Deterioration of Organic Polymers

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This paper is a general review of deterioration processes in polymers. It is pointed out that changes in properties with aging are usually the result of chemical reaction with components of the atmosphere. The mechanisms of these reactions and some methods of preventing or retarding them are discussed.

ORGANIC compounds which have enough inherent strength to be used as structural materials—e.g. rubbers, plastics, textiles, and surface coatings—belong to a class called polymers. The deterioration of these materials in service is a serious problem, probably equal in dollar value to corrosion of metals, and one or another aspect of it has been under study in the Laboratories for years.[1] Everyone is familiar with the tendering of cotton cloth and with the loss of strength of rubber with time, but except among people who work with them there is not a wide recognition of the fact that plastics also suffer extensive damage from the weather. This is probably because organic corrosion is usually not visible in its early stages even though deep-seated changes may be taking place throughout the body of the material. In its advanced state, however, such deterioration is easily observable, manifesting itself in loss of strength, erosion, warpage, development of cracks, loss of transparency, or in other ways depending on the material and the application. These changes are of obvious importance in most engineering uses, particularly in the Bell System where apparatus frequently is expected to last thirty or forty years, and it is therefore desirable that they be understood. It is the purpose of this article to review in a rather general way the causes and mechanisms of deterioration.

Even casual consideration reveals that both chemical and physical changes may occur. The loss of plasticizer from a plastic, for example, can induce warping and embrittlement without a change having occurred in the chemical nature of any of the component molecules. Alternate periods of high and low humidity can cause swelling and shrinking in such hydrophilic materials as nylon and cellulose acetate and if stresses are present this can result in permanent distortion[2] (Fig. 1). The swelling of rubber in contact with oils is another example of physical change (Fig. 2). These phenomena are generally well understood and are taken into account in careful engineering. The effect of chemical changes can be even more striking as illustrated in Figs. 3, 4 and 5, but their mechanisms are more obscure and require more detailed discussion.

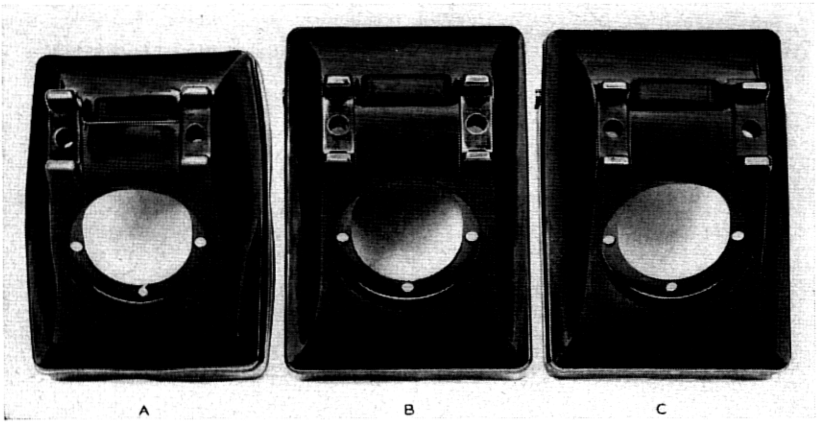


Fig. 1—Cellulose ester telephone housings.
A—Acetate after 7 cycles of high and low humidity.
B—Original.
C—Butyrate after 7 cycles of high and low humidity.

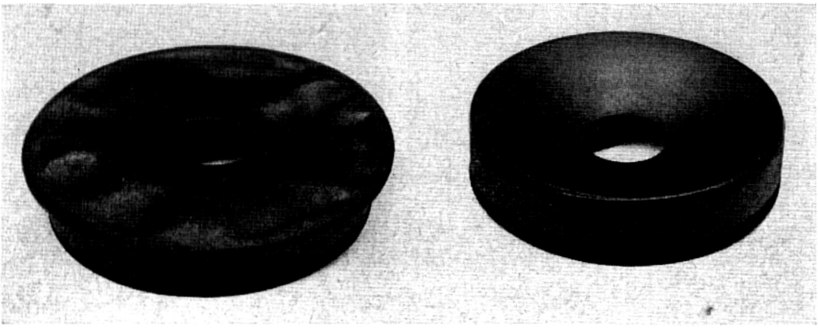


Fig. 2—Neoprene ear pad after one year's use, at left, and original at right.

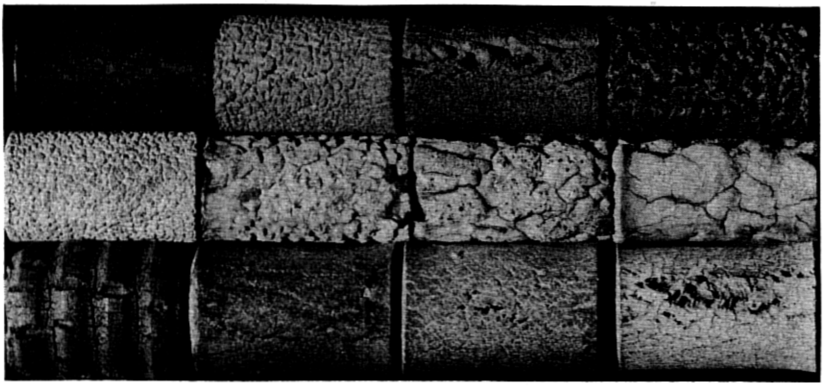


Fig. 3—Samples of rubber in various stages of weathering.

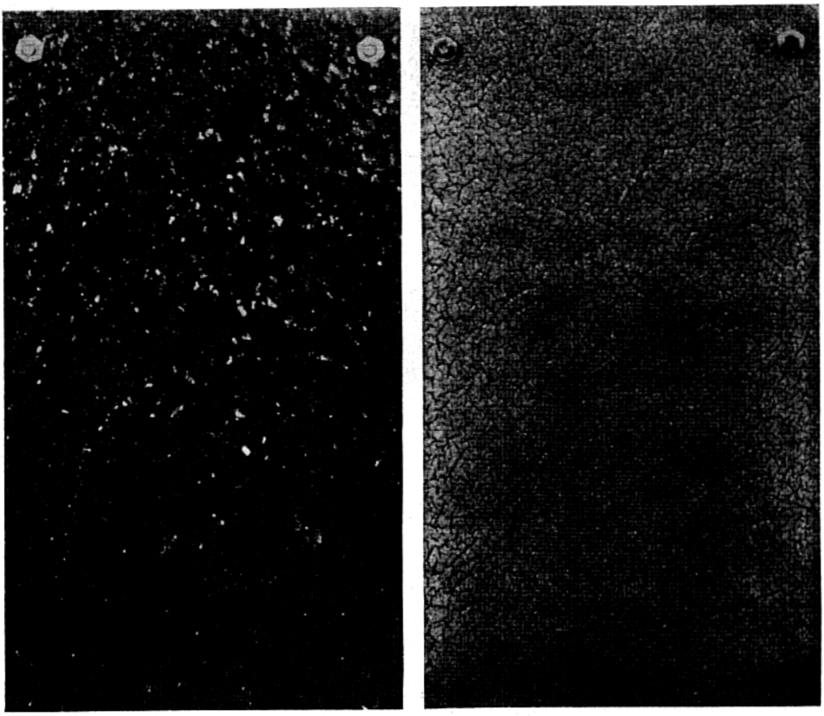
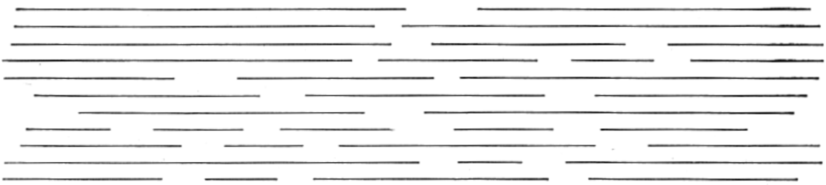


Fig. 4—Cellulose acetate panels exposed in Florida for six months.

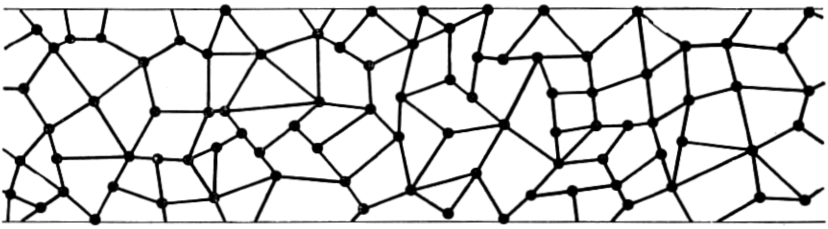
Fig. 5—Samples of rubber garden hose cracked by ozone.

The value of polymers as structural materials is derived entirely from the fact that they are composed of very large molecules. They are generally classified in two broad groups, the essentially linear or chain-like polymers comprising the thermoplastics and rubbers, and the very highly branched three-dimensional networks which are called thermoset materials. The fundamental difference between these groups is shown diagrammatically in Fig. 6 in which, for convenience, the linear polymers are shown as straight lines instead of in their usual randomly kinked shape.

The linear polymers are made up of molecules of finite average size, from a hundred to a thousand or more times as long as they are wide[3] and the strength of the material is dependent on the size of these molecules much as the strength of a cotton thread is dependent on the length of the individual fibers of which it is composed. The forces holding the aggregate together are the cumulative interchain forces. In thermoplastics these forces may be quite strong. In rubbers they are weak until the rubber is vulcanized. Vulcanization connects the chain-like molecules into a loose three-dimensional network, but the number of cross-links is very low compared to typical thermoset polymers being only about one or two for every hundred chain atoms.[4] Vulcanized rubbers are therefore still largely linear polymers and their deterioration follows the pattern of the thermoplastics. The



SCHEMATIC REPRESENTATION OF A LINEAR POLYMER



SCHEMATIC REPRESENTATION OF A THERMOSET POLYMER

Fig. 6—Schematic representation of a linear polymer, above, and of a thermoset polymer, below.

thermoset materials, of which the phenolic resins are typical examples, are so highly interconnected that the molecular weight can be considered to be infinite. Each molding, for example, may consist of a single molecule. Because of their extensive internal cross-bracing their deterioration is usually a surface phenomenon.[5] It will be discussed later in this memorandum. The paragraphs which follow immediately will refer to linear polymers.

Any material chosen for an engineering application obviously must possess desirable characteristics and "corrosion" or deterioration changes these characteristics in some undesirable way. There are three ways in which a system of chain-like molecules can change: 1) the chains may be cut into smaller pieces, 2) the chains may be tied together by cross-links, and 3) the nature of any side groups along the chain may be modified. All of these changes have been found to occur during normal weathering of polymers and the properties of the product are determined by the extent of each change.[6]

The first type, chain scission, is usually the most serious because it cuts at the very essence of polymeric nature which is high molecular weight. As molecular weight is lowered, strength is lowered and ultimately is lost completely. To continue the analogy to a cotton thread, the individual fibers become so short that they cease to overlap each other adequately. Tough horny polyethylene, for example, deteriorates to something akin to paraffin wax. If chain scission occurs extensively in rubbers, portions of chains are cut loose from the relatively few cross-links and the product will appear to have become unvulcanized. This phenomenon is well known with natural rubber and is called "reversion".[7] (Fig. 7)

The second type of change caused by aging, the introduction of ties or cross-links, is not usually of great importance in plastics unless carried to an extreme when the rigidity and brittleness of thermoset polymers might result. As a matter of fact, the introduction of a few cross-links in a thermoplastic, without accompanying chain scission, probably serves to toughen the material. In rubbers, however, where high elongation is a desired property and is derived from the uncoiling of the molecules under stress, introduction of cross-links beyond those necessary for vulcanization tends to "shorten" the material and can eventually stiffen it to the point that it loses serviceability. The introduction of cross-links increases the density, and frequently when the surface of a plastic or rubber has been cross-linked extensively it develops an "alligator" or "mud crack" pattern resulting from excessive shrinkage.

The third type of change, the modification of side groups, normally has little effect on the strength of a polymer, but may have a pronounced effect on the dielectric properties, solubility, moisture absorption, etc., depending

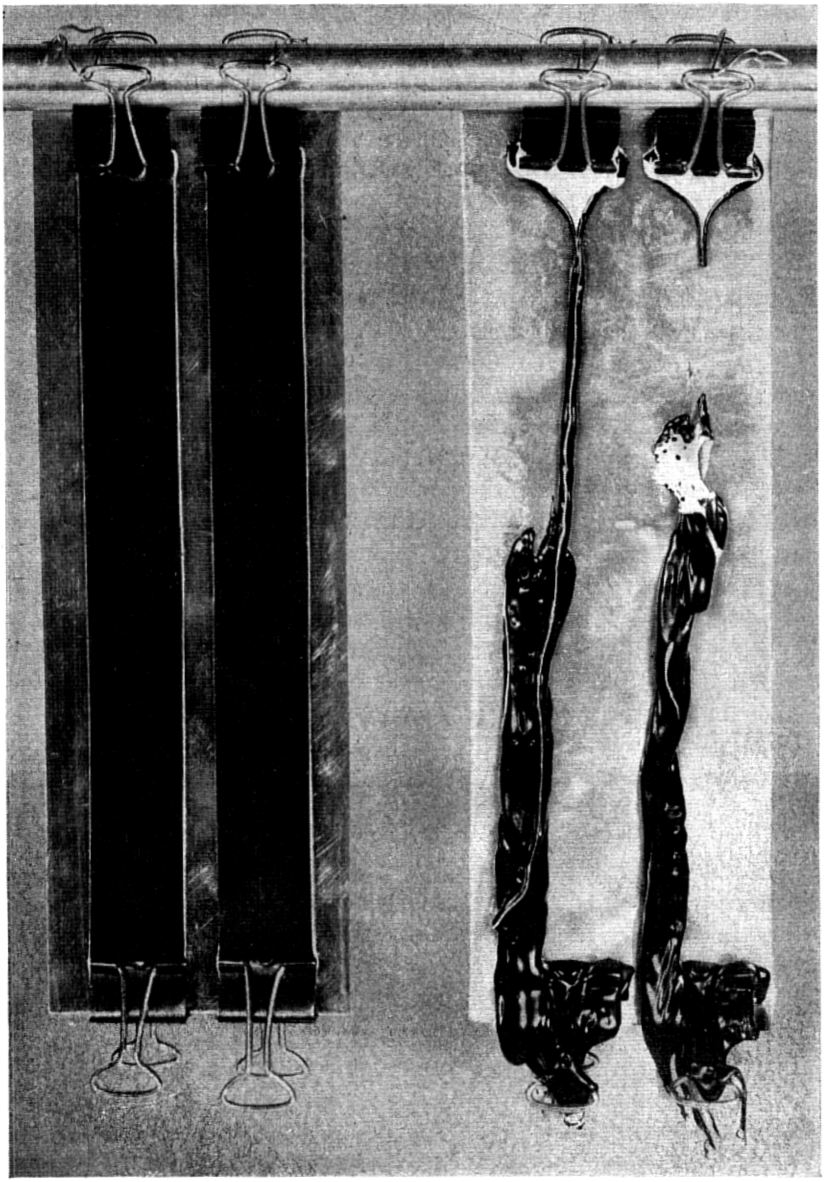


Fig. 7—Natural rubber tapes before and after oxygen bomb treatment.

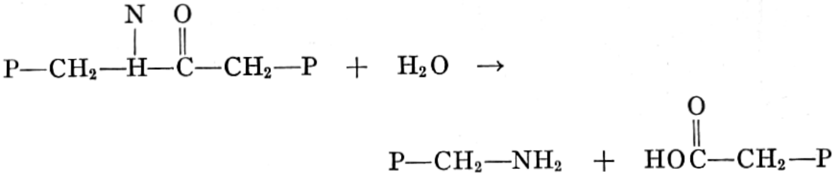
on the nature of the groups introduced or modified. As indicated above, during normal deterioration all of these types of change are proceeding simultaneously to greater or less extent. The rates of the reactions vary from one material to another, and the same conditions which degrade natural rubber to a soft gum may cause neoprene or GR-S to become harder and stiffer.

Returning now to the thermoset polymers, one sees that neither occasional chain scission nor occasional cross-linking can have an important effect on the mechanical properties of a thermoset polymer since every part of the structure is tied to the rest of it by many bonds. For this reason the most conspicuous changes of thermoset materials on exposure to weather are on the surface and are of the third type discussed above.

From the viewpoint of physical structure all of the elements of deterioration are covered in the above paragraphs. However, nothing has been said about the agencies which cause the chemical changes or the mechanisms by which they are brought about. These agencies and mechanisms become the most important objects of study. One type of change—the cross-linking of molecules—in certain cases can occur by self-reaction under the influence of heat or light in complete absence of other chemicals. Self-reaction is not, however, an important effect in materials which are in engineering use. The changes which lead to the loss of utility of polymers during aging are caused by *chemical reaction with the environment.* Usually this environment is the atmosphere. There are normally three substances in the atmosphere which under various circumstances may be considered reactive toward organic compounds, namely water vapor, ozone, and oxygen. The next section will discuss the ways in which these chemicals bring about the destruction or organic polymers.

WATER

The chemical reaction of water with organic compounds is limited to materials which contain hydrolyzable groups either as part of their original composition or as a result of oxidation. Examples of such groups are esters, amides, nitriles, acetals, and certain types of ketones. The reaction is illustrated with an amide linkage, the unaffected portions of the molecule being represented by the letter P:



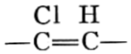
$$\mathrm{P{-}CH_2{-}\overset{N}{\overset{|}{H}}{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}P} + \mathrm{H_2O} \rightarrow \mathrm{P{-}CH_2{-}NH_2} + \mathrm{HO\overset{O}{\overset{\|}{C}}{-}CH_2{-}P}$$

When these vulnerable groups are present as substituents on a polymer chain composed exclusively of carbon-to-carbon bonds their hydrolysis may affect certain properties of the material (dielectric constant, power factor, insulation resistance, water absorption) but in general the molecular weight of the polymer is unaffected. When the vulnerable group is a link in the skeletal chain, however, the result of hydrolysis is much more serious because it constitutes scission of the primary chain and hence a lowering of molecular weight. Polymers which are subject to this kind of scission are polyesters, polyamides, cellulose and cellulose derivatives (ethers and esters). Hydrolysis is accelerated by high temperature and is catalyzed by acids and alkalies, and hence many polymers of the classes listed are stable only when kept neutral. Polyesters in particular are usually easily hydrolyzed and it is this fact which has been the main barrier to their greater commercial utilization. Hydrolysis as such is a well known reaction and is taken into account in current engineering with materials which are subject to it. For example, nylon molding powder is shipped dry in sealed containers to keep the moisture content low until after the molding operation which requires that the nylon be heated to a high temperature,[8] and cellulose esters undergo repeated careful neutralizations and washes after esterification to reduce acidity.[9] The extent to which water plays a role in the deterioration of hydrocarbon materials which are first attacked by oxidation is not yet known, but it is certainly secondary to the oxidation itself. An important effect of rain in outdoor weathering is the washing away of water soluble oxidation products with consequent exposure of new surface. Another effect is the removal of water soluble compounding ingredients. This may be distinctly beneficial as in the case of polyester rubbers vulcanized by acid-producing catalysts,[10] or harmful as in certain polyvinyl chloride formulations which contain water soluble protective agents.

OZONE

Ozone is an extremely reactive chemical which is present in the air in extremely small amounts, ranging from 0 to 10 parts per hundred million. In this low concentration it has not been shown to have any effect on chemically saturated materials, but it is a very serious hazard for unsaturated compounds. Natural rubber and several synthetic rubbers fall in this class (Fig. 8). Ozone is a specific reagent for carbon-to-carbon double bonds, forming an ozonide which undergoes rearrangement resulting in chain scission.[12] When rubber is not being stretched the attack of ozone appears to be negligible, but when it is under stress the attack has very serious consequences resulting in transverse cuts which may sever the piece of rubber.[11, 13] Apparently the initial attack, starting in regions of highest local stress, cuts enough chains to cause a crack to open, and this exposes new surface and concentrates the stress so that the crack grows.

The practical significance of the reaction of ozone on rubber is very great since almost all rubber articles which undergo any appreciable stretching in service are in some degree subject to attack. Exceptions are articles composed of certain specialty rubbers such as silicones, Hypalon*, and some Thiokols. These are saturated materials and hence are not attacked. Neoprene and Butyl rubber are more resistant than natural rubber or GR-S, Butyl because it is only slightly unsaturated, and neoprene because its double bond is considerably deactivated by the adjacent chlorine atom.[14]



$$-\overset{\text{Cl}}{\text{C}}=\overset{\text{H}}{\text{C}}-$$

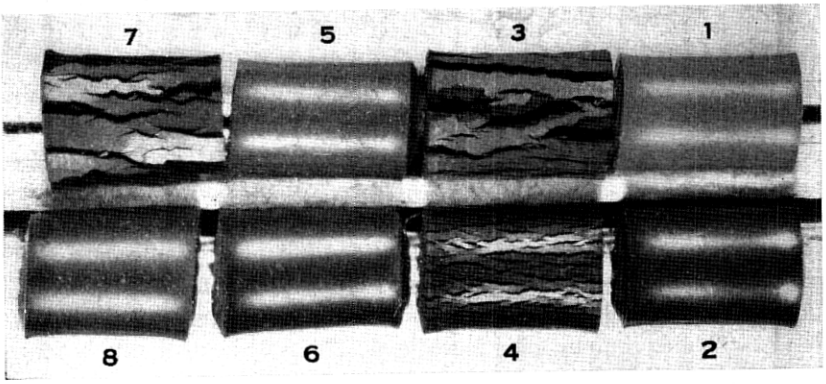


Fig. 8—Samples of various rubber compounds after exposure to ozone. (1) Silicone; (2) Hypalon; (3) Buna-N; (4) natural rubber; (5) & (6) Neoprene; (7) GR-S; (8) Butyl.

Large additions of pigments or plasticizers lower the ozone resistance of neoprene. The measure which has been found most effective for protecting rubber compounds from ozone is the inclusion of several percent of wax. The amount required varies with the type of wax, the polymer, and the other compounding ingredients, the absorptive power of any pigments present being an important factor. By proper compounding neoprene can be made extremely resistant to the attack of ozone, and the other unsaturated rubbers can be greatly improved. The chief effect of temperature changes on the cracking of rubber by ozone is in changing the solubility of wax in the rubber. At elevated temperature the wax film may redissolve and leave the rubber unprotected. This is illustrated in Fig. 9 which shows a tape wrapping which has been attacked on the sunny side, not by the light, but by ozone enabled to reach the rubber because the sun's heat had redissolved the wax in it.

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* A chlorinated, sulphonated polyethylene manufactured by the Du Pont Company.

OXYGEN

The degradative agent of most general attack and of greatest economic importance is oxygen, which is capable sooner or later of bringing about change in almost any organic material. Even disregarding the oxidation of dead organic matter in nature, which is aided by bacteria and fungi, one finds many examples of oxidation familiar to the layman. The development of rancidity in foods is a common one. The production of sludge-forming acids in engine oils, and the spontaneous combustion of rags soaked with linseed oil are others. The loss of strength of cotton cloth after a few years of service is very largely due to oxidation although mildew or other fungus attack may have played a part depending on circumstances.[15, 16, 17] That changes in polymers are indeed the result of oxidation is easily demonstrated in the laboratory by exposing samples to heat or to ultraviolet light in the presence and in the absence of oxygen The results of such an experiment are shown in Table I, in which solution viscosity is used as a measure of molecular weight. It is seen that in nitrogen neither heat nor light brought about any serious loss of molecular weight.

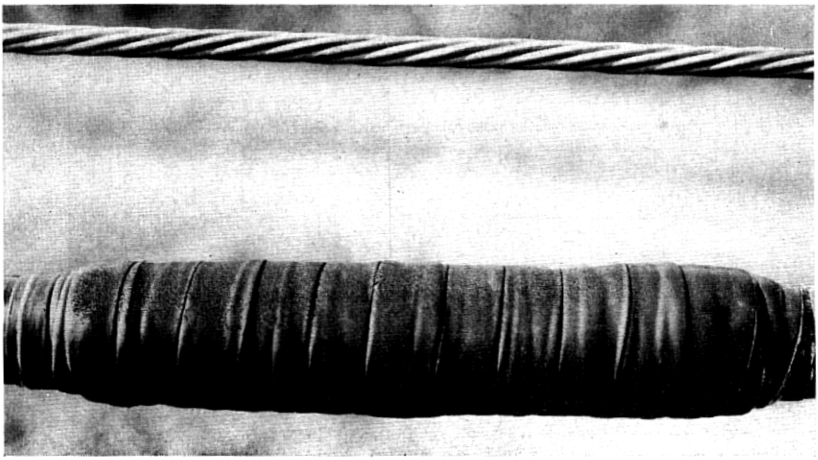


Fig. 9—A tape-wrapped splice after 6-weeks of exposure outdoors. An example of the acceleration of the ozone reaction by heat.

Similar work has been reported with natural rubber with the conclusion that in an inert atmosphere rubber would retain its original properties "for at least thirty years".[18]

Gross Effects of Oxidation of Polymers

Severe oxidation of organic polymers results in the drastic changes mentioned in the introduction and is easily detected. Photo-oxidation of polyethylene,[19] nylon and cellulose esters,[20] for example, causes crazing, cracking, embrittlement, and in extreme cases granulation of the sample. (Fig. 10) In polyvinyl chloride it leads to hardening and discoloration.[21] In natural rubber, GR-S, and neoprene it causes the development of "mud-crack" patterns or "alligatoring" of the surface and loss of elongation. Thermal oxidation leads to embrittlement of thermoplastics, to "shortening" or loss of elongation in neoprene,[22, 23] nitrile rubbers, and GR-S, and to reversion or the development of tackiness in Butyl rubber and sometimes in natural rubber. As pointed out earlier, these varying effects result from the relative rates of cross-linking and chain-scission reactions. The mechanisms by which oxygen can attack polymers are discussed in the next paragraphs.

TABLE I

SOLUTION VISCOSITY OF CELLULOSE ACETATE BUTYRATE

Original	1.77
After 4 Weeks Exposure to UV Light at Room Temperature	
In Nitrogen	1.60
In Oxygen	.15
After 150 hrs. at 150°C	
In Nitrogen	1.78
In Oxygen	.52

Mechanism of Oxidation Leading to Chain Scission

The reaction of organic compounds with atmospheric oxygen, frequently called "auto-oxidation" or "autoxidation", has been of interest to chemists for a long time and a voluminous literature on the subject has accumulated.[24, 25, 26] While most of the work done has been on small molecules rather than on polymers it is becoming apparent that much of the mechanism of oxidation is the same and what has been learned on small molecules can be applied to large.[27, 28, 29] This is fortunate since polymers do not lend themselves readily to normal chemical manipulations. While it might be expected that different compounds would be attacked by oxygen in different ways a general mechanism has emerged which appears to be characteristic for aliphatic hydrocarbon structures and is probably applicable to many of the polymeric materials in current engineering use. It can be described as an autocatalytic free radical chain reaction.[30, 31, 32]

The sequence of events is believed to be as follows: Free radicals are produced in the substrate from the energy of heat or of light. They may arise from the decomposition of unstable groupings such as the —O—O—

bond in peroxides or by the dissociation of a relatively more stable bond such as —C—C— or —C—H. Needless to say, the ease with which such cracking occurs is influenced by chemical structure. These free radicals, which may be produced in very minute amount, react with oxygen to form peroxidic radicals. This is illustrated by the following chemical equation in which the radical is represented by the letter R and the fact that it is "free" or reactive is indicated by the dot.

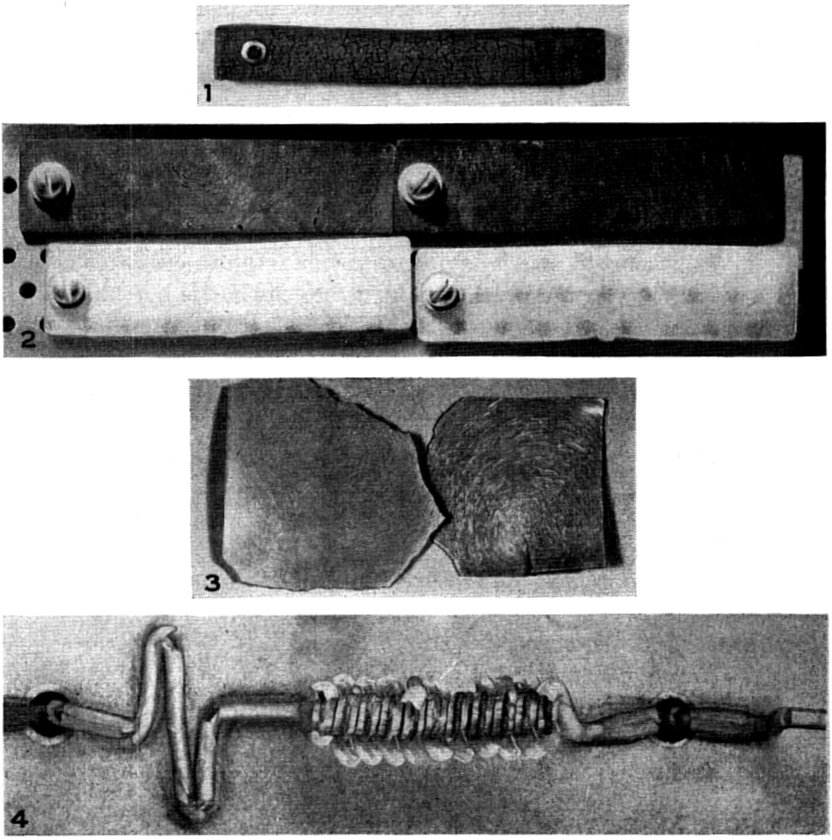


Fig. 10—(1) Cellulose acetate exposed six months at Murray Hill, N. J.
(2) Nylon test panels exposed 5 months at Yuma, Arizona.
(3) Clear Polyethylene sheet exposed 3 years at Murray Hill, N. J.
(4) Clear polyethylene coated wire exposed 3 years at Murray Hill, N. J.

$$R\cdot + O_2 \rightarrow R{-}O{-}O\cdot$$

The peroxidic radicals are also reactive entities, but their affinity is for hydrogen atoms and they tend to abstract hydrogen from some other molecule of substrate, thus:

$$\mathrm{ROO\cdot} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R\cdot}$$

(These equations were written by Bäckström for the oxidation of benzaldehyde[30] and have been adopted by many others.)[31, 6, 33] The latter reaction results from molecular collision with formation of intermediate additive complexes which decompose into the indicated products and in general many ineffective collisions will occur before reaction takes place. The molecule of substrate which loses hydrogen in this way is now a free radical and it repeats the process, reacting first with oxygen and then with another molecule of substrate. This *linear* chain reaction continues until two radicals unite by collision with each other, thus terminating two chains. The word linear is italicized in the previous sentence to emphasize that this part of the reaction is not in itself autocatalytic. The autocatalytic nature of the oxidation stems from the fact that the product of the reaction as outlined is a hydroperoxide, ROOH. Such compounds are relatively unstable and slowly decompose into free radicals which initiate new chains. This might go as follows:

$$\mathrm{ROOH} \rightarrow \mathrm{RO\cdot} + \mathrm{\cdot OH}$$
$$\mathrm{RO\cdot} + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R\cdot} \text{ and } \mathrm{\cdot OH} + \mathrm{RH} \rightarrow \mathrm{HOH} + \mathrm{R\cdot}$$

Thus, though the original rate of generation of free radicals from cracking might have been very low, the combined rate increases quite rapidly since each molecule of peroxide produced in the chain reaction becomes a potential source of new radicals. Eventually the rate reaches what appears to be a steady state and finally levels off. A typical oxygen absorption curve for a liquid hydrocarbon is shown in Fig. 11. The region of fast reaction has received attention from those interested in the oxidation of small molecules but it is unimportant to people interested in polymers because it has been shown by various workers that only slight oxidation is required to destroy the useful properties of a polymer.[34] By the time oxidation has proceeded far enough to be getting into a rapid rate it has already resulted in enough chain scissions to have lowered the molecular weight below useful levels. (A simple calculation will illustrate this point. Suppose a polymer molecule whose molecular weight is 32,000 reacts with one molecule of oxygen (mol. wt. 32) and a chain scission results. The molecular weight of the polymer molecule will have been halved by reaction with .1% of its weight of oxygen. Not every reaction with oxygen results in chain scission of course;[27] but, even so, the amount of oxygen required to ruin the polymer is very small.)

The principal effect of the reactions described above is to introduce the hydroperoxide group into the polymer at various points. It is in the decomposition of these peroxides that chain scission occurs. Studies of the decomposition of the tertiary peroxides produced by oxidation of various dialkyl phenyl methanes have shown that the product is invariably an alkyl phenyl ketone in which the alkyl group is the shorter of the two originally present.[35]

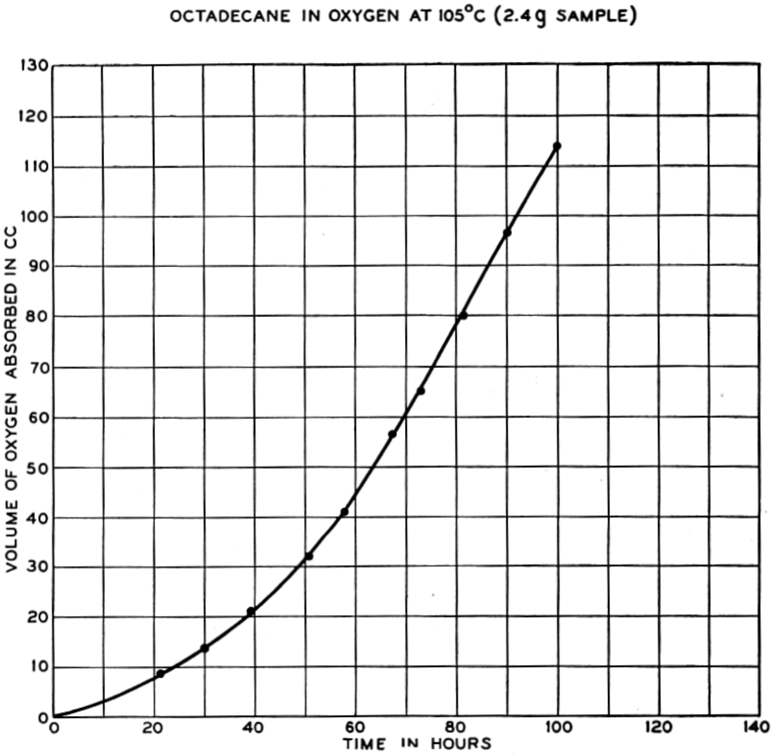
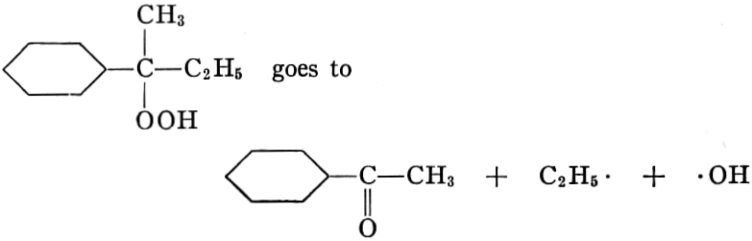


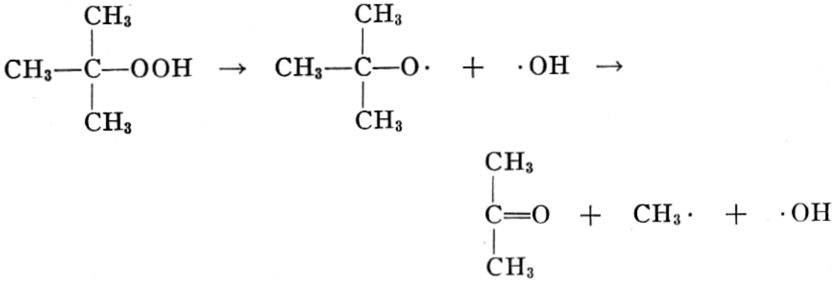
Fig. 11—Octadecane in oxygen at 105° C. (2.4 g sample)

Thus:



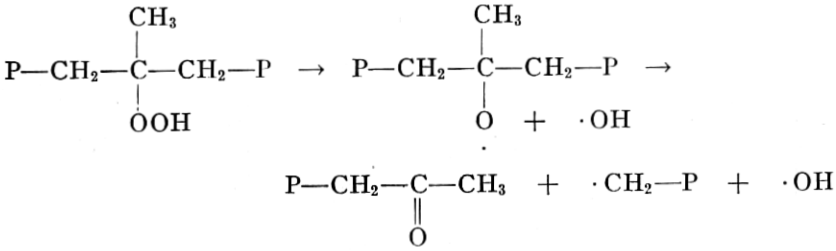
$$C_6H_5-C(CH_3)(OOH)-C_2H_5 \text{ goes to } C_6H_5-C(=O)-CH_3 + C_2H_5\cdot + \cdot OH$$

the C—C bond attaching the ethyl group having been broken. The decomposition of tertiary butyl hydroperoxide has been shown similarly to proceed by the following reactions:[36, 37]



$$\mathrm{CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OOH} \rightarrow \mathrm{CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O\cdot} + \cdot\mathrm{OH} \rightarrow \mathrm{\overset{CH_3}{\underset{CH_3}{C}}{=}O} + \mathrm{CH_3\cdot} + \cdot\mathrm{OH}$$

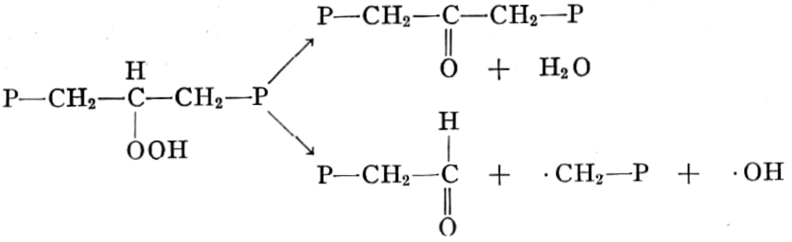
Here again a carbon-to-carbon bond has been broken. The implication of this work for a substituted polyethylene, for example, is quite clear. If oxidation occurred at a tertiary hydrogen as it most probably would,[38, 39, 40] the decomposition of the resulting tertiary peroxide would be as follows (the unaffected portions of the polyethylene chain being represented by the letter P):



$$\mathrm{P{-}CH_2{-}\overset{CH_3}{\underset{OOH}{C}}{-}CH_2{-}P} \rightarrow \mathrm{P{-}CH_2{-}\overset{CH_3}{\underset{\dot{O}}{C}}{-}CH_2{-}P} + \cdot\mathrm{OH} \rightarrow \mathrm{P{-}CH_2{-}\underset{O}{\overset{}{\underset{\|}{C}}}{-}CH_3} + \cdot\mathrm{CH_2{-}P} + \cdot\mathrm{OH}$$

Thus the polyethylene chain would be cut.

The course of events is less clear for secondary peroxides. Here at least two paths are possible:



$$\mathrm{P{-}CH_2{-}\overset{H}{\underset{OOH}{C}}{-}CH_2{-}P} \nearrow \mathrm{P{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}P} + \mathrm{H_2O}$$

$$\mathrm{P{-}CH_2{-}\overset{H}{\underset{OOH}{C}}{-}CH_2{-}P} \searrow \mathrm{P{-}CH_2{-}\overset{H}{\underset{O}{\underset{\|}{C}}}} + \cdot\mathrm{CH_2{-}P} + \cdot\mathrm{OH}$$

If the decomposition proceeds according to the top arrow, no chain scission results, whereas if it takes the lower course the polymer is divided. The aldehyde is subsequently oxidized to acid. The fact that short fatty acids are produced in the oxidation of straight chain hydrocarbons such as octadecane is proof that secondary peroxides or peroxidic radicals can decompose by the chain splitting process. That they do not decompose exclusively by that mechanism is shown by the high yield of tetralone obtained from the decomposition of tetralin hydroperoxide.

The mechanisms outlined, while certainly not complete, are adequate to account for the chain scission type of oxidative deterioration of many plastics and rubbers. The degradation of chlorine bearing plastics such as polyvinyl chloride and polyvinylidene chloride, while also being caused by oxygen and being energized by light and heat, is not believed to follow the patterns outlined above. The first step here is reported[21,41,42] to be the elimination of hydrogen chloride with introduction of a double bond, which makes the loss of more HCl easier and also increases the oxidizability.

TABLE II
FIELD RESULTS ON SAMPLES OF NATURALLY AGED NEOPRENE JACKETING (FROM DROP WIRE)*

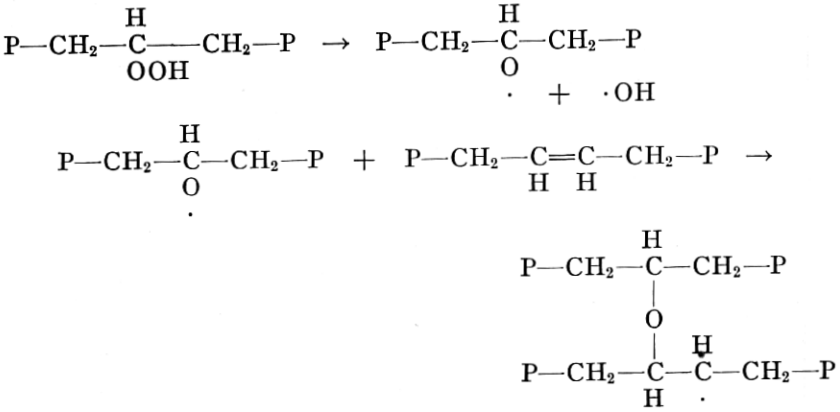
Months Exposure at		Tensile Strength psi	Elongation, %
Original		2218	330
Chester, N. J.	15	2635	215
	31	2655	225
	57	2510	205
Stone Harbor, N. J.	21	1990	190
	64	2485	185
	78	2615	175
Miami, Fla.	14	2540	195
	48	2215	140
	60	2260	125
	74	2410	150
	87	2450	130
	109	2520	120
San Antonio, Tex.	11	2395	160
	22	2300	145
	34	2585	180
	45	2165	135
Brawley, Cal.	15	1980	165
	58	2405	165

* From a paper by G. N. Vacca, R. H. Erickson and C. V. Lundberg(22)

Cross-Linking Resulting from Oxidation

The second important effect of oxidation of polymers is cross-linking. This is of great consequence only with unsaturated compounds and these are principally the rubbers. If cross-linking is the dominant reaction (as it usually is on neoprene, GR-S, and the nitrile rubbers) the result is a decrease in elongation and an increase in hardness without a loss in tensile strength.

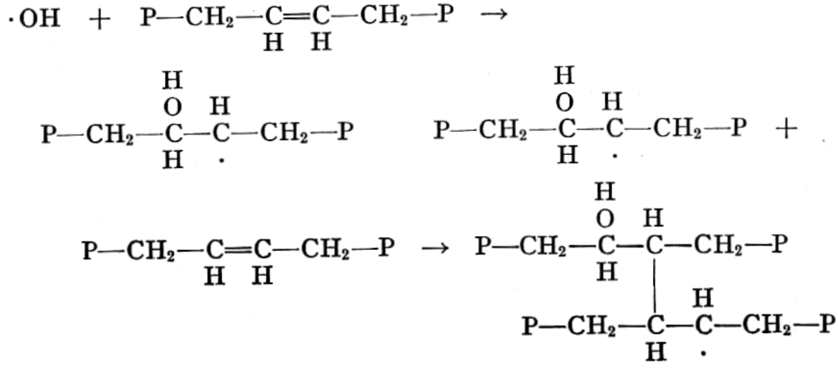
The strength may actually increase as shown in Table II. The rubber tends to "shorten" and ultimately ceases to be rubbery. Carried to an extreme condition, oxidized rubbers can resemble hard rubber or the phenolic resins. The detailed mechanisms of cross-linking are not worked out but certain deductions can be made about the reaction. That it is not just a polymerization of the double bonds can be shown by the fact that its rate in the absence of oxygen is extremely slow. That it is probably induced by free radicals can be inferred from the work on "vulcanization" of unsaturated polyesters with peroxides in which it was evident that a free radical attacking a double bond initiated the cross-linking reaction.[10, 43] The sequence might be as follows:[28]



$$\mathrm{P{-}CH_2{-}\overset{H}{\underset{OOH}{C}}{-}CH_2{-}P} \rightarrow \mathrm{P{-}CH_2{-}\overset{H}{\underset{\underset{\cdot}{O}}{C}}{-}CH_2{-}P} + \cdot\mathrm{OH}$$

$$\mathrm{P{-}CH_2{-}\overset{H}{\underset{\underset{\cdot}{O}}{C}}{-}CH_2{-}P} + \mathrm{P{-}CH_2{-}\underset{H}{C}{=}\underset{H}{C}{-}CH_2{-}P} \rightarrow \begin{array}{rcl} \mathrm{P{-}CH_2{-}} & \overset{\mathrm{H}}{\mathrm{C}} & \mathrm{{-}CH_2{-}P}\\ & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{P{-}CH_2{-}} & \underset{\mathrm{H}}{\mathrm{C}} & \mathrm{{-}\overset{H}{\underset{\cdot}{C}}{-}CH_2{-}P} \end{array}$$

Thus a link has been introduced. The new radical can react with another radical, it can react with oxygen to form another peroxide group, it can react with a double bond in another chain to form an additional cross-link, or when antioxidant is present it can react with antioxidant. The hydroxy radical resulting in the original decomposition of the peroxide could initiate a similar series of reactions resulting in one or more cross-links as follows:



$$\cdot\mathrm{OH} + \mathrm{P{-}CH_2{-}\underset{H}{C}{=}\underset{H}{C}{-}CH_2{-}P} \rightarrow \mathrm{P{-}CH_2{-}\overset{\overset{H}{O}}{\underset{H}{C}}{-}\overset{H}{\underset{\cdot}{C}}{-}CH_2{-}P}$$

$$\mathrm{P{-}CH_2{-}\overset{\overset{H}{O}}{\underset{H}{C}}{-}\overset{H}{\underset{\cdot}{C}}{-}CH_2{-}P} + \mathrm{P{-}CH_2{-}\underset{H}{C}{=}\underset{H}{C}{-}CH_2{-}P} \rightarrow \begin{array}{rcl} \mathrm{P{-}CH_2{-}\overset{\overset{H}{O}}{\underset{H}{C}}{-}} & \overset{\mathrm{H}}{\mathrm{C}} & \mathrm{{-}CH_2{-}P}\\ & | & \\ \mathrm{P{-}CH_2{-}} & \underset{\mathrm{H}}{\mathrm{C}} & \mathrm{{-}\overset{H}{\underset{\cdot}{C}}{-}CH_2{-}P} \end{array}$$

The factor that determines whether or not cross-linking will be dominant in the aging of an unsaturated material must be the chemical structure of the polymer (and its peroxide.) The mode of decomposition of the peroxide which, of course, is a function of structure probably has the most important effect. While cross-linking can occur in saturated materials, as shown by the vulcanization of saturated polyester rubbers with peroxides, its rate is never high enough to result in a condition that could be called deterioration. Both polyethylene and cellulose acetate butyrate can undergo enough gelation on outdoor exposure to become insoluble, but if this were the only change occurring their toughness would be improved rather than degraded by it. Their deterioration in strength is due entirely to chain scission.

Modification of Side Groups by Oxidation

All the oxidation reactions discussed result in the introduction of oxygen into the polymer composition. If the polymer is one which already contains a high percentage of oxygen such as cellulose or even nylon, this may have little effect. If the polymer is a hydrocarbon, however, its power factor will be raised markedly. As a matter of fact the measurement of power factor is a very sensitive way of detecting the addition of oxygen to polyethylene. Except where the polymer is being used for its low power factor, however, the change in side groups will be secondary to the change resulting from chain scission and cross-linking.

Acceleration of Oxidation

The foregoing description of the mechanisms of auto-oxidation makes apparent several ways in which oxidation may be accelerated beyond what might be called the natural rate for a pure material. Since oxidation is a free radical process an obvious way to accelerate it is to add free radicals or materials which produce free radicals. Addition of peroxides to organic compounds generally accelerates the rate of oxidation.[33] Similarly the oxidation of a relatively stable material is accelerated if there is left in it a small amount of a chemical which itself is easily oxidized to peroxides. For example, an addition of turpentine greatly accelerates the air-oxidation of paraffin wax.[44] The addition to polyethylene of an unsaturated polymer such as natural rubber would probably have a similar effect.

It is apparent that the amount by which the rate of oxidation of a substrate is accelerated by peroxides, whether the latter are added as such or are self-generated, is dependent on the rate of decomposition of the peroxide. The latter rate can be accelerated by the presence of certain metallic ions and hence they act as catalysts for oxidation reactions. Copper is particularly active in this regard in natural rubber, and the rubber industry long ago learned to avoid it[45] (Fig. 12). Other metals which have been found to

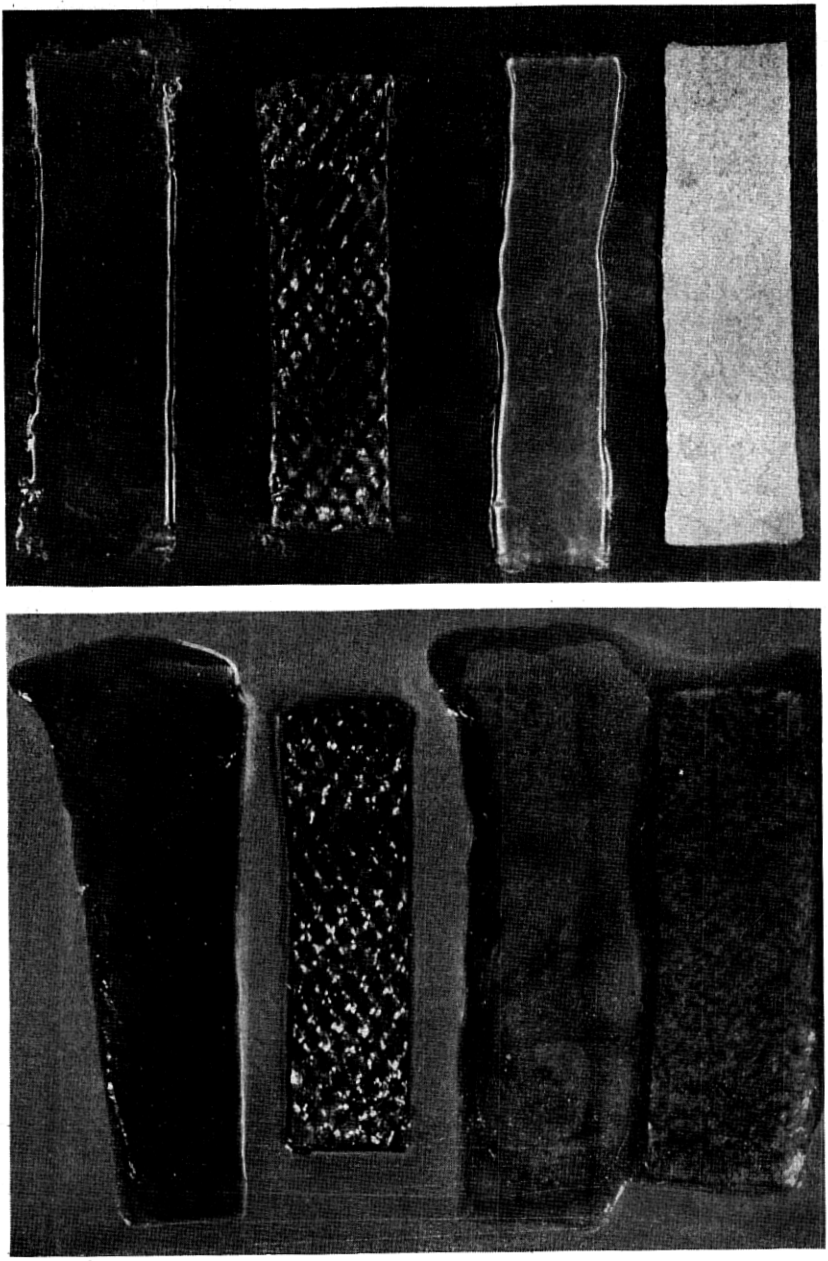


Fig. 12—Various samples of natural rubber oven aged on tin, above; and on copper, below.

cause poor aging at various times are cobalt, manganese, and iron.[46] Since the "drying" of paint is an oxidative reaction, and since rapid drying is a desirable feature, the paint industry has found it advantageous, to use certain metallic salts as "paint dryers".[47]

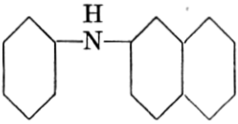
Retardation of Oxidation

Antioxidants

It was discovered by Moureu and Dufraisse about 1918[48] that the oxidation of many organic compounds could be very greatly retarded by the addition of small quantities of certain other chemicals, which they called "antioxygens." Although the mechanisms which they postulated for the action of these materials were later found to be incorrect, their discovery led to the wide use of such protective agents in industry, particularly in rubber which needs this protection badly. The action of what are now called "antioxidants" becomes clear when one understands the free radical chain mechanism of oxidation outlined above. Antioxidants are chain stoppers.[4] By interposing themselves in the chain reaction they terminate it by giving rise to relatively inert free radicals[50, 51] (stabilized by resonance). For example, the antioxidant, designated HA, could act in the following way:

$$ROO\cdot + HA - ROOH + \cdot A$$

In this case the antioxidant satisfies the peroxidic radical by giving it the hydrogen atom it needs, but the residual radical ·A is not sufficiently reactive toward oxygen to continue the chain. A typical antioxidant is β-phenyl naphthylamine,



It was pointed out earlier that many ineffective collisions of the radical ROO· with substrate molecules occur before reaction takes place. If the reactivity of ROO· toward HA is sufficient that few ineffective collisions take place, then small concentrations of HA in the substrate will be adequate to stop each chain at a very early stage. This not only saves all those substrate molecules which would otherwise have become links in these chains but, by so doing, it limits the number of molecules of peroxide produced and thus keeps the rate of initiation of new chains at a low level. The degree of protection by antioxidants varies with the length of the "natural" chain reaction (which is a function of the ratio of effective to ineffective collisions in the absence of an inhibitor and depends on chemical structure) and on the efficiency of the antioxidant but, in some cases, particularly with liquids, very remarkable protection is obtainable as shown in Fig. 13. (The oxidation of the control sample is so fast at this high temperature that the autocatalytic period is not evident.) The effect is less in solids but is still of great value. Antioxidants are of the greatest benefit where the rate of initiation is low, a condition usually true of thermal oxidation. The reason is that since antioxidant is *consumed*[52, 27] in doing its job the rather limited amounts which can be added from a practical point of view (usually not over 1 or 2%) do not last long if the rate of chain formation is very high. This explains the oft stated fact that an antioxidant is far more effective if added before oxidation starts, than if added after oxidation has proceeded for a while.[53] In the latter case enough peroxide will have been produced to overwhelm the antioxidant relatively quickly. This is also the explanation of

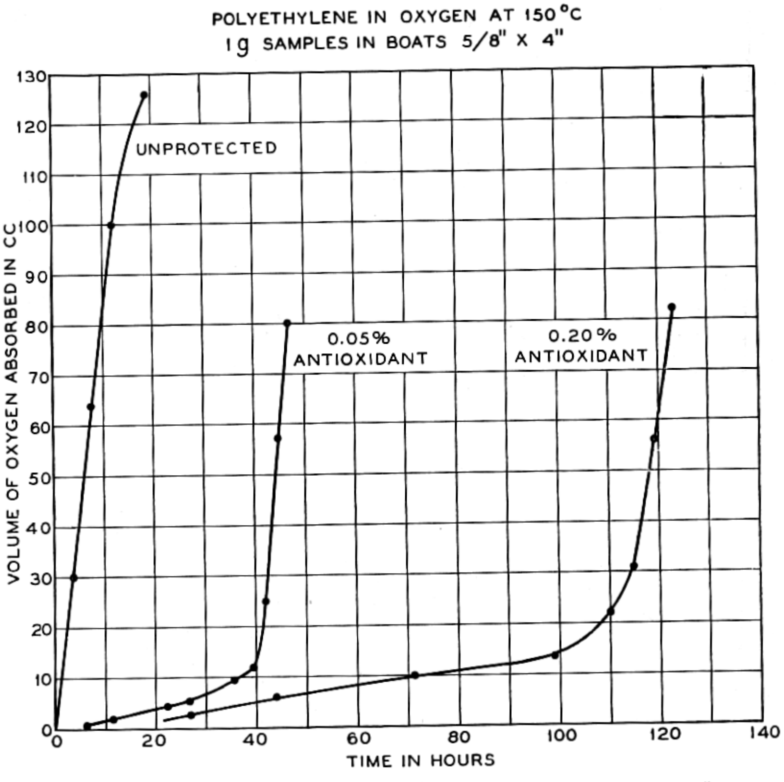


Fig. 13—Polethylene in oxygen at 150° C, 1 g samples in boats $\frac{5}{8}''$ × 4″.

the fact that antioxidants are limited in their effectiveness against photooxidation. The rate of initiation of chains in a material exposed to sunlight is so great that any antioxidant present is used up relatively fast. Furthermore, the oxidation of the antioxidant itself is rapid in sunlight and hence if it were not removed in the one way it would be in the other.

There are many chemicals in current use as antioxidants and more are being created all the time. Most of them are either phenols or aromatic amines. It is frequently asked why one antioxidant is more effective than another, if indeed such differences do exist. The answer is not altogether clear but certain statements can be made about it. In the first place, for any given substrate there are usually several antioxidants which are equally good. However, gradations of effectiveness of many commercial antioxidants can be demonstrated. Many factors can exert an influence on this. Some are solubility in the substrate, volatility, inertness toward the substrate. Beyond these are the reactivity of the antioxidant toward free radicals, both hydrocarbon and peroxidic, and the relative stability of the free radical left when the antioxidant reacts. Undoubtedly, some intermediate level of reactivity is desirable in an antioxidant[54, 55] and this desired level probably varies from one substrate to another.

Light Screens

It was mentioned above that antioxidants are of little effect against relatively strong photooxidation because of the overwhelming rate of generation of chains. The most serious problems of deterioration in the Bell System are, of course, in outdoor applications, and it is quite clear that this is because of exposure to short wave light. The extensive commerical use of unprotected material outdoors came about because of a lack of appreciation of this fact. Once this vulnerability or organic materials to light is appreciated the remedy is obvious, at least in principle, and that is to shut off the light. For this purpose there are many pigments available as well as many light-absorbing organic compounds. A great deal of work has been done with various substrates in testing the effects of the absorbers, and this can be summarized as follows:

In the class of light colored pigments, none offers complete protection. Most of them have a slight effect; a few are fairly helpful; and a few are actually harmful, acting as photosensitizers. Of the darker pigments several are quite effective but the outstanding ones are lead chromates, iron oxides and carbon black, the last being the best. A study of the effect of various types of carbon black in various concentrations in polyethylene has been reported[19] wherein it is shown that under the most favorable conditions the useful life of polyethylene, as judged by accelerated tests, can be extended at least 30 fold. It was shown in this work that for best results the carbon black should be finely divided and well dispersed. The use of polyethylene as a sheath material on outdoor cable would not have been practical without the protective effect of carbon black. The efficacy of carbon black as a light screen is apparently quite general although detailed studies have been made only with polyethylene, rubber,[56] cellulose esters,[57] and polyvinyl chloride,[58] in all of which it is effective.

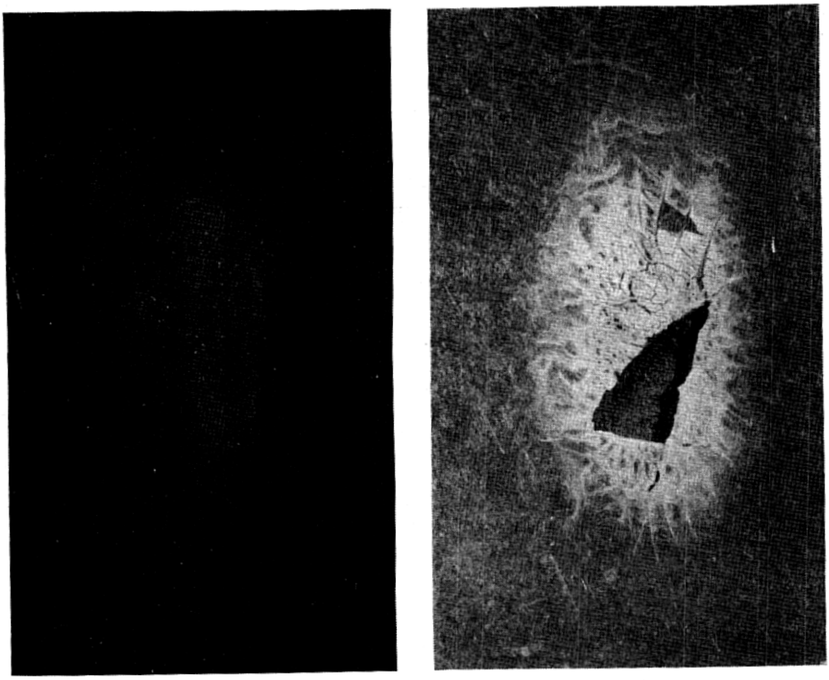


Fig. 14—Cellulose Acetate Butyrate panels exposed to concentrated beams of UV light filtered through pyrex bottles filled with water. Sample at left contains 1% carbon black. Sample at right contains 1% Salol.

In many applications of plastics and rubbers, colors are desirable and for these the use of carbon black is, of course, precluded. Some success has resulted from the use of organic materials which are transparent to visible light but which absorb in the ultraviolet. For example, phenyl salicylate, known as Salol, at a concentration of 1% is a fairly effective protective agent for transparent cellulose esters.[20] Such effects appear to be quite specific, since Salol is not nearly so effective in most other polymers (it is reported to be effective in Saran[59]), and many other compounds which are even better absorbers of ultraviolet light are much less effective in cellulose esters. Some of them actually are sensitizers. Even in cellulose esters Salol at a concentration of 1% is a poor second to carbon black, giving in accelerated tests less than half the life imparted by 1% of a well dispersed, finely divided carbon black.[57] (Fig. 14)

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