ample, in the case of "isomerization" of ethylene mentioned above, the reaction coördinate for isomerization would appear to correspond closely to the normal torsional mode, as defined for the ground state. Now double bond twist in fact simultaneously involves change of C–C distance, etc. (see ref. 5); and although such interactions might be negligible for some purposes, as in the handling of small vibrations, the treatment of the reaction coördinate should take account of it, and in-plane as well as out-of-plane modes would be involved.

Acknowledgment.—We thank Dr. E. W. Schlag for interesting comment, and Mr. Friedemann Schneider who assisted in several of the computations.

SEATTLE, WASHINGTON

[CONTRIBUTION NUMBER 183 FROM THE RESEARCH CENTER OF THE UNITED STATES RUBBER COMPANY]

Oxidation of Hevea Vulcanizates Containing Carbon Black[1]

BY E. M. BEVILACQUA

RECEIVED APRIL 3, 1959

The oxidation by molecular oxygen of a mixture of natural rubber and carbon black vulcanized with cumyl peroxide has been studied. Yields of volatile acid and of levulinaldehyde (at 140°) are independent of the presence or absence of carbon black. It is concluded: (1) the mechanism of rubber oxidation is not affected by the carbon, except as to rate; (2) volatile product yield gives an absolute measure of chain scissions which may be used to calibrate physical estimates; (3) an upper limit can be set to covalent bond formation during vulcanization involving reaction between allylic radicals and carbon, small compared to the total effective crosslink density. It is suggested that carbon black behaves as an antioxidant by virtue of reactions similar to those occurring with conventional antioxidants.

The oxidation of unvulcanized natural rubber and of other long chain polyisoprenes proceeds through cyclic peroxidic intermediates whose detailed structure depends upon the temperature of oxidation. The principal product is a hydroperoxide. At low temperatures high yields of stable hydroperoxides may be obtained. The structure of these was characterized by the work of Bolland and Hughes[2] on squalene peroxide. The structure of the "low temperature" peroxide formed in rubber has not been investigated directly because of analytical difficulties, but moderate yields can be obtained, and its properties are consistent with a structure similar to that formed from squalene.[3,4] At very high temperatures the predominant cyclic intermediate has a different structure from that formed at low temperatures.[5] It may not be converted to a stable hydroperoxide, but rather an intermediate radical decomposes directly,[6] leading to breakage of carbon-to-carbon bonds in the hydrocarbon chain. Associated with this decomposition is a group of low molecular weight compounds, including levulinaldehyde, formaldehyde and formic acid, acetic acid, carbon dioxide and (by inference) water.[5] The yield of each of the compounds depends to some extent on the experimental arrangement used to study their formation, but under a given set of conditions yields of one or more of these compounds form a good index of scission reactions in the hydrocarbon chain. So far as is known the ratio of scission to other reactions of the polymer with oxygen is determined solely by the temperature, through its effect on the ratio of "low temperature" to "high temperature" peroxide intermediates.

Using the correlation of index compounds with scissions as a means of studying the oxidation of vulcanized rubber,[7] it was found that no major change in the mechanism of breakdown of the polymer is introduced by crosslinking. The yields of volatile compounds per mole of oxygen reacted with vulcanized rubber are the same within experimental error as those obtained with raw rubber when allowance is made for the effects of temperature on product yield, in both peroxide-cured and efficient sulfur-cured vulcanizates. The vulcanizates used for the comparison were chosen to avoid complications arising from the use of inefficient vulcanizing systems. They gave the same relationship between solubility and swelling and between solubility and oxygen consumed as the conventional (Santocure[8] accelerated) gum compounds studied by Horikx,[9] implying the same scission mechanism for all vulcanized rubber.

A next logical step in the investigation of the detailed mechanism of the deterioration of rubber is the inclusion of the additional complication of fillers. This report describes a series of experiments with natural rubber containing carbon black (MPC), vulcanized with cumyl peroxide.

Experimental

Since results reported previously[7] have shown that the behavior of a peroxide vulcanizate and of an efficiently cured sulfur vulcanizate during oxidation are quite similar, for the work reported here the experimentally less complicated peroxide cure was used. Two different sets of samples were used in the course of this work. In the first set the

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[1] This is the sixth in a series on chain scission in the oxidation of Hevea. For the fifth, see ref. 7.

[2] J. L. Bolland and H. Hughes, *J. Chem. Soc.*, 492 (1949).

[3] E. H. Farmer and A. Sundralingham, *ibid.*, 125 (1943).

[4] B. C. Sekhar, *Rubber Chem. Tech.*, **31**, 425, 430 (1958).

[5] E. M. Bevilacqua, *Rubber Age* (*N. Y.*), **80**, 271 (1956).

[6] This conclusion is not fully established experimentally, but consideration of the structure of the probable intermediate[5] suggests that a "zipper effect" should be found, leading to high yields of low molecular weight products per apparent scission if the intermediate $RO_4\cdot$ resulting from successive additions of two oxygen molecules has significant stability. The observed yields instead correspond to a primary yield of one molecule of "scission products" per scission.

[7] E. M. Bevilacqua, THIS JOURNAL, **80**, 5364 (1958).

[8] Trademark name (Monsanto Chemical Company) for N-cyclohexyl-2-benzothiazole sulfenamide.

[9] M. M. Horikx, *J. Polymer Sci.*, **19**, 445 (1956).

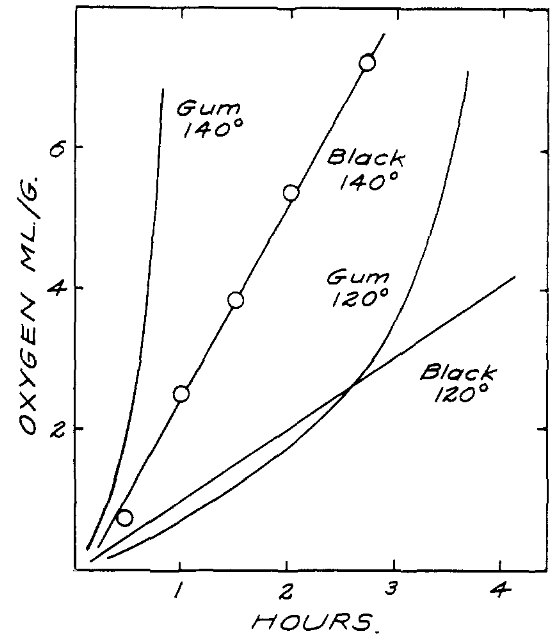

Fig. 1.—Representative curves of oxygen absorption of simple vulcanizates as a function of time. "Black" samples contained 50 parts of Spheron 6.

ingredients of the composition (pale crepe 100, Spheron[10] 6 (MPC) 50, cumyl peroxide 2.5) were assembled on a cool mill before calendering. In a later set the black and rubber were mixed, then the master batch heated in closed molds in a press for 3 hr. at 162° before cooling to room temperature for addition of the peroxide. Both sets were calendered to a thickness of about 0.25 mm. and wrapped in Holland cloth to be stored at 10° in the dark until immediately before use.

The samples which had been heat-treated before addition of the peroxide showed the expected differences[11] in properties from those assembled in a conventional manner. The resistivity of control samples was higher than that of samples not heat-treated, and the 300% stress was raised. An apparently irreversible change in the master batch is produced by this treatment, which has been attributed to improved dispersion of black in the rubber.[11,12] The moderately high activation energy required for the process has led to the suggestion that a chemical reaction between black and rubber occurs which makes it possible for the filler aggregates to be torn apart on further mixing[13] after the heat treatment and also prevents the flocculation of the filler when the master batch is heated during vulcanization.[11] Although the concentration of linkages to carbon expected to be formed in this process is much lower than the total number of crosslinks formed during the vulcanization reaction,[14] these bonds, if they have a distinct structure, might be expected to cause some observable difference in the behavior of samples during oxidation.

Oxidation experiments were made with samples obtained by wrapping a single layer of the prepared master batch on a glass form and curing it *in vacuo* at 150°. Cured samples were cooled to room temperature before opening the containers. Samples were leached with cold methanol to remove reaction products of the vulcanizing agent. Oxidation was carried out in a simple apparatus which has been described previously.[15] It consists of a closed loop, in which gas is continuously circulated during an experiment and to which is attached auxiliary equipment for measuring volume changes in the system.

For high yields of the volatile products, which are an index of scission reactions, it is desirable to work at as high a temperature as possible.[5,16] The work with vulcanizates described previously was restricted to a temperature of 120° because of the rapid oxidation of the simple gum compounds. It was found possible in the present experiments to use a temperature of 140°, the carbon black acting as a moderately effective antioxidant. Typical curves of oxygen absorption as a function of time are shown in the first figure.

In the work described here all volatile products for which analyses were made were collected in a trap at −80° through which the gas passed on leaving the oven. Analyses were made for levulinaldehyde by means of the iodoform reaction,[15] and for volatile acid (other than carbon dioxide) by titration with dilute alkali. Oxidized samples were removed from the oven promptly after the desired amount of oxygen had been consumed and were cooled to room temperature. The solubility and swelling of these samples were determined in chloroform as described previously.[15]

Discussion

Experimental results are presented in the figures and in Table II. The first results of importance are the yields of volatile products; these are plotted in Fig. 2 in comparison with previously reported results. Origins for the curves in Fig. 2 are shifted vertically to avoid overlapping of plotted points.

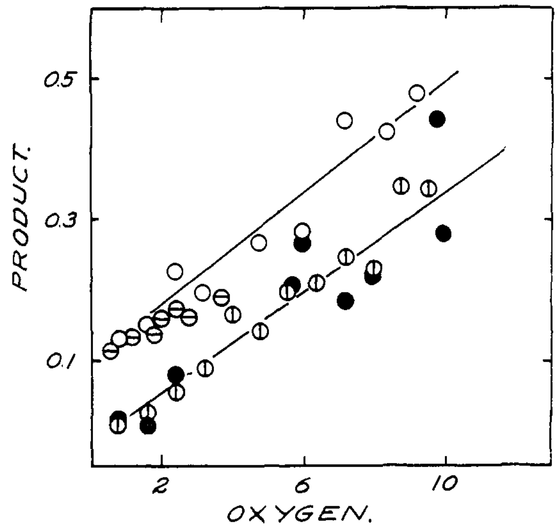

Fig. 2.—Volatile products as a function of oxygen consumed, both in moles/10^4 grams rubber: ○, levulinaldehyde from "black" samples; ⊖, levulinaldehyde from unvulcanized crude rubber; ⦶, total acids from "black" samples; ●, total acids from gum vulcanizate.

The upper set of data represents the yield of volatile methyl ketone (levulinaldehyde), the lower set the yield of volatile acid. The open circles are plotted from results obtained with the conventionally mixed black-loaded compounds studied here. The barred circles represent the yields of aldehyde previously reported for unvulcanized rubber.[15] In the lower set of points the open circles use data from the present set of heat-treated black-loaded samples, and the solid circles are from previously reported data,[7] this time for samples vulcanized with cumyl peroxide but containing no filler. All were obtained at 140°, except that the last set of data was obtained at 120°. The close correspondence between the yields of important index products shows that there is no

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[10] Trademark of Godfrey L. Cabot, Inc., for channel blacks.

[11] B. C. Barton, H. M. Smallwood and G. H. Ganzhorn, *J. Polymer Sci.*, **13**, 487 (1954).

[12] R. H. Gerke, G. H. Ganzhorn, L. H. Howland and H. M. Smallwood, U. S. Patent 2,118,601 (May 24, 1938).

[13] A. M. Gessler, *Rubber Age* (*N. Y.*), **74**, 59 (1953).

[14] G. Kraus and J. Dugone, *Ind. Eng. Chem.*, **47**, 1809 (1955).

[15] E. M. Bevilacqua, THIS JOURNAL, **79**, 2915 (1957).

[16] E. M. Bevilacqua, *J. Org. Chem.*, **21**, 369 (1956).

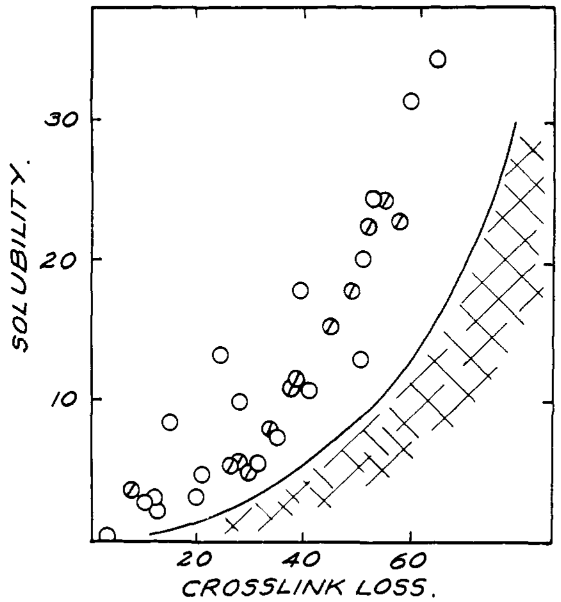

Fig. 3.—Solubility (% of rubber) as a function of crosslink density (% loss relative to control) of oxidized vulcanizates. Black samples: O, conventional, ⦶ heat treated; solid line, calculated according to Horikx; hatched area, experimental results for gum vulcanizates.[7,9]

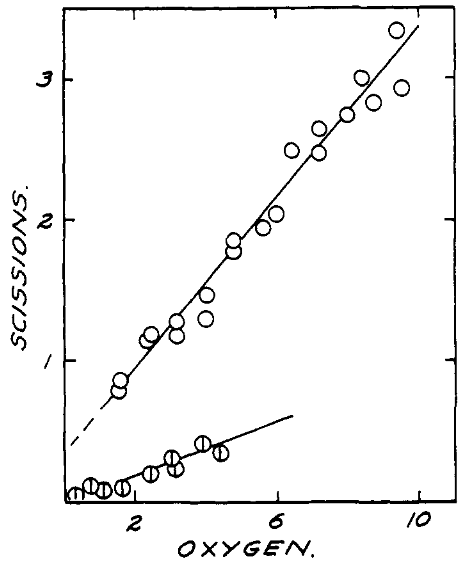

Fig. 4.—Scissions (calculated from solubility) as a function of oxygen consumed: O, black vulcanizates; ⦶, unvulcanized control. Assumptions given in text; units moles/10^4 grams.

significant difference in mechanism of breakdown of the hydrocarbon in the presence of carbon black.

Horikx[9] first pointed out that a decision might be made between scission primarily at crosslinks and scission at random in the polymer network on the basis of the solubility and swelling properties of the samples after oxidation. Horikx's experimental results for Santocure accelerated vulcanizates and those of Bevilacqua[7] for peroxide and efficient sulfur cures were consistent with the idea that scission is predominantly random, in the oxidation of gum vulcanizates. A similar comparison of swelling and solubility of the samples containing carbon black after oxidation is shown in Figs. 3 and 4. In Fig. 3 the solubility is plotted against the loss in crosslink density in the insoluble portion (referred to the crosslink density before oxidation). For the calculation of these quantities it was assumed that all soluble material was rubber and that volume changes in the insoluble portion involved the rubber only. In Fig. 4 the scission yield is plotted against the volume of oxygen consumed, the yield being calculated from the expression[9]

$$n = \nu_0\left(\frac{1}{\gamma} - \frac{1}{\gamma_0}\right) \qquad (1)$$

where ν_0 is twice the initial cross-link density in the sample, calculated from the Flory–Huggins relation[17] and γ is the mean number of attachments per primary molecule (crosslinking index).

To be consistent with earlier work, the unmodified equation of Flory (see p. 578, ref. 17) was used, together with the value of μ derived by Horikx,[9] which apparently is slightly low.[18] This introduces a slight, consistent, quantitative shift in the derived quantities calculated from the experimental data but has no effect on the conclusions of this report. The crosslinking index is related to the soluble fraction (s) by the expression

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

for $\gamma \geq 0.5$ and a "most probable" distribution of primary chain lengths.[19]

In Fig. 3 the anticipated relation between solubility and crosslink density loss is shown by a solid line, and the area occupied by data obtained from the study of gum vulcanizates is indicated by cross-hatching. In Fig. 4 typical data pertaining to unvulcanized rubber[14] are plotted for comparison with the results obtained for samples containing carbon black. Obviously, if these results can be interpreted literally, hydrocarbon scission occurs much more efficiently in the presence of carbon black than in its absence, since soluble material is formed more readily than would be anticipated on the basis of experience with gum compounds.

Since the yields of acid and of aldehyde show that scission efficiency is the same in the black samples as in gum rubber, some error must be implicit in the interpretation of the experimental data leading to the plots of Figs. 3 and 4. Calculations of derived quantities in these figures from the experimental values are based on a number of assumptions. These include: 1. carbon black is not oxidized. 2. The presence of carbon black has no effect on the empirical constant (μ) in the Flory–Huggins[17] theory. 3. The Flory–Huggins theory gives a quantitative estimate of covalent bonds. 4. Restriction of swelling in the presence of carbon black involves covalent bonds. The first assumption can be tested experimentally. The expected per cent. carbon black by weight in the samples made up according to the formulation given earlier

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[17] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953.

[18] G. Gee, *Trans. Faraday Soc.*, **42**, 585 (1946); G. M. Bristow and W. F. Watson, *ibid.*, **54**, 1731 (1958).

[19] A. Charlesby, *J. Polymer Sci.*, **11**, 513 (1953).

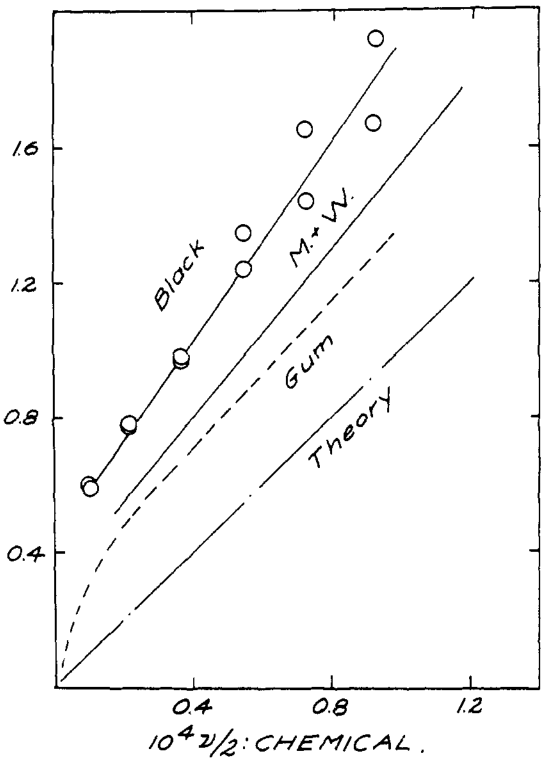

Fig. 5.—Physical and chemical estimates of crosslink density (moles/gram). Vulcanizates cured with cumyl peroxide: upper curve, samples containing 50 parts MPC. Next two curves gum vulcanizates: M. & W., Moore and Watson[22]; gum, this report.

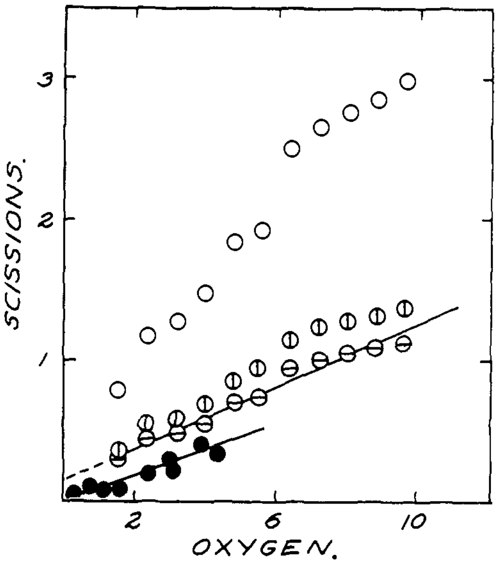

Fig. 6.—Chain scissions as a function of oxygen consumed (moles/10^4 grams): O, from Fig. 4; ⦶, calibrated by data in Fig. 5; ⊖, corrected as described in text; ●, raw rubber.

in the discussion, and cured and extracted as described, is 34.5. The amount found in a control sample by analysis was 35.0. In a sample which was severely oxidized, the amount found was 34.8%. These values confirm that carbon is not oxidized to volatile products in sufficient amount to account for the observed high solubility as an artifact. Although the second assumption has not been subjected to experimental test, it also seems reasonable. It has been discussed previously by Kraus,[20] who came to the same conclusion.

It has long been recognized that the theory of the swelling of a polymer network in a solvent may be quantitatively in error because of entanglement of long polymer chains, which would restrict swelling without a physical crosslink being required.[17] On a somewhat different basis, Kuhn[21] estimated the initial slope of the curve of stress at low strain as a function of crosslink density to be about seven-thirds as high as that predicted by the theory, ignoring entanglements. Experimental tests of the theory have shown initial slopes of this order of magnitude or more in several systems. Since low extension modulus is closely related to restraints on swelling in solvents, corresponding divergency in swelling behavior may be anticipated. For natural rubber an absolute calibration of swelling has been made by Mullins, Moore and Watson[22] over a wide range of crosslink densities. These workers found that, in the range of crosslink density of interest here, the covalent bond density in gum vulcanizates is about one-half that estimated from physical measurements on the polymer. The observed density of network chains ($\nu = 2 \times$ crosslink density) determined from swelling measurements on the samples of this report before oxidation was about 4.00×10^{-4} mole/gram for those which had been heat treated before addition of the peroxide and 3.35×10^{-4} for the conventional samples. These values contrast with the amount of crosslinking agent taken, which is equivalent to $\nu = 1.85 \times 10^{-4}$ mole/gram. Thus a portion of the discrepancy between observed and expected results can be attributed to the entanglement effect. In order to determine whether this would account for the entire discrepancy, a direct comparison was made, on a series of vulcanizates containing 50 parts of MPC and cured with cumyl peroxide, between crosslink density estimated from swelling measurements and crosslink density estimated on the assumption that one mole of peroxide leads to one mole of crosslinks and that the peroxide is 100% efficient. The experimental basis for these assumptions has been reviewed in detail by Moore and Watson.[22]

The comparison is shown in Fig. 5. The highest curve consists of the experimental data for black loaded samples. The next highest is taken from the published results[22] describing the absolute calibration for gum stocks. The third curve was obtained from data on gum stocks prepared in this Laboratory, under the same assumptions as for the samples containing carbon black. The slope of this curve is 85% of the slope of that of Moore and Watson. The difference between the two curves includes the effects of any impurities in the commercial peroxide used in these experiments, of inefficiency of vulcanization under our conditions, of inhibitors in the crepe used, of failure to correct for the finite molecular weight of the polymer.

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(20) G. Kraus, *Rubber World*, **135**, 67 (1956).

(21) W. Kuhn, *J. Polymer Sci.*, **1**, 380 (1946).

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

An alternative approach to correcting the estimate of scission efficiency in Fig. 4 is to attempt to apply the physical theory of the effect of filler on modulus to the experimental results. No one has explicitly considered the applicability of the derivations of Smallwood[23] or of Guth,[24] dealing with modulus effects, to the restriction of swelling of a polymer network in the presence of filler, but it is of interest to compare this with the direct calibration in Fig. 5. The comparison is made in Table II, the data from which are plotted as Fig. 6 for convenience. In Fig. 6 the yield of chain scissions in moles per 10^4 grams, calculated from equation 1, is plotted against oxygen consumed by the polymer (in the same units). The highest set of points are reproduced from Fig. 4; these include results from both the conventional and the heat treated samples, which are indistinguishable. The other curves referring to vulcanized rubber are derived from data for the heat treated vulcanizate only, by appropriate corrections to the estimate of crosslink density obtained from swelling measurements. The points with vertical bar were obtained on the assumption that the calibration given in Fig. 5 is correct. The next circles were obtained by performing two manipulations on the value of ν_0. For this calculation it was assumed that the theory of modulus reinforcement given by Smallwood[23] predicts correctly the effect of carbon black on swelling of the polymer. The value of ν_0 obtained by this correction was assumed to be equal to the physical crosslink density in an equivalent gum stock. This, corrected in accordance with the calibration by Moore and Watson, gives the chemical crosslink density. The difference between the curves represented by vertical and horizontal bars can be entirely accounted for by assuming that the efficiency of cure with peroxide is the same (85%) in the black vulcanizates as was observed for gum stocks.

TABLE I

EFFECT OF HEAT TREATMENT

Heat-treated	Log resistivity (ohm-cm.)	300% Stress (pounds/in.^{2})
Yes	13.0	925
No	6.7	780

TABLE II

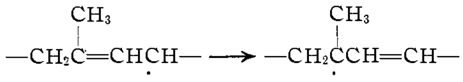
SCISSION EFFICIENCY IN BLACK STOCKS

Oxygen consumed moles/104 g.	Scissions (moles/10^4 g.) 1^a	2^a	3^a
0.80	0.08	0.04	0.03
1.60	0.79	.37	.30
2.40	1.18	.55	.45
3.20	1.27	.59	.48
4.00	1.48	.69	.56
4.80	1.86	.86	.71
5.60	1.93	.89	.73
6.40	2.50	1.16	.95
7.20	2.67	1.23	1.01
8.00	2.76	1.28	1.04
8.80	2.86	1.32	1.09
9.60	2.97	1.37	1.13

[a] Assumptions: (1) Flory–Huggins theory is quantitative; (2) calibration in Fig. 5 is absolute; (3) Smallwood theory and Moore and Watson calibration constitute corrections required to Flory–Huggins theory.

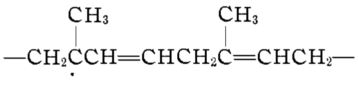
The last set of data in the figures are representative of results with unvulcanized rubber.[15] The slope of the line drawn through these points is 0.095; the slope of the line through the "corrected" points for the vulcanized rubber containing black is 0.108. The difference of ~15% is well within the combined experimental errors.

The corrected curve still shows an intercept of some magnitude which remains to be accounted for. It is possible that we are now observing an effect which is real and represents a genuine distinction between vulcanized rubber and raw rubber, obscured in earlier studies because of the poorer reproducibility of swelling measurements in the gum stocks unprotected by an antioxidant. On theoretical grounds it is expected that the hydrocarbon structure near crosslinks in both sulfur-cured and peroxide-cured rubber might be more readily oxidized than the undisturbed structure in the polymer chain.[5] Evidence from the study of the oxidation of raw rubber shows that extensive double bond shift occurs in radical reactions of polyisoprenes at high temperatures. At the temperature used for vulcanization in the experiments described here (150°) the shift is substantially complete[5,25]



$$-CH_2\overset{\overset{CH_3}{|}}{C}=CH\underset{\cdot}{C}H- \longrightarrow -CH_2\underset{\cdot}{\overset{\overset{CH_3}{|}}{C}}CH=CH- \qquad (3)$$

This results in formation of a 1,4-diene



$$-CH_2\underset{\cdot}{\overset{\overset{CH_3}{|}}{C}}CH=CHCH_2\overset{\overset{CH_3}{|}}{C}=CHCH_2- \qquad (4)$$

with a methylene group between two unsaturated carbon atoms. All other conditions being equal, vulcanized rubber containing a small amount of this structure should be oxidized faster than raw rubber. There is no experimental (or theoretical) basis for predicting whether or not such a structure will also undergo scission more efficiently than the 1,5-diene, since the scission reaction is not known to be directly related to the chain carrying steps in oxidation. If scission during oxidation of a structure like (4) were more efficient, the expected effect on over-all scission efficiency would be just that found, as represented by the corrected curve in Fig. 6. The observed scission efficiency would be high at first. The most readily oxidized structures, present in low concentration, would disappear at low extents of oxidation, the scission efficiency then decreasing to that for the oxidation of unvulcanized rubber. No direct experimental test of this interpretation has been obtained thus far. However, both Veith[26] and Horikx[9] found evidence for highest scission efficiency during early stages of oxidation in rubber vulcanized with more conventional compositions than those used here. Further, Veith's observed efficiencies (estimated[7] as initially 0.2–0.25 mole scissions/mole oxygen) are higher than Horikx's (0.05–0.10 when adjusted

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(23) H. M. Smallwood, *J. Applied Phys.*, **15**, 758 (1944).

(24) E. Guth, *ibid.*, **16**, 20 (1945); Proc. Second Rubber Tech. Conf. (London), 1948, p. 353.

(25) E. M. Bevilacqua, THIS JOURNAL, **77**, 5394 (1955).

(26) A. G. Veith, *J. Polymer Sci.*, **25**, 355 (1957).

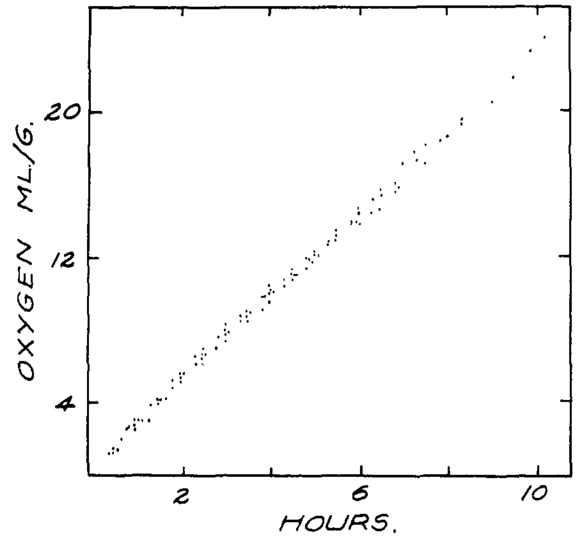

Fig. 7.—Reproducibility of oxidation rates in heat-treated carbon black vulcanizate. Data for eight replications at 140°.

for effects of entanglements), which is consistent with the present interpretation. The high estimates were obtained using stress relaxation to follow scission; this is most sensitive at early stages of oxidation, where solubility measurements suffer from a high experimental error. It is in the early stages that highest scission efficiency is anticipated.

It may be noted here that the alternative possibility mentioned in the description of the preparation of samples cannot be entirely excluded on the available evidence. The intercept of the curve for vulcanized rubber on the scission axis is at about 2×10^{-5} mole/gram, which is of the order of magnitude to be expected for covalent bonds to the carbon black, formed during processing,[14,27] or during vulcanization.[28] No difference was found between heat treated and conventional samples, but the reaction between rubber and black may be rapid enough at vulcanizing temperatures to obscure any difference in bond densities resulting from differences in processing or from the thermal reaction of black and rubber, within the experimental error of the present investigation. When a mixture of pale crepe with 50 parts of Spheron 6 was heated 3 hr. in a press at the temperature used for vulcanization, the fraction associated with the carbon gel had an effective crosslink density of about $\nu/2 = 0.17 \times 10^{-4}$ mole/gram, corresponding to a covalent bond density of $\sim 0.8 \times 10^{-5}$.

A final result of interest from this work is that it is now possible to make somewhat more explicit the hypothesis of Szwarc[29] for the effectiveness of carbon black as a thermal antioxidant. It is well known that at low temperatures and with high black loadings an apparent acceleration of oxidation of rubber[30] (and of SBR)[31,32] occurs in the presence of carbon black. On the other hand carbon black, at high temperatures and at low black loadings, has been reported to retard oxidation of both natural rubber and synthetic rubbers.[33] Referring again to Fig. 1, it is evident that carbon black is a moderately effective antioxidant under the conditions used in this work. It is now proposed that reinforcing carbon blacks are simply antioxidants against thermal oxidation at all temperatures. As with other antioxidants[34] there is an optimum concentration at which the rate of oxidation is a minimum. No directly pertinent studies on the effect of temperature on the optimum concentration for other antioxidants have been reported, but it can be seen qualitatively that an effect might be anticipated, since the optimum results from the balance between the two independent effects, one the shortening of the oxidation chain length by the provision of an alternate mode of termination and the other the continuation of the oxidation chain by a relatively unreactive antioxidant radical. For carbon black the optimum at low temperatures occurs at low concentrations and is rather sharply defined. As a result it rarely has been observed. The lowest temperature for which the effect has been reported is 70°, in the work of Shelton and Wickham.[32] The similarity between the effects of black and of other antioxidants is striking (Fig. 6 of the reference cited). Veith[27] observed retardation of oxidation of purified rubber by carbon at slightly higher temperatures. Experimental observation of the effect may depend quite critically on such factors as dispersion because it depends on a reaction at the surface of the black. At high temperatures the optimum rises to higher concentrations and becomes much more diffuse, so that the antioxidant effect is detected readily.

The reproducibility of the rate of oxidation of samples from the same master batch is illustrated by Fig. 7 in which all the experimental points for eight separate runs are plotted, points which fall in the same position being indicated only once. This good reproducibility is quite characteristic of mixtures containing high concentrations of an effective antioxidant.

Four reactions must be considered among alternative possibilities for termination steps which shorten the reaction chain in the presence of carbon black

$$R\cdot + C \longrightarrow RC \qquad (5)$$

$$RO_2\cdot + C \longrightarrow RO_2C \qquad (6)$$

$$R\cdot + C(H) \longrightarrow RH + C\cdot \qquad (7)$$

$$RO_2\cdot + C(H) \longrightarrow RO_2H + C\cdot \qquad (8)$$

It is not possible to assess the relative importance of these reactions in natural rubber at present. Either (5) or (6) if it occurs would account for the results obtained by Watson[35] in his study of "car-

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(27) J. Duke, W. K. Taft and I. M. Kolthoff, *Ind. Eng. Chem.*, **43**, 2885 (1951); W. F. Watson, *ibid.*, **47**, 1281 (1955); D. S. Villars, *J. Polymer Sci.*, **21**, 257 (1956).

(28) E. M. Dannenberg, M. E. Jordan and H. M. Cole, *ibid.*, **31**, 127 (1958).

(29) M. Szwarc, *ibid.*, **19**, 589 (1956).

(30) G. J. Van Amerongen, *Ind. Eng. Chem.*, **45**, 377 (1953); A. G. Veith, *ibid.*, **49**, 1775 (1957).

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bon gel" formation. Of these two reactions 6 is the more likely. The reaction

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (9)$$

is very fast, competing so successfully with reaction 10

$$R\cdot + R\cdot \longrightarrow RR \qquad (10)$$

that the latter cannot be detected in the presence of oxygen at pressures approaching atmospheric. But on the evidence in this report, reaction 5 occurs to an undetectable extent compared with reaction 10. Although other radical reagents inhibit carbon gel formation, oxygen, which is one of the most efficient radical acceptors in Hevea, does not.[35] This also suggests reaction 6. The occurrence of either (5) or (6) would not explain the formation of carbon radicals capable of continuing the reaction chain as would (7) and (8). Alternative formulations such as (5a) and (6a) may do so

$$R\cdot + C \longrightarrow RC\cdot \qquad (5a)$$

$$RO_2\cdot + C \longrightarrow RO_2C\cdot \qquad (6a)$$

in analogy with, say, addition to an olefinic bond. Studies with graphitized carbon black may help decide between these alternatives.

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Analysis of the Double Pulse Galvanostatic Method for Fast Electrode Reactions

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A rather rigorous analysis is made for the double pulse galvanostatic method for the kinetic study of very fast electrode reactions. An equation is derived for potential–time curves. The ratio of pulse heights is calculated for conditions in which the potential–time curve has a horizontal tangent at the end, t_1, of the first pulse. It is shown that a plot of overvoltage at time t_1 against $t_1^{1/2}$ is linear for curves with a horizontal tangent at t_1. The overvoltage extrapolated at $t_1 = 0$ does not include any concentration polarization component, and the calculation of the exchange current is immediate. Exchange currents for very fast reactions can be seriously in error when concentration polarization is neglected at the end of the first pulse. Theory and experiment are in good agreement for the discharge of mercurous ion on mercury in 0.98 *M* perchloric acid at 25°. Instrumentation is described in detail.

Fast electrode processes are studied by relaxation methods in which either the potential of the electrode being studied or the cell current is changed abruptly or periodically.[3] In galvanostatic methods, a single or a double current pulse is applied to the cell, and potential–time variations are determined. The cell current at any time is the algebraic sum of the faradaic and capacity currents. An analysis of the single pulse method was made by Roitern, Juza and Polujan[4] for electrolysis without concentration polarization and by Berzins and Delahay[5] for processes with concentration polarization. It was found[5] that to minimize concentration polarization the duration of electrolysis must be decreased as the exchange current increases. Even so, very fast electrode reactions cannot be studied by the single-pulse method because an important fraction of the cell current in the initial moments is primarily non-faradaic.[6] This limitation is removed in the double pulse method which was developed by Gerischer and Krause[7] and applied by these authors to the discharge of mercurous ion on mercury. The first pulse, which is of higher amplitude than the second pulse, primarily charges the double layer for the overvoltage required at the current density of the second pulse (Fig. 1). A potential–time curve with a horizontal tangent at time t_1 at the end of the first pulse is obtained when the ratio of pulse heights is properly adjusted (Fig. 2). This ratio is determined by trial and error. Gerischer and Krause assumed that concentration polarization is quite negligible at time t_1, and they readily calculated the exchange current density from the overvoltage at t_1. They realized that their interpretation is approximate, and they determined an order of

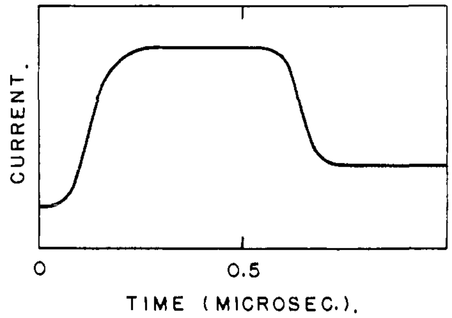

Fig. 1.—Tracing of double pulse. The length of the second pulse was approximately 10 microseconds. See Experimental for discussion of distortion.

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[3] (a) For a review, see for instance P. Delahay, *Ann. Rev. Phys. Chem.*, **8**, 229 (1957); (b) also, P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

[4] W. A. Roitern, W. A. Juza and E. S. Polujan, *Acta Physicochim. U.R.S.S.*, **10**, 389, 845 (1939).

[5] T. Berzins and P. Delahay, THIS JOURNAL, **77**, 6448 (1955).

[6] Gerischer and Krause (ref. 7a) state that the potentialities of the single pulse galvanostatic method are the same as for faradaic impedance measurements because a step function can be expressed by a Fourier series. This does not seem correct, however, because a *steady state* is achieved in faradaic impedance measurements whereas transients are observed in the single pulse method. The limitation is rather the one stated above.

[7] (a) H. Gerischer and M. Krause, *Z. physik. Chem., N.F.*, **10**, 264 (1957); (b) **14**, 184 (1958).