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The Mechanism of Ozone Cracking. I. Ozone Cracking of Plastic Films

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INTRODUCTION

Stress cracking of organic construction materials was first observed in stretched vulcanized rubber in the presence of ozone. This growth of cracks under the combined influence of tensile stresses and traces of ozone is related, as a phenomenon, to the crazing of organic glasses caused by certain vapours and to the stress cracking of plastics in the presence of surface-active liquids. A general theory of stress corrosion has, however, not yet been given. Even for the well-documented case of ozone cracking the fundamental mechanism is still not clear, according to recent reviews of available information.[1,2] The suggested analogy between stress cracking of plastics and ozone cracking of rubbers would become more plausible if materials of similar mechanical properties could be compared. Instead of studying stress cracking of rubbers below their transition temperature it was more convenient to follow, at ambient temperature, the ozone cracking of olefinic plastics.

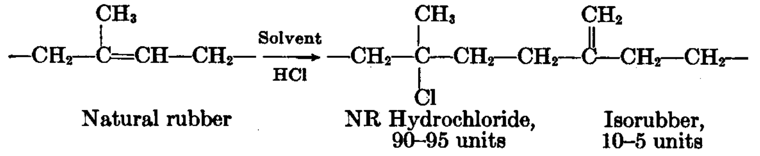
Delayed fracturing in an ozonized atmosphere was reported some time ago,[3] not only for stretched gutta-percha but also for high-styrene resins, chlorinated rubber (with some residual double bonds) and rubber hydrochloride (with some residual double bonds). Talen and Scheffer had previously mentioned the ozone sensitivity of commercial rubber hydrochloride (Pliofilm) in contrast to the apparent tolerance for atmospheric ozone of paint films prepared from drying oils.[4]

Films of rubber hydrochloride were found most convenient for detailed observations. It will be shown that delayed fracturing of these films in the presence of ozone is identical with the phenomenon well-known for rubbers, but that events during the induction period differ from those observed with low-modulus polymers. That ozone indeed reacts with the surface is borne out by chemical evidence. Microscopic and stress optical observations on initiation and growth of cracks are to be reported, and a phenomenological theory will be developed.[5]

EXPERIMENTAL

Structure and Properties of Natural Rubber Hydrochloride

The hydrochlorination of natural rubber in latex goes nearly to completion.[6] Films and fibers prepared from this material are resistant to the attack even of concentrated ozone. However, hydrochlorination of rubber in organic solvents is accompanied by an isomerization process and, as these "isorubber" groups are less readily hydrochlorinated, the HCl addition remains incomplete:[7]



$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \xrightarrow[HCl]{Solvent} -CH_2-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH_2-\overset{CH_2}{\overset{\|}{C}}-CH_2-CH_2-$$

The combined evidence of ICl addition and infrared analysis points to only 6–8% residual double bonds. The polymers used here contained 30.5 ± 0.5% Cl, corresponding to about 83% saturation. Half of the residual number of double bonds are presumably lost by cyclization during HCl addition.

Solutions of this polymer degrade readily under the influence of ozone, as is indicated by viscosity changes and IR spectra.[8] The corresponding reaction with the unstrained *solid* film is very slow. Changes in the IR spectrum are observed only after exposure for hours to oxygen containing as much as 1% ozone.[7] At the same time the surface of the film becomes insoluble and brittle. Similar mechanical changes in the unstrained surface are produced by rapid (photochemical) or slow (shelf aging) oxidation. While already a very dilute atmosphere of ozone rapidly causes stress cracking, the surface of such cracked film is apparently unchanged, as will be shown.

Films prepared in the laboratory and commercial Pliofilm (Goodyear Tire and Rubber Company), have identical chemical properties; they do not differ in ozone sensitivity. It was convenient, therefore, to use a series of grades of Pliofilm. The chlorine content of the polymer was the same in different charges. Three types were used in this investigation: N2 (normal), P4 (plasticized), and FF (frozen food), manufactured to standard nominal gauges, which corresponded nearly to the measured thickness in microns. The plasticizers were isolated, analyzed, and found to be different in each type: butyl–stearate in type N and a mixture of stearate and phthalate in type P, while type FF contained also sebacate. The prestretched type N1 was mechanically similar to type N2 after prestretching about 200%. The essential data are compiled in Table I.

Such films are highly crystalline[9]; a value of 40% for type P4 has been estimated from x-ray measurements.[10] The crystalline phase melts near 110°C. and the polymer loses HCl at a slightly higher temperature of about 130°C. The modulus of elasticity was determined from the first

TABLE I
Properties of Rubber Hydrochloride Films

	Pliofilm designation and gauge			
	N1, 40	N2, 80	P4, 120	FF, 250
Thickness, μ	10	19	29	66
Plasticizer content, %	5	4	10	15
Density (23°C.)[a]	1.147	1.139	1.130	1.136
E modulus, 10^9 dynes/cm.[2]	32	11	8	6

[a] Determined by a density gradient method.

part of the stress–strain curve. It is raised by a factor of 3 on prestretching and lowered by an increase in plasticizer content, the former effect being more pronounced than the latter. Dynamic moduli determined by a vibrating-reed method near 20 cycles/sec. are 4–7 times higher. A significant softening influence of moisture is observed and the method is accurate only with thicker films, as a clamped thin film curls on absorption of moisture. The modulus in the direction of casting is only about 10% higher than that perpendicular to it. However, for the prestretched film N1 the modulus in the fiber direction (Table I) is about 30% higher than that measured perpendicular to it. It is seen from Table I that films differing in modulus by a factor of 2 were available. The stiffness was 10^2–10^3 times higher than that of conventional rubbers.

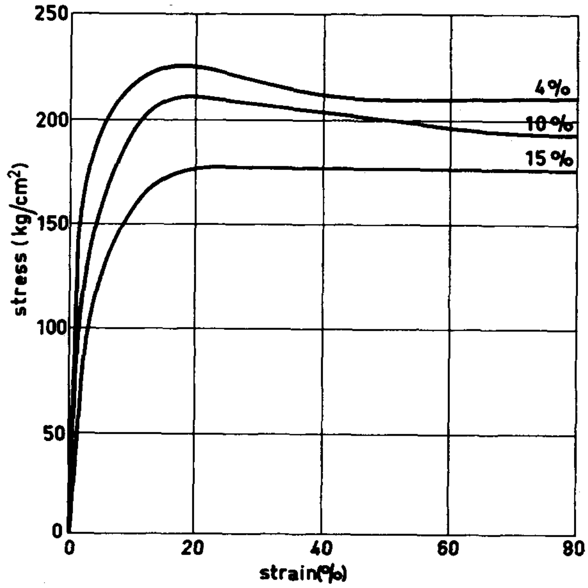


Fig. 1. Nominal stress versus strain of natural rubber hydrochloride films. Plasticizer contents from 4 to 15%, as indicated. Strain rate 2%/min.

Stress–strain diagrams, Figure 1, for the three types of Pliofilm most used were taken on an Instron-type instrument. The strain rate of 2%/min. was applied also in prestraining films for fracturing experiments.

The plasticized films begin to yield at 20% extension. The apparent maximum in the curve is due to the superposition of rapid stress relaxation during extension. To reach always the same steady state on exposure to ozone, it is necessary to standardize a period of rest.

At higher elongations necking takes place and the amount of local deformation differs from that recorded as overall extension. The true stress–strain curve (Fig. 2) was obtained with the aid of the microdynamometer discussed below (see Fig. 5). Extension and change of cross section of *small* inked volume elements were followed under the microscope. Small changes in volume of the measured elements were observed and taken into account in calculating the true stresses. Deformation is comparatively small in the elastic region and increases nearly linearly with stress. A second area of linear deformation is found at high strains, when the actual stress is much higher than the stress calculated on the original cross section. The prestretched material N1, which does not neck, is mechanically similar to this strained, originally softer, film P4.

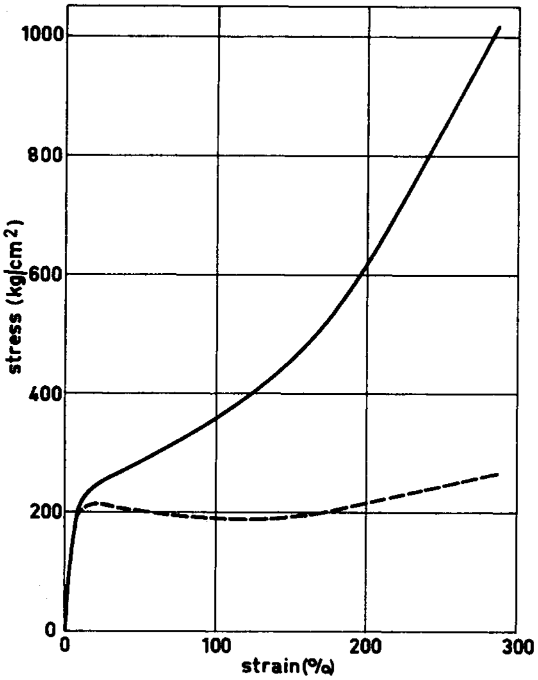


Fig. 2. Actual stress versus strain (—) and nomimal stress versus strain (- - -) for film type P4 mostly used in this study. Overall strain rate 2%/min.

Partial recovery at all degrees of strain takes place, rapidly followed by a further time-delayed recovery (Fig. 3). This rapid elastic reaction, even after extensive plastic flow in the highly strained region has taken place, determines the course of cracking. It will be shown[5] that the shape of a growing crack is influenced by it.

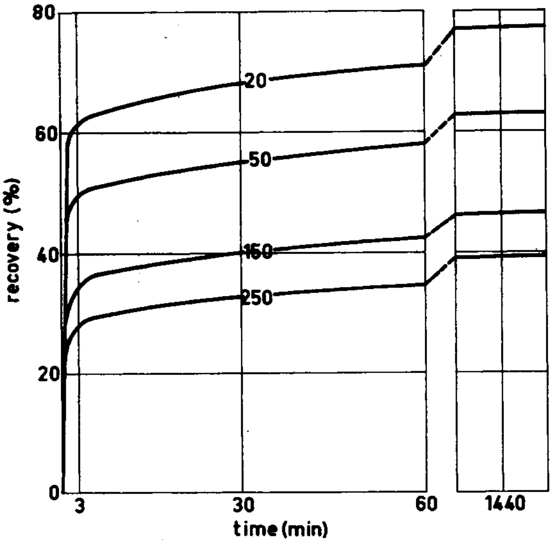


Fig. 3. Delayed elastic recovery of film type P4; prestrained from 20 to 250%, as indicated. Overall strain rate 2%/min.

Stress Cracking

Time-delayed fracturing was at first measured with a simple device: Strips of film were prestrained and kept at a particular elongation for 5 min. They were then placed in a cylinder filled with ozonized oxygen and the time to fracture was observed. Average values for 15 measurements at each elongation are shown in Figure 4. No fracture of the stressed films occurred, even after days, in the absence of ozone.

As with rubbers, a minimum elongation is needed to produce fracture, but the corresponding minimum stress is surprisingly high, about 30% of the yield value. The delay time decreases exponentially with increasing stress but goes through a minimum near the yield point. After that, localized necking causes uneven stress distribution, and a large spread in the time to fracture is observed. The loop in the curve, however, is quite reproducible. Therefore, results for the harder film type, N2, and the softer type, FF, did not differ essentially in their dependence on strain.

More elaborate equipment was developed to follow this time dependence of fracturing both more accurately and at lower ozone concentrations.

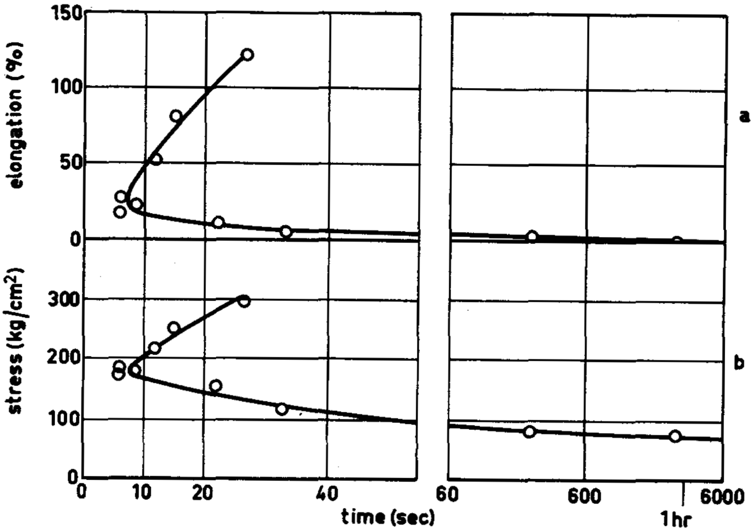


Fig. 4. Delayed fracturing of film type P4 in 100 ppm ozone as a function of prestraining. Relaxation time before exposure, 5 min. Each point is the average of 15 measurements. Exposure in cylinders filled with ozonized oxygen.

Stress Relaxation Measurements

A Perspex cell with windows made from microscope slides was designed to allow simultaneous exposure of a plastic film and observation through a magnifying glass or a microscope (Fig. 5). A gas stream introduced at the inlet filled the cell within a few seconds. The gas leaked out through the slits guiding the film. Ozone was destroyed at these points by plucks of cotton wool (not shown in the photograph).

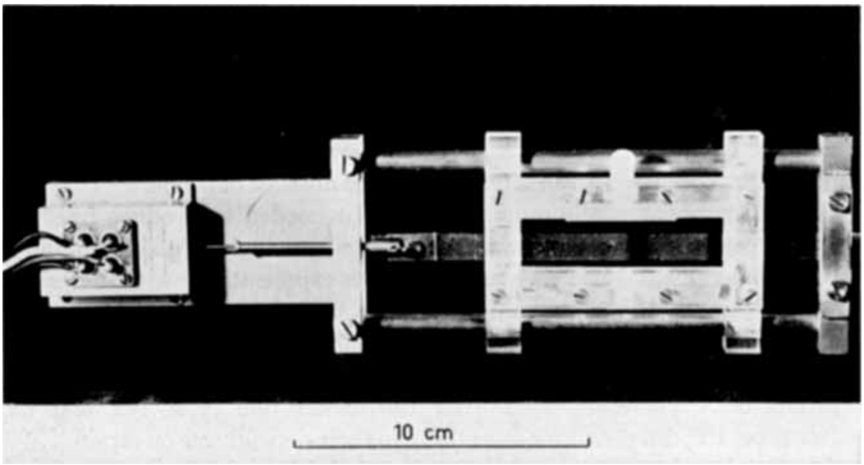


Fig. 5. Microdynamometer and reaction cell.

A flow sheet of the microdynamometer is given in Fig. 6. Automatic straining at a preset rate is effectuated by a reduction gear driven by a synchronous motor. Elongation is measured between markers on the film. Stresses are taken up by an unsupported strain gauge, a Statham transducer, type G 1–48, for plastics, and the more sensitive type G 1–4 for rubbers or for the measurement of small stresses in plastic films. Changes in force due to stress relaxation at constant elongation are registered on the galvanometer (G) with an accuracy of 0.1% of the total stress.

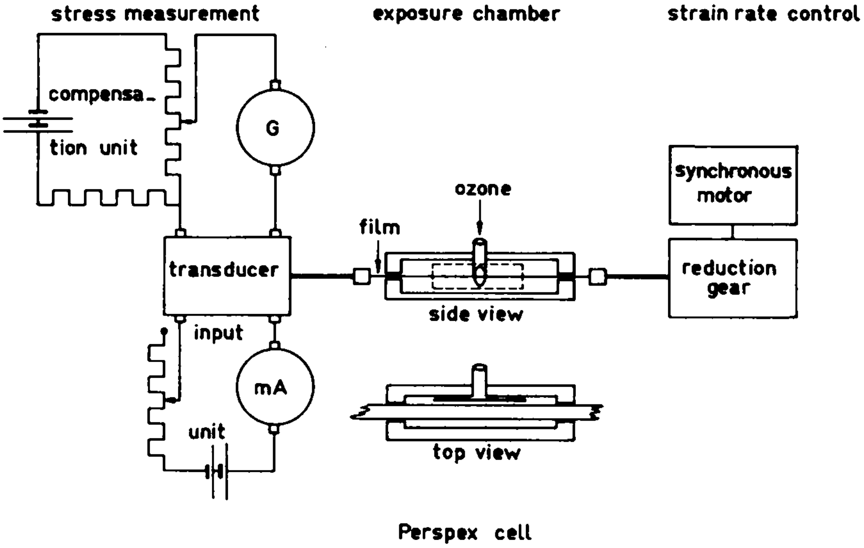


Fig. 6. Flow sheet of arrangement for stress relaxation measurements.

Low concentrations of ozone, about 5 ppm, were obtained from pure oxygen with a high-pressure mercury UV lamp (Philips No. HPK, 125-w., Type 57 203 B). Concentrated ozone was prepared by electrolysis[11] and diluted with pure oxygen to the desired concentration and humidity.

RESULTS

The sensitivity of our microdynamometer is illustrated by the well-known stress relaxation of rubbers with 5 ppm ozone. Relaxation begins prior to surface cracking, even when the rubber is protected by an effective antiozonant. The roughness of the surface of natural rubbers and butadiene styrene rubbers increases at the same time. Butyl rubber relaxes at a slower rate and in moist ozone becomes tacky; no cracks are formed during this first phase.[12] While relaxation is a sensitive indicator of *surface* attack, it does not necessarily run parallel to cracking.

The behavior of natural rubber–HCl films was rather unexpected.

Although on admission of ozone (point A in Fig. 8) a sudden small drop in stress was registered, further stress decay is not observed even after the first crack (point B) becomes visible. Only when gross tearing sets in does catastrophic stress relaxation become apparent. It was found that the first instantaneous drop (A) was due to moisture only; it is reversible and produced also by a stream of moist air or nitrogen (Fig. 8*a*). In all further experiments ozonized oxygen of 90% R.H. was applied.

Although the film surface chemisorbs ozone rapidly (see below), very little stress relaxation occurs, the induction period A–B, and even the crack growth period, differs thus from the corresponding phenomenon found with rubber surfaces (Fig. 7). This striking and unexpected discrepancy in mechanical reaction between a rubber and a plastic film on ozonization becomes intelligible only after microscopical inspection of the surfaces. As has been shown,[12] a rubber surface roughens rapidly on ozonization. The hard Pliofilm surface, on the other hand, seems to absorb considerable quantities of ozone without any change in surface structure on a microscopic scale.

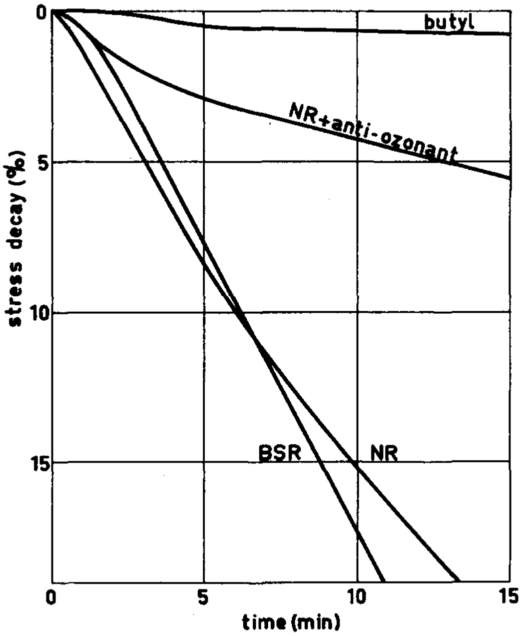


Fig. 7. Stress relaxation of rubbers in 5 ppm ozone at 20% strain.

Definite proof that fracturing is due only to ozone is obtained by intermittent admission of the gas stream. After switching off of ozone and flushing of the cell with nitrogen during comparatively long periods, the crack or even the half-torn film did not grow at all, while the process continued at the same rate on readmission of ozone.

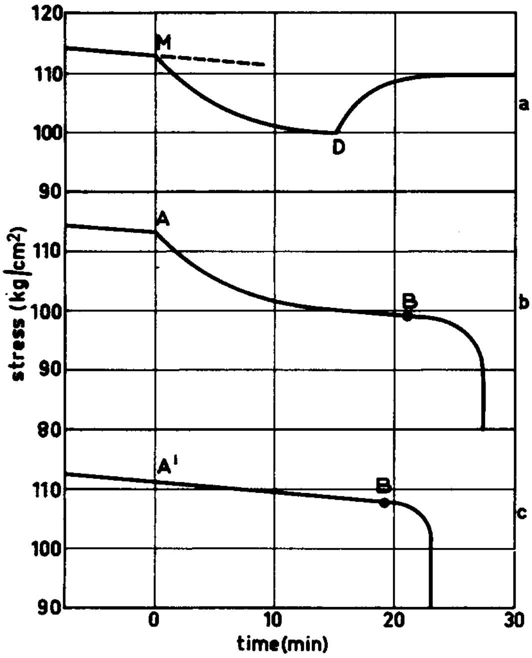


Fig. 8. Stress relaxation of rubber hydrochloride film: (*a*) influence of moisture and atmospheric nitrogen; M = moist nitrogen admitted, D = dry nitrogen admitted; (*b*) and (*c*) influence of moisture and ozone. (*b*) At point A, 5 ppm O_3 in oxygen of 90% R.H. admitted, at point B, first crack visible. (*c*) At point A′ 5 ppm O_3 in oxygen of 60% R.H. admitted to film conditioned at 60% R.H.

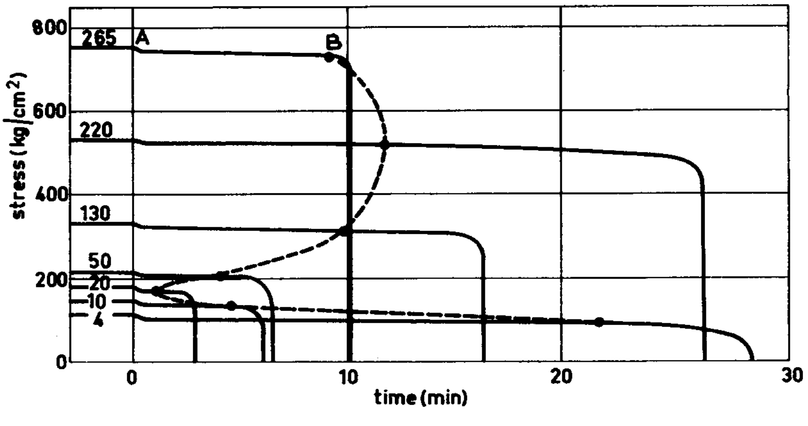


Fig. 9. Stress relaxation and delayed fracturing in 5 ppm ozone. Overall prestrain from 4 to 265%, as indicated. Ozone admitted at point A, first crack visible at point B.

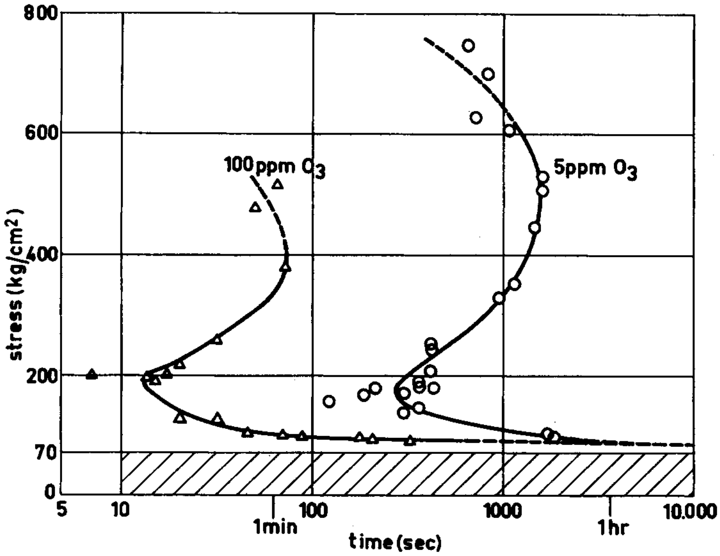


Fig. 10. Stress dependence of delayed fracturing at 100 ppm and 5 ppm ozone: (shaded area) no fracture after many hours; relaxation time after prestraining 30 min.; rate of prestraining 2%/min.

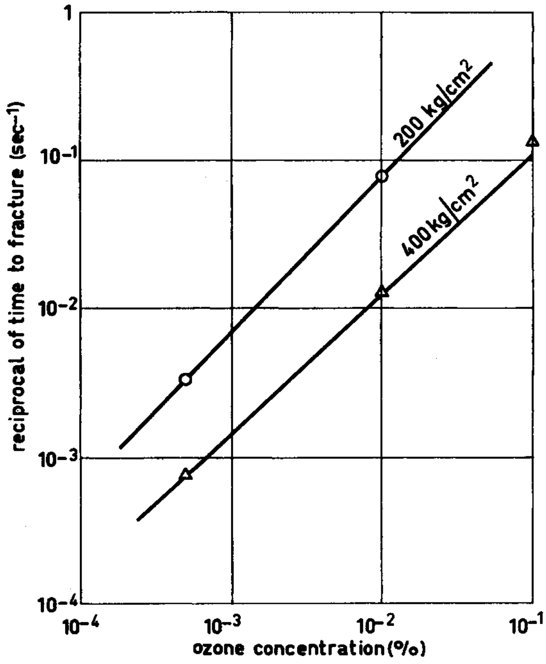


Fig. 11. Influence of ozone concentration on time to fracture at 200 kg./cm.^{2} (near yield point) and at 400 kg./cm.^{2} stress. Conditions same as in Figure 10.

Measurements at well-defined higher strains were made also with the small exposure cell described above. Results from the crude observations (see Fig. 4) are confirmed on careful exposure of selected areas between markers (see Fig. 9). Catastrophic fracture occurs rapidly near the yield point, while at higher strains both the time to formation of a visible crack and that to growth of this crack become longer. Once the film is well orientated by still higher prestraining, cracking accelerates but the type of fracture now becomes different.[5]

Results for ozone concentrations differing by a factor of 20 are summarized in Figure 10. The salient features of these measurements are as follows. (*1*) Below a stress level of about 70 kg./cm.^{2} no cracking takes place even at the highest ozone concentration. (*2*) Ozone sensitivity increases exponentially with stress and goes through a maximum near the yield point of the material. (*3*) The *rate of* cracking is controlled only by ozone concentration. Near and above the yield point, time to fracture decreases linearly with increasing ozone concentration, as is shown in Figure 11. This is probably true also for fracture near the limiting stress level.

Formation and Properties of the Ozonized Layer

Direct evidence of surface ozonization was procured from gravimetric and volumetric measurements. Additional experiments gave some impression about the localized nature of the reaction and of the resulting changes in mechanical properties.

Gravimetric and Volumetric Determinations

Experimental. It was shown (Fig. 8) that the films are hygroscopic. To obtain meaningful and reproducible results on a microbalance the films had to be carefully kept dry during the whole operation. A second source of error was due to electrostatic charges, which are large enough to influence the results of weighing. During weighing the sample was exposed to a weak β-radiation emitter. With these precautions individual measurements were reproducible to $\pm 0.012\%$ weight increase, which corresponds to an ozone uptake of 4.5×10^{-9} moles/cm.^{2}.

For volumetric determinations, the procedure applied by Tucker[13] and Erickson et al.[14] was followed with some modifications. A film of known surface area was placed in a glass tube and a known amount of ozone–oxygen mixture was admitted. After the desired period of exposure the gas was washed with oxygen into a reaction vessel with KJ. The liberated I_2 was titrated. This discontinuous determination of surface reactivity has the advantage that ample time is given for contact with the surface. Accuracy was now 4×10^{-10} moles/cm.^{2} within one run, and 2×10^{-9} moles/cm.^{2} between different runs. Reproducibility of blank titrations was excellent even after 12 min. of contact of the gas with the glass vessel. The ozone concentration changed slightly during the experi-

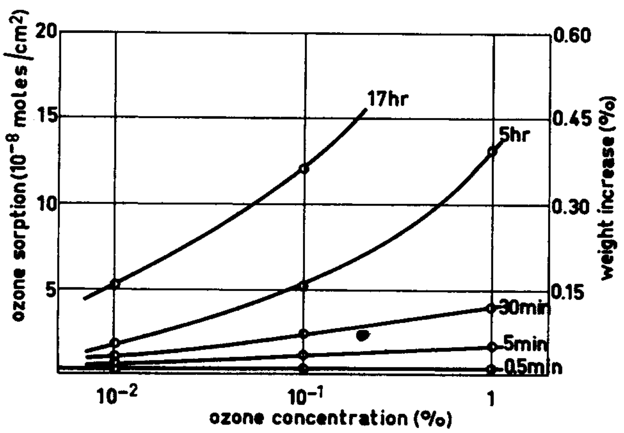


Fig. 12. Gravimetric determination of ozone sorption by film type P4. Influence of ozone concentration.

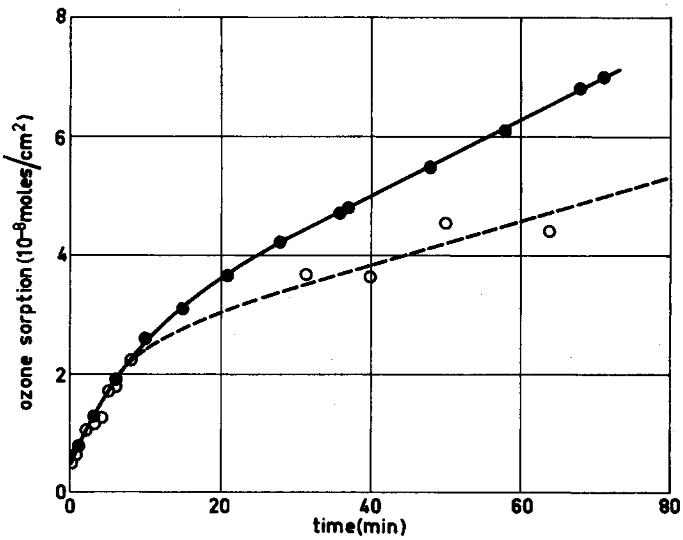


Fig. 13. Volumetric determination of ozone sorption by film type P4 at 1% O_3: (●) volumetric measurements; (O) gravimetric data from Figure 12.

ment. This, however, is not relevant for a relative comparison at different levels of ozone concentration.

Results. The rate of ozonization is a function of time and of ozone concentration, as is shown in Figure 12. At short times of exposure (0.5–5 min.) the influence of ozone concentration is very small. After 30 sec. 2×10^{-9} moles/cm.^{2} are taken up and about twice that quantity after 5 min. Additional measurements at $5 \times 10^{-4}\%$ ozone yielded similar figures. It is evident that only a thin surface layer reacts rapidly. Once the reaction has become diffusion controlled more ozone is taken up after a lapse of hours and at higher ozone concentration, but only the fast surface reaction is of importance in a discussion of cracking.

Accurate volumetric determinations are possible only at high ozone concentrations, but as the rate at first contact with the surface is nearly independent of ozone concentration this limitation is not serious. Assuming that both surfaces of the film react to the same degree, the titrated loss of ozone can be calculated as amount O_3 chemisorbed by the surface (Fig. 13). Surprisingly enough, agreement with the gravimetric determinations shown also in Figure 13 is quantitative for periods up to 10 min., and still reasonable over hours. This proves that only ozone reacts with the surface: an induced reaction with oxygen should lead to higher values in the gravimetric determination. That an autocatalytic oxidation takes place in ozonization has been shown for reactions in solution[8]; a simpler kinetic process seems to govern the solid surface reaction.

Although the plastic film contains only a small fraction of the number of double bonds present in the surface of butadiene styrene rubber or natural rubber, chemisorption of ozone is quite similar. Erickson et al.[14] found at the parts per million ozone level a reaction of about 4×10^{-10} moles/cm.^{2} after 1 min. while Pliofilm reacts even with 2×10^{-9} moles/cm.^{2} during the same period. An unprotected rubber surface has taken up much more ozone after some hours. Tucker[13] exposed natural rubber and neoprene *sponge* to a 0.12% ozone stream, $2\text{–}3 \times 10^{-7}$ moles/cm.^{2} are taken up; it follows from Figure 12 that at the same ozone concentration the weight gain of Pliofilm is distinctly lower even over periods of hours.

The Nature of the Surface Reaction

Some calculations and additional experiments were performed, to trace the correlation between chemical cause and mechanical effect.

The depth of the ozonized layer is calculated from Figures 12 and 13 to be $\sim$600 A. for the instantaneous reaction. The formation and decomposition of an ozonide is highly exothermic. About 35 kcal./mole are released for the reaction $O_3 \rightarrow O + O_2$, together with part of the energy from opening of the double bond; a total amount of 40–50 kcal./mole will be available. For quantities given in Figure 13 about 27 cal./cc. heat of reaction are calculated. Assuming a specific heat of 0.5 cal./g. for the polymer and the specific gravity given in Table I, a local heating of 70°C. above ambient temperature of the ozonized layer could be expected. In order to trace any violent reaction a thermocouple was placed in a crack. Within the (small) experimental error no increase in temperature was recorded on further ozonization, nor was any visible light observed (in a dark room) although light is frequently emitted in autoxidation. Why chemisorption of ozone causes fracturing can thus not be understood from chemical observations alone.

Another group of experiments gave more direct proof of structural changes. The formation of acidic groups on continued ozonization is indicated by an increasing affinity for basic dyestuffs, such as fuchsin, which are absorbed readily from an aqueous solution by the ozonized layer but not by the original film. That ozonization causes crosslinking can be deduced from the formation of an insoluble layer. The original film is soluble in chloroform while solutions of the exposed film have the following properties:

Exposure, hr.	0	0.5	1	2	4	17
Solution turbidity	Clear	Haze	Slight	Flakes	Many flakes	Haze

Again the effect is observable only after long periods of exposure to 1% O_3 and therefore not a direct measure of the mechanism of cracking. Additional support for the assumption that the surface layer has different mechanical properties is found in the stiffening of the films. Three different types were measured in a vibrating-reed apparatus and an increase of dynamic modulus was noted after exposure to 1% O_3 during 1 hr. That the films become not only stiffer but also less plastic is readily established by folding tests. While there is no doubt left that ozonization leads to mechanical changes, the time necessary to produce *observable* differences is much longer than that needed for ozone cracking of a stressed film.

DISCUSSION

Although these plastic films are much less unsaturated than rubbers, the chemisorption of ozone is quite similar both in quantity of ozone taken up and in the distinctly self-sealing nature of the reaction. As with rubbers, the stress-cracking reaction itself is by far the most sensitive indicator of the chemical interaction.

The films are about 10^3 times stiffer than rubbers; therefore, less strain is needed to produce cracking. However, as with rubbers, a distinct *minimum* stress level exists below which no cracking at all is taking place. The absolute value of this minimum stress is obviously a function of the modulus; a quantitative correlation will be discussed later.[5]

Our earlier experiments[3] were beset with erratic results. It is now clear that, unless the minimum stress level is first established, fracturing cannot be reproduced. For example, ozone cracking of gutta-percha was reported earlier[3] but is not confirmed by Braden and Gent,[15] as they tested below the critical stress. Again, Talen, in his study of the properties of drying oil films[4] stressed only to 5.5 kg./cm.^{2}, perhaps a value too low to produce ozone cracking.

Evaluation of this minimum stress level seems to have been neglected generally, in following the stress corrosion of organic materials. Once this level has been passed, the rate of crack growth increases exponentially with stress. As with rubbers,[16] ozone sensitivity goes through a maximum near a certain elongation. Unlike rubbers, these plastic films develop only a few cracks, insufficient to cause appreciable stress relaxation prior to gross tearing. What determines the initiation of cracks and the rate of growth can be understood only from direct observations of crack morphology.[5]

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Synopsis

Stretched films from partly unsaturated natural rubber hydrochloride develop cracks and fracture in ozonized oxygen. Cracking occurs only above a minimum stress level of about 70 kg./cm.^{2}. Ozone sensitivity increases exponentially with stress, but goes through a maximum near the yield point of the thermoplastic films. Contrary to rubbers, these high-modulus materials do not undergo overall stress relaxation prior to fracturing induced by ozone. The rate of surface ozonization of an unstretched film is estimated gravimetrically and volumetrically; it is found to be similar to that of rubber surfaces. Physical and chemical changes of the ozonized surface are reported. Results are briefly compared with ozone attack on other (nonrubber) materials.

Résumé

Des films étirés de caoutchouc naturel hydrochloré, partiellement insaturé, présentent des crevasses et finalement des cassures sous l'influence d'oxygène ozonifié. Ces crevasses sont liées à une tension minimum d'au moins 70 kg/cm^2. La sensibilité vis-à-vis de l'ozone augmente exponentiellement avec la tension, mais passe par un maximum aux environs de la limite élastigue des films thermoplastiques. Contrairement aux caoutchoucs ces matériaux à module élevé ne subissent pas de rélaxation à la tension avant la cassure provoqué par l'ozone. La vitesse d'ozonisation en surface d'un film non étiré, est évaluée par gravimétrie et par volumétrie; on a trouvé que celle-ci est similaire à celle des surfaces de caoutchouc. Des changements physiques et chimiques de la surface ozonifiée ont été décrits. Les résultats sont brièvement comparés avec l'attaque d'ozone sur d'autres matériaux non-caoutchouteux.

Zusammenfassung

In gedehnten Folien aus teilweise ungesättigtem Naturkautschukhydrochlorid entstehen in ozonhaltigem Sauerstoff Risse und schliesslich tritt Bruchbildung ein. Für die Rissbildung besteht eine Spannungsschwelle von mindestens 70 kg/cm.^{2}. Die Empfindlichkeit für Ozon nimmt exponentiell mit der Spannung zu, geht aber in der Nähe der Fliessgrenze des Thermoplasten durch ein Maximum. Im Gegensatz zu Kautschuk erleidet dieses steife Material vor dem ozon-induzierten Zerreissen keine Spannungsrelaxation. Die Geschwindigkeit der Oberflächenozonisierung wurde gravimetrisch und volumetrisch an der ungedehnten Folie bestimmt; sie ist von ähnlicher Grösse wie die für Kautschukoberflächen gefundene Geschwindigkeit. Physikalische und chemische Änderungen der ozonisierten Oberfläche werden beschrieben. Die Ergebnisse werden kurz mit den bei Ozonangriff an nicht-kautschukartigen Materialien erhaltenen verglichen.

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