

## Oxidation and Heat Aging of Carboxyl-Terminated Polybutadiene

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### Synopsis

Liquid carboxyl-terminated polybutadiene (CTPB) on aging in air increased in viscosity and molecular weight and eventually gelled. Simultaneously, the acid content decreased without formation of anhydride, the changes being a function of the hydrocarbon portion of the molecule. Cured stocks of CTPB underwent changes on heating in air which were largely resinification due to oxidation. However, chain scission or hydrolysis also occurred, resulting in reversion of cure which could be observed in vacuum-aged material or in the interior of the stocks. Commercial resins were compared, and a difference noted between CTPB prepared by ionic and free-radical methods. The idea was presented that the greatest depth of oxidation was determined by the plane beneath the surface where the rate of oxidation equalled the rate of arrival of oxygen by diffusion. This idea was developed mathematically from Fick's diffusion law and an equation derived which related the depth of oxidation to the temperature, the energies of activation for reaction and diffusion, and the rate constants for reaction and diffusion. By using the equation, relative rates of oxidation were determined and the energy of activation for diffusion of oxygen in CTPB was found to be 13.6 kcal./mole.

### INTRODUCTION

During the past few years several low molecular weight carboxyl-terminated butadiene polymers have become commercially available. These are Butarez CTL-I and II (Phillips Petroleum Company), Telagen CT (General Tire and Rubber Company), Hycar CTB (B. F. Goodrich Chemical Company), and HC-434 (Thiokol Chemical Corporation), and have been described in the literature.<sup>1-5</sup> They are prepared by both ionic<sup>1-3,5</sup> and free-radical processes.<sup>4-6</sup> These materials are liquids of molecular weight 3500-6500 and viscosities ranging from 225 to 400 poise. On heating with either imines or epoxides of functionality greater than two, they are converted to crosslinked elastomers of low tensile strength.

A number of investigators have commented upon the many phenomena which can occur during the crosslinking of these carboxyl-terminated polybutadienes (CTPB) and the difficulty of distinguishing between such changes as curing reactions, oxidative resinification, and hydrolysis. In this work we attempted to follow the changes which occur on heating cured and uncured samples of CTPB.

## MATERIALS

Products were obtained from four manufacturers, one of whom (General Tire and Rubber Co.) supplied us with samples of varying molecular weight.

A few of the properties of these materials are shown in Table I. It should be emphasized that the values given are as of the time of use and in at least one case may have been quite different when first received. The properties listed are those of some importance in this work and by no means represent a full description of the resins.

In order to form crosslinked rubbers for use in this work, the various resins were formulated and cured as shown in Table II. Stoichiometric proportions of crosslinking agents were used. When epoxides were employed, catalysts were also present.

## CHANGES IN THE LIQUID POLYMERS

It was observed early in the work that liquid CTPB changed during prolonged storage in the laboratory. Figure 1 shows the increase in viscosity for a sample of Butarez CTL-I over a 40-month period. This sample was in a container with a large air space and was opened frequently. The temperature in the room sometimes reached 100°F. Simultaneously with the increase in viscosity, the carboxyl content of the resin decreased from 1.21% to 1.05% indicating either that chain scission had occurred or that anhydrides had formed. Efforts to detect acid anhydrides by infrared methods or by titration with  $\text{NaOCH}_3$  and  $\text{KOH}$  failed. It was concluded that the anhydride carboxyl, if present at all, had to be less than 5% of the total initial carboxyl content whereas, more than 12% had disappeared. Loss of carbon dioxide on the other hand has been observed by several workers<sup>7</sup> during the oxidation of unsaturated acids.

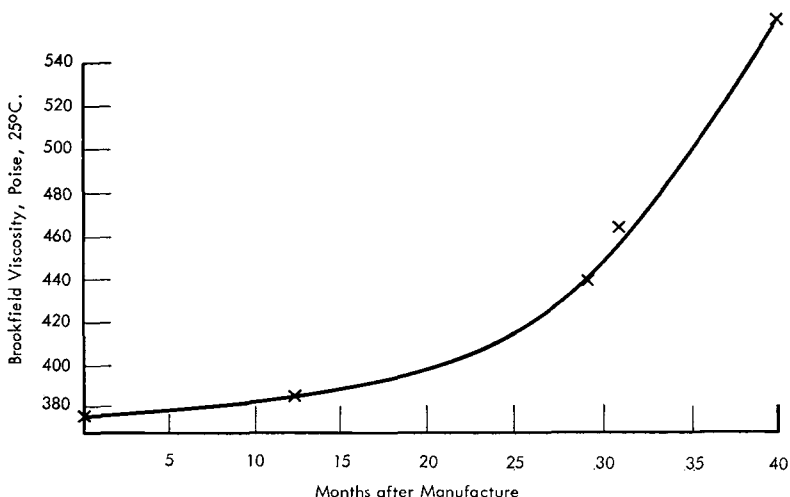


Fig. 1. Influence of storage time on viscosity of CTPB.

TABLE I  
Some Typical Properties of Carboxyl-Terminated Polybutadiene<sup>a</sup>

Product	Production method	Molecular weight (corr.) <sup>b</sup>	Equivalent weight (corr.) <sup>b</sup>	Viscosity (25°C.), poise	Water content, %	pH <sup>c</sup>	Antioxidant present <sup>d</sup>	Antioxidant content, %
Butarez CTL-I <sup>e</sup>	Ionic	5400	4000	260	0.063	5.5	2246	1.25
Butarez CTL-II	Ionic	6400	3000	290	0.053	6.1	2246	1.30
Telagen CT	Ionic	5800	2900	225	0.037	5.4	2246	0.90
Hycar CTB	Free radical	4800	2300	395	0.14(?)		2246	0.87
HC-434	Free radical	3800	1875	230	0.057	5.9	PBNA	0.94

<sup>a</sup> Results are measured values at the time of use and not necessarily as received.

<sup>b</sup> Molecular weights and equivalent weights have been corrected for the effect of the antioxidant present.

<sup>c</sup> The pH is on an extract.

<sup>d</sup> 2246 is antioxidant 2246 from American Cyanamid Company; PBNA is phenyl beta naphthyl amine.

<sup>e</sup> Butarez CTL-I is formed from Butarez CTL-II by adding 30 parts of nonfunctional polybutadiene to 70 parts of Butarez CTL-II.

TABLE II  
Composition of Stocks

	A	B	C	D	E	F	G	H	J
Butarez CTL-I	100								
Butarez CTL-II		100				100	100	100	100
Telagen CT			100						
Hycar CTB				100					
HC-434					100				
Tris[1-(2-methyl)-aziridiny]phosphine oxide	2.10	2.90	2.51	3.40	4.15	5.12	5.12	3.83	3.83
Kopox 170 <sup>a</sup>						5.12			
Epon X801 <sup>b</sup>						0.47	0.25	0.25	0.25
Ferric acetyl acetate									
Triethylenediamine <sup>c</sup>									
Dimethylbenzylamine									
Cure									
Time, hr.	72	72	72	72	72	72	72	72	72
Temp., °C.	80	80	80	80	80	95	95	95	95

<sup>a</sup> Poly(phenyl glycidyl ether), Koppers Company, Inc.

<sup>b</sup> Epopropyl phenyl glycidyl ether, Shell Chemical Company.

<sup>c</sup> Dabco, Houdry Corporation.

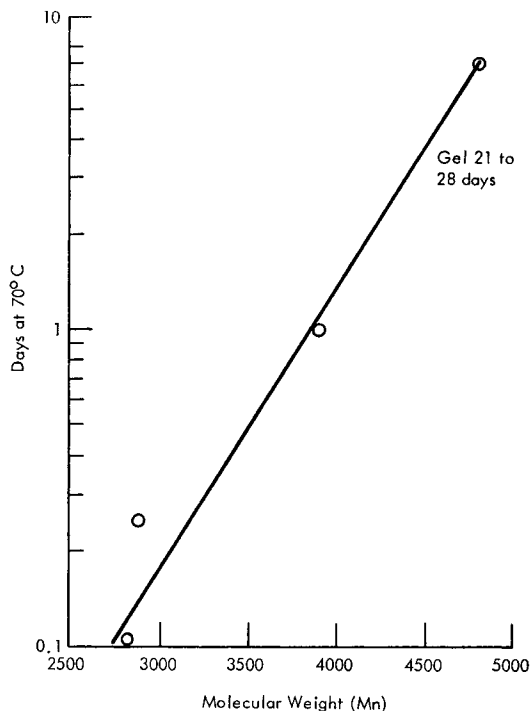


Fig. 2. Influence of air aging of CTPB prepolymer on molecular weight.

Against the instability at relatively low temperatures of the above single sample may be cited the fact that other samples stored in full containers or in the refrigerator remained with only minor increases in viscosity for 16 months. Representatives of the Thiokol Chemical Corp. have reported that the carboxyl content, viscosity, and antioxidant content of their HC-434, doubtless properly stored, remained unchanged for 24 months.

Figure 2 shows the increase in number-average molecular weight of a new sample of Butarez CTL-I heated in air in a thin layer at 70°C. There was evidence, based on the crosslink density of cured stocks of this material, that at the same time as molecular weight was increasing, chain scission was also occurring. That the molecular weight increase is a function of the hydrocarbon portion of the CTPB molecule is shown by the fact that a similar increase takes place during the oxidation of liquid polybutadiene. Figure 3 shows the increase in viscosity of liquid polybutadiene when ferric acetyl acetonate (FeAA) is present and oxygen is bubbled through the mixture.

In the same figure is shown for comparison, a carboxyl-terminated polybutadiene, Telagen CT. Telagen CT oxidized more rapidly than the polybutadiene, in fact 3.6 times as fast. This result may be connected with the fact that Telagen CT contained 27% vinyl olefin groups while the polybutadiene contained only 9% vinyl groups.

Increase in viscosity and molecular weight on heat aging in air continues with CTPB and with liquid polybutadiene until the resins gel. A film of Butarez CTL-I gelled in 21–28 days at 70°C. and in 4 days at 95°C. An antioxidant-free sample of Butarez CTL-I gelled in 20 hr. at 95°C. as did an antioxidant-free sample of liquid polybutadiene. Samples of liquid polybutadiene containing the phenolic antioxidant 2246 (American Cyanamid Company), remained fluid for 1 week at 95°C.

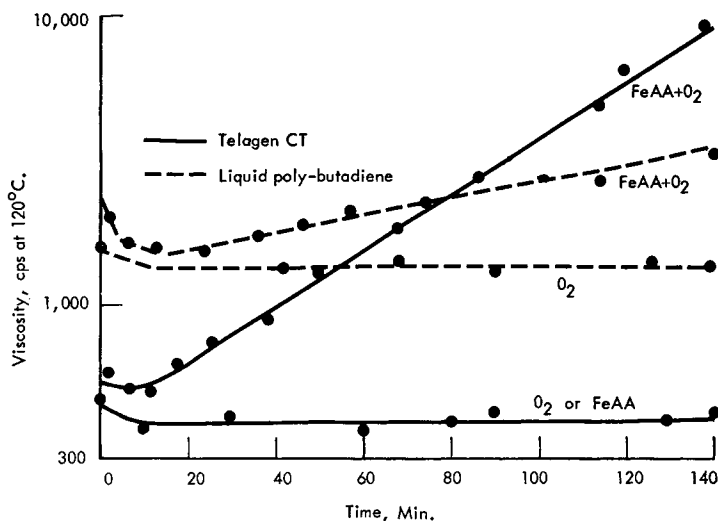


Fig. 3. Oxidation of butadiene prepolymers: (—) Telagen CT; (--) liquid polybutadiene.

Thermal breakdown of liquid CTPB was investigated briefly. Thermal rupture of CTPB or polybutadiene can be observed below 275°C. only in the case of noncrosslinked material and in the complete absence of oxygen. Liquid CTPB degrades at a measurable rate above 245°C. while polybutadiene shows degradation at somewhat lower temperatures. Liquid products are produced. If oxygen enters the system or if the materials are crosslinked, temperatures of 250–275°C. simply cause the polymers to resinify.

### HYDROCARBON NETWORK OXIDATION

When the CTPB prepolymers are crosslinked, the changes which can occur on aging are complex. All unsaturated hydrocarbons are subject to changes at elevated temperatures or in the presence of light or ozone. Vulcanizates of carboxyl-terminated polybutadiene are subject to these changes as well as to changes in the state of cure of the stocks. Reactions which can occur on heating CTPB stocks beyond the normal cure time are as follows.

### Continued Cure

Crosslinking of CTPB stocks as normally practiced is probably inefficient. On continued heating in the absence of oxygen cure often rises. In some cases the crosslink density may double. It is believed that increase in hardness in the interior of the stock is partly and perhaps mainly due to a continuation of the curing reaction.

### Bond Rupture by Reaction

CTPB can dissolve 0.11% water. If water is present, particularly if the material is acidic, hydrolysis of certain branch point bonds occurs ( $O=P-N$ ) and the stock may "melt" after a few days at 100°C. Hydrolysis takes place readily in imine cured stocks but has not been observed in epoxide cured stocks. There is some evidence that impurities other than water, possibly alcohols or amines, can cause similar changes.

### Thermal Rupture

Breakdown of high molecular weight uncured polybutadiene takes place above 200°C. in the complete absence of oxygen to produce principally vinyl cyclohexene. We have not observed thermal rupture in crosslinked CTPB at 265°C.

### Crosslinking or Resinification by Oxygen

In the presence of atmospheric oxygen at elevated temperatures unsaturated hydrocarbons, including CTPB, form free radicals which form carbon-to-carbon crosslinks.<sup>8,9</sup> CTPB is ultimately converted to a hard, horny resin by this process.

### Chain Scission by Oxygen

Instead of crosslinking, the effect of oxygen at elevated temperatures may be to break the hydrocarbon chain.<sup>8,9</sup> If this reaction predominates over the crosslinking reaction, the product becomes softer, and cured stocks may be converted to a liquid. Minor differences in the hydrocarbon structure influence the relative rate of chain scission and crosslinking. For instance, polybutadiene resinifies, whereas *cis*-polyisoprene softens by oxidation. Chain scission has been detected in uncured CTPB, but the predominant effect at the surface of cured stocks of CTPB is nearly always resinification.

The processes leading to reversion of cure, chain scission and hydrolysis, may be difficult to distinguish. On the other hand, the two hardening processes, continued cure and resinification, can be observed separately in the interior of the stock and at an air surface.

### OXIDATION OF CROSSLINKED CARBOXYL-TERMINATED POLYBUTADIENE

Heat-aging studies have been carried out on stocks of all CTPB commercially available. Measurements of hardness and crosslink density by solvent swelling have been made on the exposed surface of stocks and on the interior of the stocks after aging in air and in vacuum. Figure 4 shows some typical data comparing the state of cure of a CTPB stock during heat aging in air and in vacuum.

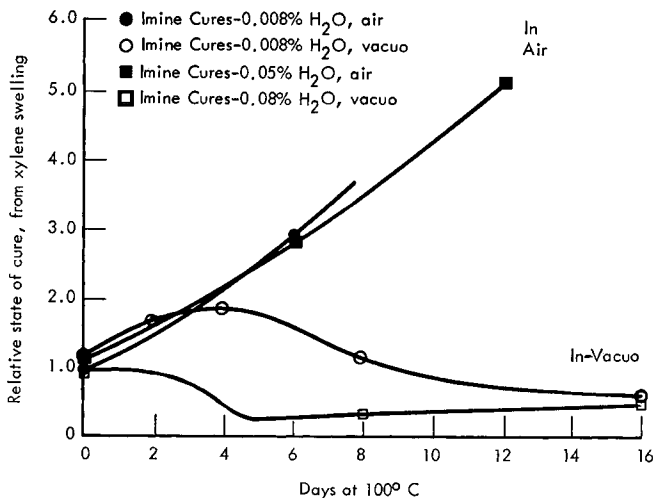


Fig. 4. Heat aging of CTPB stocks at 100°C.: (●) imine cures, 0.008% H<sub>2</sub>O, air; (○) imine cures, 0.008% H<sub>2</sub>O, vacuum; (■) imine cures, 0.05% H<sub>2</sub>O, air; (□) imine cures, 0.08% H<sub>2</sub>O, vacuum.

A great difference exists between the two sets of curves. The results are most readily explained by two competing processes: (1) oxidation which produces a hardening, a shorter break, and eventually a brittle material, and (2) scission or hydrolysis which produces a softer stock with a higher elongation at break. In the presence of air, hardening is the predominant effect at the surface.

It was found that oxidation darkened the color of CTPB even in samples containing no antioxidant. The changes were more rapid in antioxidant-free stocks. This result indicates that the color change involves a CTPB reaction. The boundary between the dark and light portions is fairly sharp, and the rate of oxidation may be followed by determining the change in intensity of color of the dark portion. These points are illustrated in Figure 5. During oxidation the hardness of the dark portion increases, while the hardness of the light-colored center of the stock sometimes decreases. The changes are abrupt at the boundary. These changes are paralleled by changes in crosslink density as measured by solvent swelling.



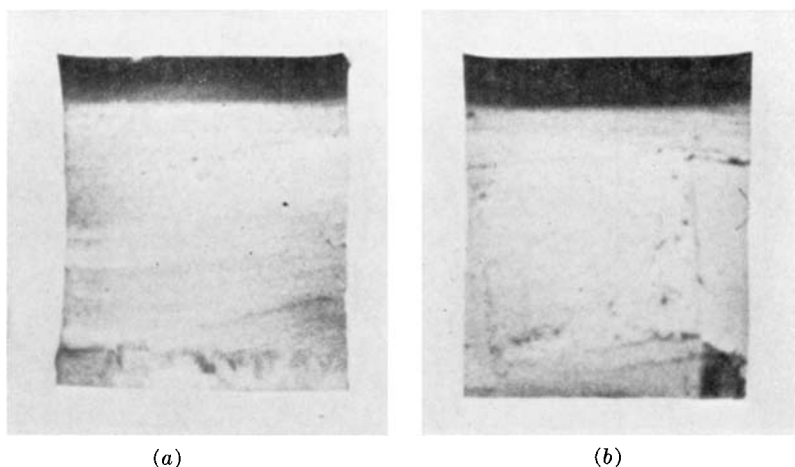


Fig. 5. CTPB, imine-cured; (a) 6 days, 100°C.; (b) 12 days, 100°C.

In samples aged below 75°C. the boundary may be difficult to see except under special lighting conditions.

The depth of the dark oxidized portion measured from the air surface decreased as the aging temperature increased. The depth varied inversely with the hardness of the surface and the surface became much harder at

TABLE III  
Surface and Interior Cure at Various Temperatures

Treatment	Depth dark band, mm.	Shore A, 5 sec.		RNB number	
		Sur-face	In-side	Sur-face	In-side
Initial, 3 days at 70°C.	8	10	6	1.11	0.97
6 days, 79°C.	7		11		1.92
6 days, 100°C.	4 <sup>1</sup> / <sub>2</sub>	14	11	1.24	1.03
6 days, 150°C.	2	68	7	4.70	0.95
12 days, 79°C.	7	19	10	1.30	1.18
12 days, 100°C.	4 <sup>1</sup> / <sub>2</sub>	20	7	1.19	0.55
12 days, 150°C.	2	76	6	7.29	1.06
Antioxidant-free, 6 days, 100°C.	4	21	8		

TABLE IV  
Crosslink Density at Various Depths

Treatment	RNB number at various depths			
	0-3 mm.	3-7 mm.	7-10 mm.	10-12 mm.
6 days, 79°C.	2.76	2.47	1.92	
12 days, 79°C.	1.30	1.28	1.19	1.18

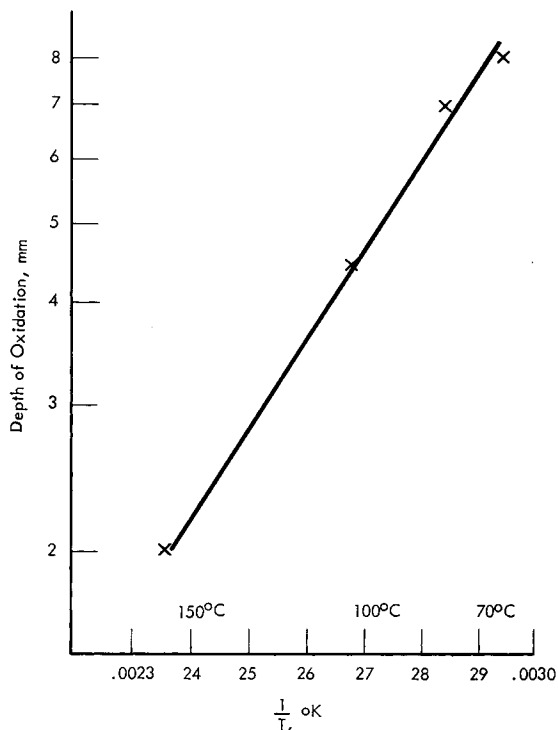


Fig. 6. Oxidation depth as a function of temperature of heat aging.

higher temperatures. The width or depth of the dark portion did not change with time of aging. These results are shown in Tables III and IV. Somewhat similar observations have been made by others for Hevea oxidation.<sup>10</sup>

We have used in Figure 4 and Tables III and IV an RNB number. The RNB number is calculated from the results of swelling tests, run in this case in reagent grade mixed xylene. Such tests have been used extensively in determining the state of cure of crosslinked stocks. The RNB value is the relative number of crosslinking bonds. It is calculated as follows:

$$\text{RNB} = V_2^{5/3} \text{ (per cent gel)}$$

where  $V_2$  is the volume fraction of polymer in the solvent swollen gel excluding filler. The RNB number is approximately proportional to the number of chemical bonds at the branch points. This treatment is derived from the modified equation of Flory<sup>11</sup> relating solvent swelling and crosslink density.

Atmospheric oxygen diffuses into CTPB stocks to a depth determined by the rate of oxidation, the faster the rate the less the distance the gas diffuses. This diffusion is observed very early in the heating period. Thereafter oxygen diffuses to no greater depth, but over the area which it has reached reaction continues as time goes on. The depth of oxidation is thus deter-

mined by the reaction time of oxygen with the polymer and the diffusion rate of oxygen at a given temperature.

Figure 6 shows the logarithm of the depth of oxidation of an imine-cured CTPB stock as a function of the reciprocal of the temperature. A straight line is obtained. We have predicted this result mathematically in a treatment given in the appendix of this paper and obtain the relationship

$$x \cong (\pi k_D c_0 / 2k_R c)^{1/2} (e^{(E_R - E_D)/RT})^{1/2}$$

from which

$$\ln x = 1/2 \ln (\pi k_D c_0 / 2k_R c) + [(E_R - E_D)/2R]/T$$

where  $x$  is the distance from the surface of the polymer where the rate of oxidation is equal to the rate of arrival of oxygen from the surface;  $k_D$  is the diffusion constant, excluding the energy of activation term;  $k_R$  is the apparent overall reaction rate constant for oxidation, excluding the energy of activation term;  $c_0$  is the concentration of oxygen at the surface, assumed to be constant;  $c$  is the concentration of oxygen at the point  $x$  beneath the surface ( $c$  may be small but is not zero at the point  $x$ );  $E_R$ ,  $E_D$  are, respectively, the energy of activation for the overall oxidation reaction and for diffusion of oxygen in the polymer.

The difference between the two activation energies as calculated from the slope of Figure 6 is 10.4 kcal./mole. If the apparent overall energy of activation for the oxidation reaction is 24 kcal./mole,<sup>12</sup> then the energy of activation for diffusion of oxygen in CTPB becomes 13.6 kcal./mole.

All of the foregoing discussion of oxidation depth is based on observations on imine-cured CTPB. If an iron compound is present, as is sometimes the case when epoxide crosslinking agents are used, the rate of oxidation increases, and correspondingly the depth of oxidation is much less. In fact, we believe that one may use the depth of oxidation as a possible means of obtaining rough comparisons of the relative rate of oxidation in the presence of various compounding ingredients (see Appendix).

In stocks filled with 40–70% filler, the air surface again was harder and darker in color than the interior. However, the edge of the dark band was diffuse and it was impossible to give a definite value to the width of the oxidized band except that it was no wider than in the absence of the filler and was about 5 mm. wide for stocks aged at 100°C. Crosslink density by swelling measurements was consistently a little less in the interior of the filled stocks than near the surface.

## BEHAVIOR OF COMMERCIAL RESINS

Having established the outlines of CTPB heat aging, various commercially offered products were compared. Gum stocks were used which were aged at 80, 100, and 150°C. Figures 7–9 show changes in cure obtained on heat aging these stocks in air at 100 and 150°C. The imine referred to in

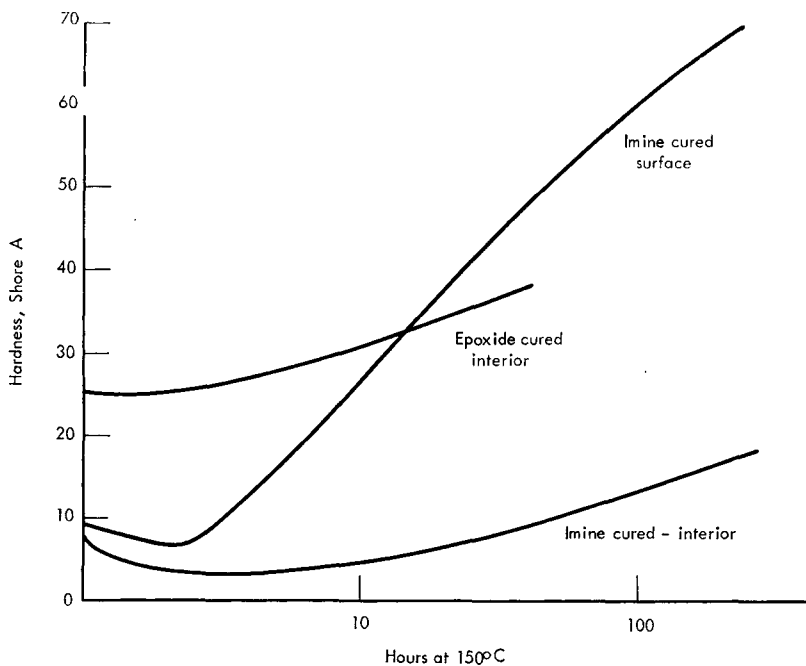


Fig. 7. Heat aging of Butarex CTL-1 gum stocks in air at 150°C.

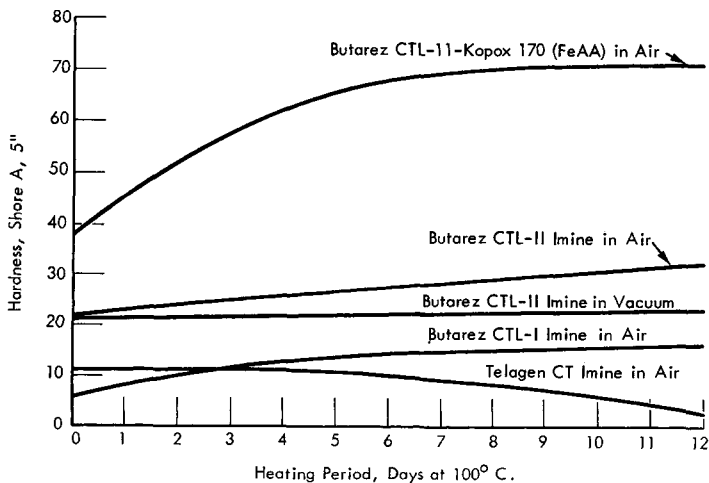


Fig. 8. Variation in surface cure on aging at 100°C.

the figures is tris[1-(2-methyl)aziridinyl]phosphine oxide. The composition of the stocks is given in Table II.

Figure 7 shows typical differences found between the interior and the air surface of a stock. The initial drop in cure is frequently found and may be due to hydrolysis of branch point bonds by the 0.03–0.06% water

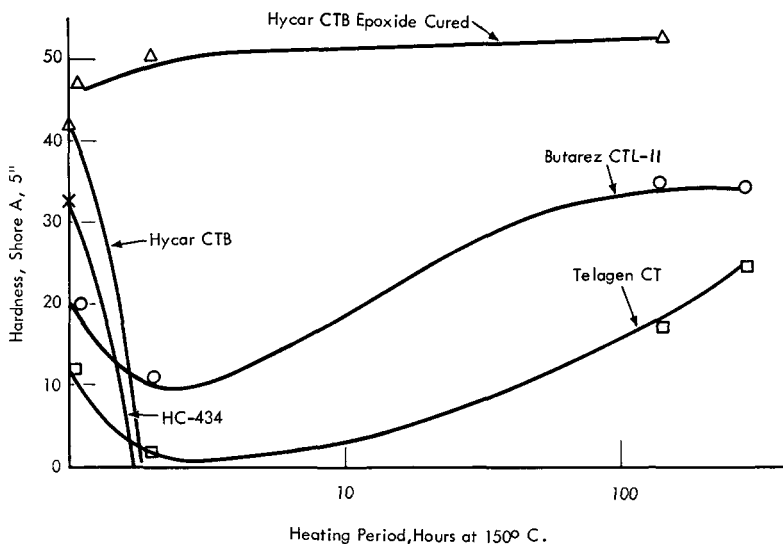


Fig. 9. Heat aging of interior of imine-cured CTPB gum stocks.

usually present in these materials. Stocks cured with epoxides do not show this initial drop in cure, and if ferric acetyl acetate is present (Fig. 8) their surface may become quite hard and brittle.

Figure 8 shows a comparison of four commercial types of CTPB stocks at 150°C. in air. These are imine-cured except for one case, which shows the increased stability to be expected from epoxide cures.

In general one may say that stocks cured with an epoxide showed greater stability than those cured with imine. The two ionic-type CTPB products behaved similarly, and the two free-radical-produced materials were similar. Aging characteristics of the CTPB produced by the two methods were different however. The products made by free-radical methods and cured with an imine (one only was tested) melted down completely in a few days at 100°C. and then resinified whether heated in air, in a vacuum, or in air over  $P_2O_5$ . The ionic products did not. On the other hand, when cured with an epoxide both types were stable. The behavior of the CTPB produced by a free-radical method and cured with an imine does not fit in with existing theories of air oxidation, nor does it seem possible that hydrolysis can take place in the stocks stored over  $P_2O_5$ .

## APPENDIX

Fick's first law of diffusion states that the rate of diffusion is proportional to the rate of change of concentration with distance<sup>13,14B</sup>

$$\delta s / \delta t = -D \delta c / \delta x$$

where  $s$  is the amount of material diffusing through a unit area of the substrate;  $c$  is the concentration of diffusing material, which decreases in

the direction  $x$ , that is,  $dc/dx$  is negative;  $x$  is the distance from the surface;  $t$  is time, and  $D$  is the diffusion coefficient. It is the weight of material diffusing across a plane of 1 cm.<sup>2</sup> in unit time under a concentration gradient,  $dc/dx$ , of unity. It contains an activation energy term.

Now, since we are considering a unit area,  $\delta s/\delta x = c$ . Hence  $\delta c/\delta x = \delta^2 s/\delta x^2$  and the diffusion law may be expressed as  $\delta s/\delta t = -D(\delta^2 s/\delta x^2)$  or by  $\delta c/\delta t = -D(\delta^2 c/\delta x^2)$ , Fick's second law.

The equations have different solutions, depending on the conditions of diffusion. Here we are interested in a solution in the case of a semi-infinite medium, the distance from the boundary or surface being variable, the surface having a constant concentration of diffusing material, and the initial concentration being zero in the medium.

If we first consider a particular plane in the medium at a distance  $x$  from the surface and parallel to it, one may derive  $(\delta s/\delta t)_x = c_0(D/\pi t)^{1/2}$ , where  $c_0$  is the concentration of diffusing material at the surface.

This equation was given but not derived by Ward.<sup>15</sup> A derivation was presented by Lennard-Jones<sup>16</sup> and can be found discussed by Crank in terms of the loss of diffusing substance rather than the gain.<sup>14b</sup>

The relationship shows the rate of change in the amount of diffusing substance present at a given point as a function of time. However, from the original statement of Fick's law, the rate of change with time of the amount of material is proportional to the rate of change of concentration with distance. That is,  $c_0(D/\pi t)^{1/2} = -D(\delta c/\delta x)$ .

If we set the time as constant, this equation may be integrated. We have first regarded distance as invariable and integrated. We now put the result back and keep another variable constant. Thus,

$$\int_{c_0}^c \delta c = -c_0/(\pi Dt)^{1/2} \int_0^x \delta x$$

$$c/c_0 = 1 - [x/(\pi Dt)^{1/2}]$$

$\delta c/\delta t$  may now be determined:

$$\delta c/\delta t = c_0 x/2t(\pi Dt)^{1/2}$$

But

$$t^{1/2} = x/\{[1 - (c/c_0)](\pi D)^{1/2}\}$$

or

$$\delta c/\delta t = c_0 \pi D [1 - (c/c_0)]^3/2x^2$$

Now if the maximum depth below the surface where oxidation is observed is near the point where the increase in concentration of oxygen with time due to diffusion is equal to the rate of oxidation, then this depth may be determined by setting the two rates equal and solving for  $x$ . The rate of oxidation of unsaturated hydrocarbons,  $-dc/dt$ , is a first-order reaction with respect to oxygen concentration at low pressures of oxygen and is zero-order at high pressures.<sup>17</sup>

If we assume a first-order reaction,

$$-\delta c/\delta t = kc$$

where  $k$  is the reaction rate constant. It includes an overall energy of activation term.

Thus

$$kc = c_0\pi D[1 - (c/c_0)]^3/2x^2$$

$$x = (c_0\pi D/2kc)^{1/2} [1 - (c/c_0)]^{3/2}$$

Neglecting  $c/c_0$  in comparison with one yields

$$x = (\pi Dc_0/2kc)^{1/2}$$

If we place activation energy terms in  $D$  and  $k$ ;

$$D = k_D e^{-E_D/RT}$$

and

$$k = k_R e^{-E_R/RT}$$

Then

$$x = (\pi k_D c_0 / 2 k_R c)^{1/2} e^{(E_R - E_D)/2RT}$$

and

$$\ln x = 1/2 \ln (\pi k_D c_0 / 2 k_R c) + [(E_R - E_D)/2R]/T$$

Since the slope of the curve  $\ln x$  versus  $1/T$  is positive,  $E_R > E_D$ . The value of  $E_R - E_D$  may be determined from the slope of the curve:  $E_R - E_D = 10,400$  cal./mole. If we take an average value of the overall energy of activation for the oxidation of polybutadiene as 24,000 cal./mole<sup>10,12</sup> then  $E_D = 13,600$  cal./mole. This value is in agreement with the energy of activation for diffusion of oxygen in poly(vinyl acetate) above the glass point, 14,000 cal./mole.<sup>18</sup>

$c$  in the above equation of course cannot be zero. It is the concentration of  $O_2$  at the point where the rate of oxidation equals the rate of appearance of oxygen by diffusion from the surface. Since the oxidation boundary is sharp in this case it follows that the concentration of  $O_2$  must approach zero very rapidly inward from the point  $x$ . Furthermore,  $kc$ , the rate of oxidation, will vary inversely with  $x^2$ , and hence relative reaction rates in various formulations of the same polymer may be assigned by measuring the depth of oxidation, that is, the value of  $x$ .

$$kc \cong c_0\pi D/2x^2$$

The approximate depths of oxidation found in Butarez CTL-II are given in Table V.

TABLE V

System with CTPB	Oxidation depth, (100°C.), mm.	Relative rate value
Imine	4 <sup>1</sup> / <sub>2</sub>	1
Imine, absence of antioxidant	4	1.3
Epoxide-triethylenediamine	3 <sup>1</sup> / <sub>2</sub>	1.7
Epoxide-dimethylbenzylamine	2 <sup>1</sup> / <sub>2</sub>	3.2
Epoxide-FeAA	<sup>3</sup> / <sub>4</sub>	36

The rate of oxidation is increased greatly by the presence of ferric acetyl acetate, FeAA, and seems to be increased by the presence of the basic compound, dimethylbenzylamine. Antioxidant 2246 has some effect, but not a great one, on the oxidation rate.

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### Résumé

Les polybutadiènes liquides terminés par des groupes carboxyles (CTPB) manifestent par vieillissement à l'air une augmentation de viscosité et de poids moléculaire et éventuellement gélifient. Simultanément, la teneur en acide décroît sans formation d'anhydride, le changement étant une fonction de la portion hydrocarbonée de la molécule. Les stocks recuits de CTPB subissent des changements par chauffage à l'air qui correspondent en grande partie à la résinification par suite de l'oxydation. Toutefois, la scission de chaînes ou l'hydrolyse se passent également avec un renversement du processus de recuit, qui peut être observé dans du matériel vieilli sous vide, ou à l'intérieur des matériaux stockés. Les résines commerciales ont été comparées et une différence notée entre le CTPB préparé par des méthodes ioniques et par radicaux libres. On admet que l'oxydation est plus prononcée en dessous de la surface où la vitesse d'oxydation est égale à la vitesse d'arrivée de l'oxygène par suite de la diffusion. Cette idée est développée mathématiquement au départ de la loi de diffusion de Fick et une équation a été dérivée qui relie la profondeur de l'oxydation à la température, les énergies d'activation pour la réaction et pour la diffusion, et les constantes de vitesses pour la réaction et pour la diffusion également. Sur la base de cette équation, des vitesses d'oxydation relatives ont été déterminées et l'énergie d'activation pour la diffusion de l'oxygène au sein de ce CTPB a été trouvée égale à 13.6 Kcal/mole.

### Zusammenfassung

Flüssiges Polybutadien mit Carboxylendgruppen (CTPB) nahm beim Altern unter Luft an Viskosität und Molekulargewicht zu und zeigte schliesslich Gelbildung. Gleichzeitig nahm der Säuregehalt ohne Anhydridbildung ab, wobei die Änderung eine Funktion des Kohlenwasserstoffteils des Moleküls war. Vulkanisiertes CTPB veränderte sich beim Erhitzen unter Luft grösstenteils durch oxydative Verharzung. Es trat jedoch auch Kettenspaltung oder Hydrolyse auf, was zu einer Vulkanisationsumkehr führte, welche bei Vakuumgealterten Material oder in Inneren der Proben beobachtet werden konnte. Handelsübliche Harze wurden verglichen, und ein Unterschied zwischen ionisch und radikalsch hergestellten festgestellt. Es wurde die Vorstellung entwickelt, dass die grösste Oxydationstiefe durch diejenige Ebene unterhalb der Oberfläche bestimmt wurde, an welcher die Oxydationsgeschwindigkeit der Geschwindigkeit der Sauerstoffanlieferung durch Diffusion gleich war. Diese Vorstellung wurde mathematisch aus dem Fickschen Diffusionsgesetz und einer Gleichung, welche die Oxydationstiefe mit der Temperatur verknüpft, aus den Aktivierungsenergien von Reaktion und Diffusion und den Geschwindigkeitskonstanten von Reaktion und Diffusion entwickelt. Mit dieser Gleichung wurde die relative Oxydationsgeschwindigkeit bestimmt, und die Aktivierungsenergie der Diffusion von Sauerstoff in CTPB zu 13,6 kcal berechnet.

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