

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, RESEARCH CENTER, U. S. RUBBER COMPANY]

Degradation of Polyisoprene Networks by Oxygen

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Volatile products of the oxidation of natural rubber vulcanized in two distinct ways are identical with those obtained from raw rubber. Rates of oxidation of the vulcanizates are similar, but faster than that of raw rubber. Solubility and swelling after oxidation are not affected by the nature of the crosslinking agent. Differences between the oxidation of vulcanized and raw rubber must be traced to some feature common to vulcanizates containing carbon-to-carbon and carbon-to-sulfur bonds in the crosslink, and external to the crosslink itself.

Introduction

The insolubility of vulcanized rubber and the relatively low concentration at which oxidation reactions completely degrade the vulcanizate have made it necessary that indirect methods be used to study the reaction of molecular oxygen with rubber. The literature contains many reports of measurements of the absorption of oxygen by vulcanized rubber, which is easy and convenient experimentally. In some of these the rate of oxygen absorption has been the only property measured. This alone gives little information about the mechanism of oxidation, although the fact that the general form of curves of oxygen absorption as a function of time can be predicted by equations based on the known mechanism of oxidation of low molecular weight olefins¹ is indirect support for similar mechanisms of oxidation of polymers.

The technologically important reaction accompanying oxidation of natural rubber is scission, not detected by gas absorption measurements. It has been studied principally by determining the decay in stress of a sample at constant strain.²⁻⁹ The results suggest that scission occurs by a first order^{7,8} process at selected sites in the network.⁵ This has been interpreted to mean that crosslinks are the primary locus of oxidation in vulcanized rubber.^{7,9} Estimates of the amount of oxygen required for breaking a bond are available only for samples vulcanized with sulfur.⁹ From these it may be calculated that initially 4-5 moles of oxygen is required per scission, when allowance is made for the effect of entanglements¹⁰ on stress. A marked difference between the relaxation of peroxide-cured and sulfur-cured samples has been reported.^{7,8}

Horikx¹¹ has made an extensive investigation of the solubility and swelling of oxidized vulcanized rubber. His results show that the hydrocarbon chain must be broken during oxidation.

The mechanism of scission of unvulcanized rub-

ber has been determined¹²; in this work it was found that low molecular weight products are an important index of scission reactions. The present report describes preliminary work on the scission mechanism in vulcanized natural rubber which has two objectives; to repeat Horikx's experiments with vulcanizates incapable of further cure, and to determine whether low molecular weight products accompany the scission reaction.

Experimental

Considerations governing the choice of temperature and experimental arrangement have been discussed previously.^{12b} The high rate of oxidation of vulcanized rubber relative to raw rubber made it necessary to work at a lower temperature (120°) than was used in the earlier study. It has not yet been determined whether scission efficiency varies with temperature in vulcanized rubber in the same way it does in raw rubber.

The apparatus is a closed loop in which gas is circulated through a cell containing the sample and one or more traps for removing volatile products in series. Auxiliary equipment for measuring gas absorbed at constant pressure is attached. Gas burets were kept at 40°, the cell at 120° and traps at 0 or -80°. All connections between parts external to the oven are of capillary tubing to minimize the volume of the apparatus exposed to uncontrolled temperature fluctuations.

It is widely assumed that both crosslinking and scission reactions occur in the oxidation of rubber, although this has not been established experimentally.¹² Many conventional rubber mixtures will increase in modulus after the initial "cure" as a result of continued vulcanization. In order to remove this complication as far as possible two series of samples were used in which continued cure is impossible. The formulas used for the vulcanized mixtures are given in Table I. The first set, which will be referred to as the sulfur samples, were made using a highly accelerated "compound" typical of those compounds used for foam sponge¹³ manufacture. These give the maximum modulus per mole of sulfur taken, which can be obtained by known methods, if the cure is continued until the modulus stops rising. The samples were coagulated on forms, dried and cured in an atmosphere of carbon dioxide at 100° for 72 hr. According to Barton's¹⁴ results, this is sufficient to produce the ultimate modulus. To destroy residual ultraaccelerator and to remove as much free zinc oxide as possible, the cured samples were leached 2 hr. at 95° in 3% acetic acid solution. This did not succeed in removing as much zinc as was expected from earlier results with foam samples, so that our estimates of acid production may be low for these stocks. However, they are of the same order of magnitude as the results for the peroxide samples, which contained no base. The latter were prepared by calendering the simple mixture at low temperature into a strip 0.010" thick and 8" wide. Pieces of this strip were cut off, wrapped around cylindrical forms and cured *in vacuo* at 150° for 2 hr. The samples were cooled *in vacuo* before opening the containers. Decomposition products of the peroxide were removed from some

(1) J. R. Shelton and W. L. Cox *Ind. Eng. Chem.*, **45**, 816 (1954).

(2) A. V. Tobolsky, I. B. Prettyman and J. H. Dillon, *J. Appl. Phys.*, **15**, 380 (1944).

(3) M. Mooney, W. E. Wolstenholme and D. S. Villars, *ibid.*, **15**, 324 (1944).

(4) A. V. Tobolsky, D. J. Metz and R. B. Mesrobian, *THIS JOURNAL*, **72**, 1942 (1950).

(5) A. M. Bueche, *J. Chem. Phys.*, **21**, 614 (1953).

(6) S. Baxter, P. D. Potts and H. A. Vodden, *Ind. Eng. Chem.*, **47**, 1481 (1955).

(7) J. P. Berry and W. F. Watson, *J. Polymer Sci.*, **18**, 201 (1955).

(8) J. P. Berry, *ibid.*, **21**, 505 (1956).

(9) A. G. Veith, *ibid.*, **25**, 355 (1957).

(10) L. Mullins, *ibid.*, **19**, 225 (1956); C. G. Moore and W. F. Watson, *ibid.*, **19**, 237 (1956).

(11) M. M. Horikx, *ibid.*, **19**, 445 (1956).

(12) E. M. Bevilacqua, (a) *THIS JOURNAL*, **77**, 5394, 5396 (1955); (b) **79**, 2915 (1957); (c) *J. Org. Chem.*, **21**, 309 (1956); (d) *Rubber Age (N.Y.)*, **80**, 271 (1956); (e) *Science*, **126**, 396 (1957).

(13) "The Vanderbilt Latex Handbook," R. T. Vanderbilt Co., Inc., New York, N. Y., 1954.

(14) B. C. Barton and E. J. Hart, *Ind. Eng. Chem.*, **44**, 2444 (1952).

samples by leaching with methanol. Two of the samples whose properties are described later had faulty seals and were extensively oxidized during cure. In spite of this the results obtained with them are not in gross disagreement with those from the other samples which showed no signs of oxidation during cure.

TABLE I
COMPOUNDS USED

	Sulfur		Peroxide	
Rubber (from latex)	100	USF ^c rubber		100
potassium oleate	2	95% dicumyl peroxide ^d		2
zinc oxide	5			
OXAF ^a	1.25			
Ethazate ^b	0.65			
Sulfur	1.5			

^a Trademark (Naugatuck Chemical Division, U. S. Rubber Company) for a zinc salt of mercaptobenzothiazole. ^b Trademark (Naugatuck Chemical Division, U.S. Rubber Company) for zinc diethyldithiocarbamate. ^c Trademark U. S. Rubber Company) for a selected grade of unsmoked natural rubber. ^d Supplied by Hercules Powder Company.

In operation a weighed sample was placed in the cell, which was attached to the apparatus, and the whole immediately evacuated by means of a Hyvac pump. Ten minutes was allowed for the sample to attain oven temperature. Oxygen was then introduced to fill the apparatus and the pump started. During this process the solution in the trap (dilute sodium hydroxide in experiments in which acid was determined) was isolated from the rest of the apparatus until the pressure was restored to atmospheric. As estimated from the behavior of the manometers after cutting off the system from the oxygen supply, less than five minutes additional were required for the gas stream to come to temperature equilibrium after the pump was started.

Oxygen was added to the circuit from the gas buret at regular intervals, so that the pressure varied less than one-half cm. from atmospheric during a run. Typical curves of oxygen absorption at 120° as a function of time are shown in Fig. 1. The rates are substantially higher than for raw rubber treated in the same way except for vulcanization. At 140°, the temperature used for raw rubber studies,¹² samples absorbed oxygen at an uncontrollably high rate. After a sample had absorbed the desired amount of oxygen it was removed from the oven as rapidly as possible, cooled in a blast of air and removed from the cell. A piece was cut off the form and weighed, then placed in a 250-ml. vessel which was filled with chloroform, evacuated until the chloroform boiled furiously for some minutes and sealed. After 24 hr. the seal was opened, the sample removed rapidly from the chloroform, blotted and dropped into a tared weighing bottle. After it was weighed the bottle was placed in a desiccator in high vacuum for 24 hr. to remove the chloroform and again reweighed. From these measurements it is possible to calculate all the quantities required.

Acid products from the oxidation were washed out of the trap with water and subjected to analysis for carbon dioxide and volatile acid. Carbon dioxide was determined by sweeping it out of the acidified solution into Ascarite, in which it was weighed. The volatile acids were determined by total recovery steam distillation.¹⁵ Levulinoldehyde yields were estimated in separate experiments, using the iodoform reaction, as described previously.^{12b} In these experiments a trap held at -80° was substituted for the alkali in the gas circulating loop.

Results and Discussion

Experimental results for the two series of rubber samples are given in Tables II and III and plotted in Fig. 2-4.

Horikx¹¹ has shown that the relationship between the change in solubility of the vulcanized rubber and the change in swelling of the insoluble fraction, in the same solvent, should serve to distinguish between two extreme possibilities for the mechanism

(15) M. W. Philpott and K. C. Sekar, *J. Rubber Research Inst. Malaya*, 14, 93 (1953).

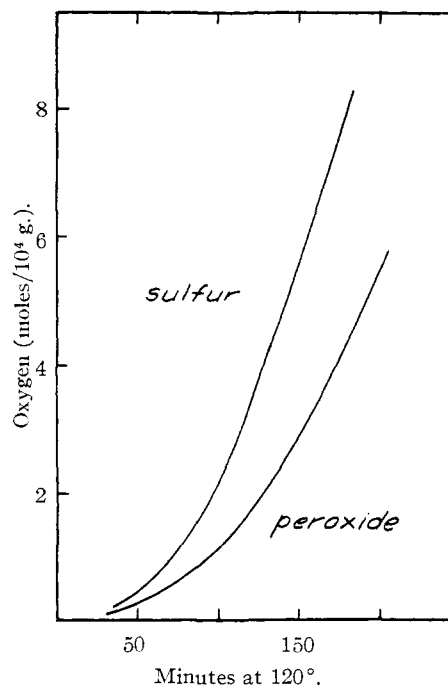


Fig. 1.—Comparison of the rates of oxidation of samples vulcanized with a peroxide and with an efficient sulfur "compound."

of degradation of cured rubber by oxygen: scission in the hydrocarbon chain or of the crosslink.

TABLE II
SULFUR CURES^a

CO ₂	Acid	Oxy- gen	Solu- ble	Swol- len wt.	ν	s	$1 - \frac{\nu_g}{\nu_0}$	γ	n
..	..	0	1.62				
0.12	0.44	1.6	16.9	35.9	0.17	5.2	0.50	3.30	0.11
.18	.24	2.4	10.7	10.5	1.38	1.9	.15	6.35	.23
.15	.49	3.2	33.0	48.8	0.10	21.3	.70	1.45	.24
.20	.48	4.1	12.7	12.6	1.04	3.5	.36	4.54	.32
.45	.48	4.8	29.8	40.9	0.15	18.8	.87	1.61	.75
.25	1.14	4.8	31.4	50.6	.09	19.7	.74	1.55	.22
.24	0.55	5.7	20.2	16.9	.65	11.4	.59	2.22	.65
.39	.31	6.0	29.2	55.4	.08	17.5	.77	1.60	.22
.67	.73	6.4	30.5	33.4	.18	18.6	.85	1.76	.68
.33	.55	7.2	30.7	32.6	.19	19.9	.84	1.56	.77
.50	.99	8.2	35.1	43.7	.11	26.4	.92	1.29	1.11

^a Explanation of column heads: CO₂; acid (evolved); oxygen (absorbed); ν , n all in moles/10⁴ g. rubber; ν = twice no. of effective crosslinks in gel; n = number of scissions (assuming chain scission); s = weight % of original material rendered soluble by oxidation ($1 - \frac{\nu_g}{\nu_0}$) = fractional loss in effective crosslinks; $\gamma = 1/[s^{1/2}(1 + s^{1/2})]$ = average number of crosslinks per molecule of "unvulcanized" rubber; swollen weight = weight ratio of insoluble portion of vulcanizate fully swollen with chloroform to dry weight.

Ignoring the very low solubility of the undegraded vulcanizate, Horikx's expressions are

$$1 - \frac{\nu_g}{\nu_0} = 1 - (1 - s^{1/2})^2 \quad (1)$$

for scission exclusively in the hydrocarbon chain and, for crosslink scission only

$$1 - \frac{\nu_g}{\nu_0} = 1 - \frac{\gamma_g}{\gamma_0} (1 - s^{1/2})^2 \quad (2)$$

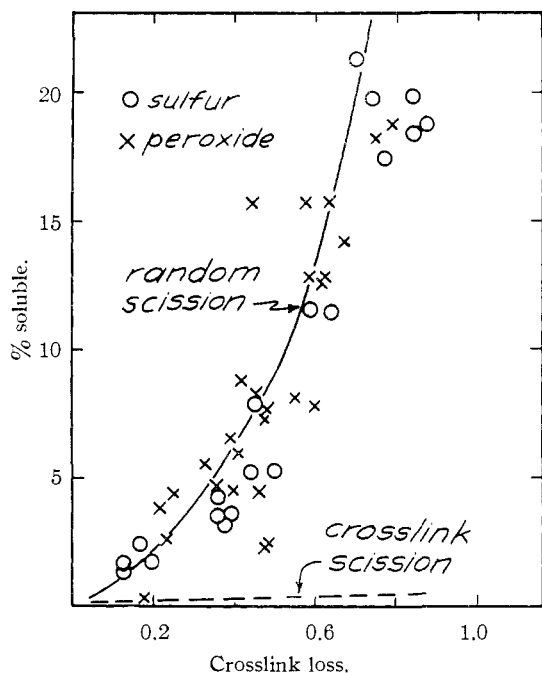


Fig. 2.—The solubility and swelling (in chloroform) of samples after oxidation.

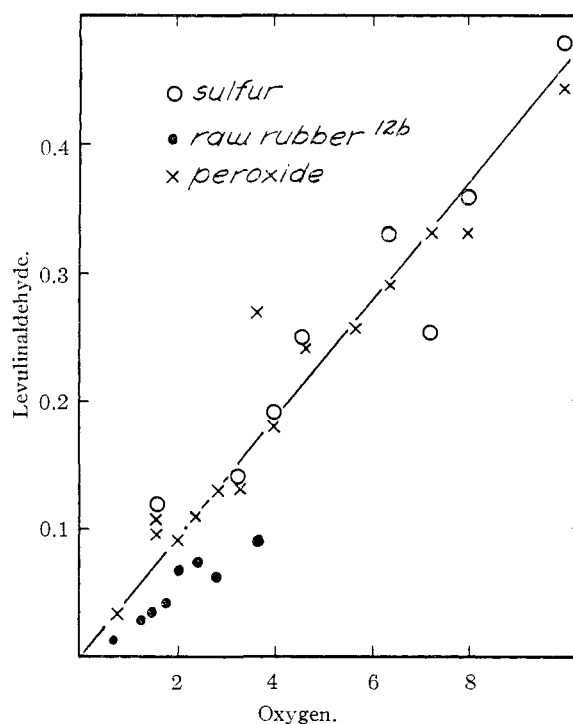


Fig. 4.—Volatile methyl ketone (levulinolaldehyde) produced during oxidation of vulcanized rubber (moles/10⁴ g.).

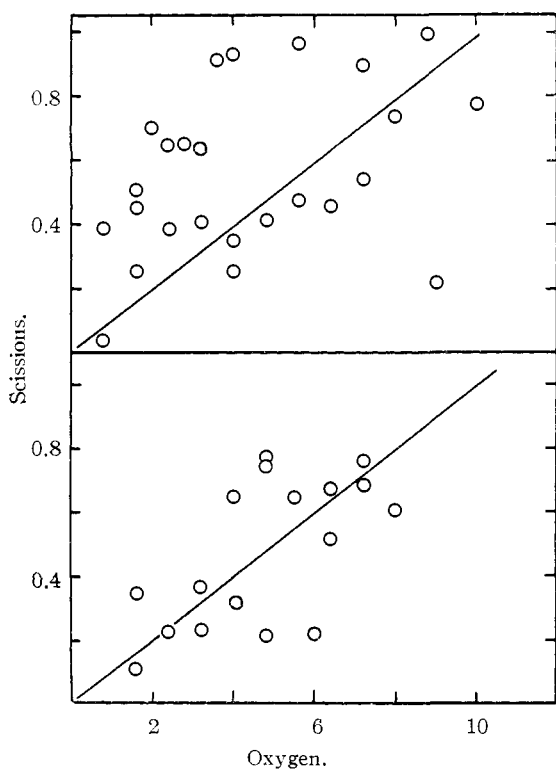


Fig. 3.—Scissions as a function of oxygen consumed: lower set, sulfur samples, upper set, peroxide samples (moles/10⁴ g.).

Here the subscript g refers to the specimen after oxidation, 0 to the original sample.

- ν = twice the concn. of effective crosslinks in the "gel"
- s = wt. fraction of the whole rubber which is soluble
- γ = av. no. of crosslinks to which one primary molecule of the network is attached

The crosslinking index (γ) may be calculated from the solubility

$$\gamma = \frac{1}{s^{1/2}(1 + s^{1/2})} \quad (3)$$

Values of ν were calculated from the swelling measurements, using the value of μ (0.30) given by Horikx. For weight ratios of swollen to unswollen polymer less than twenty¹⁶

$$\nu = \frac{\ln(1 - v_2) + v_2 + \mu v_2^2}{-\rho \bar{V}_1 \bar{V}_2^{1/2}} \quad (4)$$

for higher ratios¹⁶

$$\nu \approx \frac{1/2 - \mu}{\bar{V}_1 q^{2/3}} \quad (5)$$

where q is volume ratio of swollen to unswollen polymer.

TABLE III
PEROXIDE CURES

CO ₂	Acid	Oxy- gen	% Solu- ble	Swol- len wt.	ν	s	$1 - \frac{2s}{\nu_0}$	γ	n
..	..	0	1.78
0.34	0.12	0.8	6.3	10.8	1.33	0.06	0.25	39	0.04
.43	.06	1.6	8.5	13.9	0.88	2.3	.50	5.9	.26
.38	.13	2.4	10.7	13.8	0.90	4.5	.49	3.9	.39
.32	.15	3.2	11.6	12.0	1.14	5.4	.36	3.5	.41
.52 ^a	.23	4.0	26.3	20.7	0.39	2.3	.48	5.9	.26
.58	.21	4.0	10.0	10.9	1.31	3.8	.26	4.3	.35
.18	.25	4.8	11.2	12.2	1.10	4.9	.38	3.7	.41
.39	.20	5.6	12.7	12.6	1.04	6.5	.42	3.1	.48
.75	.27	6.4	12.2	12.8	1.02	6.0	.43	3.3	.46
.39	.18	7.2	14.1	15.6	0.74	7.9	.58	2.8	.54
.70	.22	8.0	19.3	16.3	.68	13.1	.62	2.0	.74
.81 ^a	.45	9.8	29.7	27.2	.25	7.7	.60	2.8	.22
.80	.28	10.0	20.3	18.3	.57	14.1	.68	1.9	.78

^a These two samples severely oxidized during cure as a result of leaking stopcock. Column headings as in Table II.

(16) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

The two curves drawn in Fig. 2 are calculated from equations 1 and 2 for a polymer having the properties of the samples used here. The upper one labeled "random scission" is calculated from equation 1, the other from equation 2. Within the experimental error the points for both sulfur and peroxide samples are in agreement with the curve representing random scission.

Having established that degradation occurs by breaking of the hydrocarbon chain, it is possible to calculate from our data the actual number of scissions per gram of rubber (n) which have occurred. This can be done by making use of the further relation given by Horikx, which follows obviously from the definitions of the quantities involved

$$n = \nu_0 \left(\frac{1}{\gamma_0} - \frac{1}{\gamma_g} \right) \quad (6)$$

Results of these calculations are plotted in Fig. 3. The solid lines have a slope of 0.1.

The value of (n) calculated from equation 6 is based on the assumption that equations 4 and 5 give an accurate estimate of crosslink density. Correcting it in accordance with the results of Moore and Watson¹⁰ yields an estimate of oxygen required per scission of *ca.* twenty moles per mole.

This is the same order of magnitude as that required for scission of raw rubber and suggests that similar processes are involved in breaking the hydrocarbon chain, an hypothesis supported by the further data given in this report.

Carbon dioxide and volatile acids are evolved during the oxidation of both sulfur and peroxide samples as would be expected if scission occurs by the same mechanism as that of raw rubber. Analysis of several samples of volatile acid from both types of vulcanizate by fractionation with chloroform-butanol mixtures on a silica column with 0.5 *N* sulfuric acid as stationary phase¹⁷ showed that both acetic and formic acid are formed. Yields of these products are not precise enough attempt quantitative correlation with scissions, but they are of the expected order of magnitude.

Good precision was obtained in analyses for levulinolaldehyde by the iodoform reaction.^{12b} These results are shown in Fig. 4. The yields of

(17) W. A. Bulen, J. E. Varner and R. C. Burrell, *Anal. Chem.*, **24**, 187 (1952).

aldehyde are close to those obtained from raw rubber in the same apparatus, the difference being accounted for readily by the different temperatures of the two experiments.

Taken together, all of these features of the evidence imply that there is no significant difference in the scission mechanism between the oxidation of vulcanized and of raw rubber, or between rubber containing sulfur crosslinks and that containing carbon-to-carbon bonds: (1) the similarity in oxidation rates of samples vulcanized by widely different methods; (2) the rapid appearance of soluble material during oxidation; (3) the similar requirements for oxygen to produce scission in raw rubber and both sets of vulcanizates; (4) production of the same volatile oxidation products from vulcanized rubber as are found from raw rubber, and especially the correlation between levulinolaldehyde and scission reactions.

If this is so, the effect of crosslinkages on the oxidation of rubber remains to be explained. All previous investigations,¹⁸⁻²² as well as this, agree that samples vulcanized so as to produce crosslinks containing sulfur oxidize more rapidly than raw rubber, and the more sulfur is combined with the rubber, the faster the oxidation. The present results show, in addition, that this effect can be attributed directly to the presence of the crosslink and is independent of its nature. From the evidence now available it appears possible to infer the structure of crosslinks in natural rubber in sufficient detail to account for a feature common to vulcanizates containing carbon-to-carbon bonds and those containing carbon-to-sulfur bonds and more important than the crosslink for its effect on oxidation. An attempt is being made to verify this quantitatively.²³

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(18) C. C. Davis and J. T. Blake, eds., "Chemistry and Technology of Rubber," Reinhold Publ. Corp., New York, N. Y., 1937, p. 513.

(19) C. Dufraisse and A. Etienne, *Rubber Chem. Tech.*, **11**, 282 (1938).

(20) W. L. Cox and J. R. Shelton, *Ind. Eng. Chem.*, **46**, 2237 (1954).

(21) G. J. van Amerongen, *ibid.*, **47**, 2565 (1955).

(22) A. G. Veith, *ibid.*, **49**, 1775 (1957).

(23) This is communication number 165 from the Research Center of the U. S. Rubber Company. I am indebted to E. Philipp for technical assistance and to C. L. Hilton, under whose supervision the spectrophotometric analyses for levulinolaldehyde were made.