, packed with broken glass tubing.⁸ A neutral 5% solution of potassium iodide⁹ was allowed to pass down the column at a rate of about 1 drop/sec. to a collecting flask at the bottom. After a period of time, generally about 20 min., the gas stream was diverted to a destroyer vessel. The column was then rinsed with distilled water, and the contents of the collecting flask were acidified with 2*N* sulfuric acid⁹ and titrated immediately with a standard solution of sodium thiosulfate.

The following additional precautions were observed. (1) The potassium iodide solution was stored in the dark and shielded from direct light while in use. (2) The sodium thiosulfate solution was also stored in the dark, and was frequently standardized against a standard solution of potassium dichromate. It contained 1 ml./l. of chloroform to inhibit bacterial action.¹⁰ (3) Before admitting the gas stream, the estimation column was rinsed out with the potassium iodide solution.

The concentration of ozone was calculated from the measured titer and the flow rate, by using the relation 1 ml. of 0.1*N* sodium thiosulfate = 2.4 mg. of ozone.

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References

1. Newton, R. G., *J. Rubber Research*, **14**, 27 (1945); *ibid.*, **14**, 41 (1945).
2. Gough, V. E., and D. M. Smith, *Trans. Inst. Rubber Ind.*, **29**, 219 (1953).
3. Braden, M., and A. N. Gent, *J. Appl. Polymer Sci.*, **3**, 100 (1960).
4. Davis, C. C., and J. T. Blake, *The Chemistry and Technology of Rubber*, Reinhold, New York, 1937, p. 18.
5. Van Pul, B. I. C. F., *Trans. Inst. Rubber Ind.*, **34**, 86 (1958).
6. Crabtree, J., and A. R. Kemp, *Ind. Eng. Chem., Anal. Ed.*, **18**, 769 (1946).

7. Farkas, A., and H. W. Melville, *Experimental Methods in Gas Reactions*, Macmillan and Co., Ltd., London, 1939, p. 156.

8. Boer, H., and F. L. J. Sixma, *Rec. trav. chim.*, **70**, 997 (1951).

9. Birdsall, C. M., A. C. Jenkins, and E. Spadinger, *Anal. Chem.*, **24**, 662 (1952).

10. Vogel, A. I., *A Textbook of Quantitative Inorganic Analysis*, 2nd Ed., Longmans, Green and Co., London, 1951, p. 333.

Synopsis

Experimental measurements are described of the propagation of a cut through a stretched rubber sheet under the action of an atmosphere containing ozone. It is shown that a well-defined rate of cut growth may be determined which is characteristic of growth through the bulk and substantially independent of the applied tensile stress when this exceeds a critical value necessary for growth to occur at all. The effect of the polymer employed, the vulcanization system used, the degree of crosslinking, and the presence of fillers and plasticizers on the characteristic rate of cut growth is examined. The effects of temperature in the range 2–80°C., and ozone concentration in the range 0.2–2.5 mg. of ozone/l. are also studied. It is concluded that the rate at which a cut advances in highly reactive polymers is principally determined by the rate of incidence of ozone molecules and, for relatively viscous polymers, by the restricted mobility of polymer chains. The degree of crosslinking and the vulcanization system adopted appear to be of secondary importance, while the presence of fillers has a negligible effect.

Résumé

On décrit les mesures expérimentales de propagation d'une incision au travers d'une feuille de caoutchouc étiré sous l'action d'une atmosphère contenant de l'ozone. Il a été démontré qu'une vitesse bien définie de propagation de l'incision peut être déterminée; elle est caractéristique d'une croissance au travers de la masse et, substantiellement indépendante de la force d'élongation appliquée pour autant que cette dernière dépasse la seuil critique nécessaire pour que la croissance se produise. L'influence du polymère

utilisé, du système de vulcanisation, du degré de pontage et de la présence de charges ou de plastifiants sur la vitesse caractéristique de croissance de l'incision est étudiée. L'influence de la température dans un domaine allant de 2 à 80°C et des concentrations en ozone de 0.2 à 2.5 mg/litre ont de même fait l'objet d'une étude. On en a conclu que la vitesse de croissance d'une incision dans des polymères hautement réactionnels est déterminée principalement par la vitesse d'incidence des molécules d'ozone, et, pour des polymères relativement visqueux, par la réduction de mobilité des chaînes polymériques. Le degré de pontage et le système de vulcanisation adopté semblent n'avoir qu'une importance secondaire tandis que la présence de charges n'exerce qu'un effet négligeable.

Zusammenfassung

Experimente über die Messung der Ausbreitung eines Schnittes in einem gedehnten Kautschukstreifen unter dem Einfluss einer ozonhaltigen Atmosphäre werden beschrieben. Es wird gezeigt, dass eine wohldefinierte Geschwindigkeit des Schnittwachstums bestimmt werden kann, die für das Wachstum in der Substanz charakteristisch und unabhängig von der angelegten Zugspannung ist, sobald diese einen für den Eintritt des Wachstums notwendigen kritischen Schwellenwert überschreitet. Der Einfluss der Natur des verwendeten Polymeren, des benützten Vulkanisierungssystems, des Vernetzungsgrades und der Anwesenheit von Füllstoffen und Weichmachern auf die charakteristische Geschwindigkeit des Schnittwachstums wird überprüft. Ebenso wird die Temperaturabhängigkeit im Bereich von 2 bis 80°C und der Einfluss der Ozonkonzentration im Bereich von 0,2 bis 2,5 mg Ozon/lit untersucht. Man kommt zu dem Schluss, dass die Geschwindigkeit, mit welcher sich ein Schnitt in hochgradig reaktionsfähigen Polymeren ausbreitet, hauptsächlich durch die Geschwindigkeit des Auftreffens von Ozonmolekülen und, bei verhältnismässig viskosen Polymeren, durch die beschränkte Beweglichkeit der Polymerketten bestimmt ist. Der Vernetzungsgrad und das verwendete Vulkanisierungssystem scheinen geringere Bedeutung zu haben und die Anwesenheit von Füllstoffen hat schliesslich einen vernachlässigbaren Einfluss.

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