Antioxidant Properties of Carbon Black in Unsaturated Elastomers.   Studies with *cis*-Polybutadiene

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Synopsis

The thermal antioxidant behavior of carbon black was studied in vulcanized *cis*-polybutadiene and related to the surface chemistry of the black.   Continuous and intermittent stress-relaxation and oxygen absorption measurements were employed to determine the antioxidant ability of the carbon blacks.   The blacks were characterized by the surface concentrations of oxygen-containing functional groups, using methods described in the literature.   Antioxidant activity was found to be highest in carbons containing relatively large amounts of bound oxygen.   These carbons are also acidic and decompose peroxides by the ionic mechanism.   This was demonstrated with dicumyl peroxide.   However, even though the acidity and ability to decompose dicumyl peroxide to phenol and acetone could be destroyed by methylation, this treatment did not seriously impair the antioxidant activity, so that the role of acidic groups appears to be minor.   Evidence is presented which suggests strongly that the antioxidant behavior of carbon blacks is due to surface quinones, possibly hydrogen-bonded with adjacent hydroxyl groups.   Measurements made on samples vulcanized in peroxide and sulfur curing systems indicate that the antioxidant behavior of carbon black is independent of the method of vulcanization in the absence of other antioxidants.   A characteristic feature of the antioxidant action of carbon blacks is their tendency to repress the oxidative crosslinking reactions, the relative amount of compensation of chain scission by crosslinking being smaller than in gum vulcanizates.

I. INTRODUCTION

The role of carbon black in the oxidation of elastomers has been shown to be that of an antioxidant by several workers.[1-4]   Others[5-8] have reported that in many instances the opposite is true and an acceleration of oxidation occurs.   Hawkins, Winslow, and associates[9-12] have made extensive inquiries as to the function of carbon blacks as antioxidants for polyolefins.   They have shown carbon blacks to act as thermal antioxidants and have demonstrated the existence of synergistic effects of carbon blacks with certain organo-sulfur compounds.

Considering the wide use of carbon blacks in rubber vulcanizates, it was felt that further investigation as to the role of carbon black as an antioxidant in such systems was desirable.

The present work was directed toward the elucidation of the relative effect of various carbon blacks on the thermal oxidation of vulcanizates and the effects of specific surface groups of carbon black on antioxidant

activity. For the main part, stress-relaxation techniques were used to follow the oxidations as considerable network damage occurs even in the initial stages of the reaction, before oxidation becomes autocatalytic. Also, network damage is the most pertinent effect in degradation of elastomeric vulcanizates in most of their end uses.

II. EXPERIMENTAL

A. Preparation of Rubber Vulcanizates

All vulcanizates were prepared from cis-polybutadiene (Phillips Chemical Co., Cis-4). This polymer was chosen because of its relative freedom from heavy metal impurities, particularly iron. Recipes for peroxide and sulfur vulcanizates are given in Table I.

TABLE I
Vulcanization Recipe

Peroxide vulcanizate		Sulfur vulcanizate	
Component	Parts	Component	Parts
cis-Polybutadiene	100	cis-Polybutadiene	100
Dicumyl peroxide[a]	Variable	Sulfur	0.7
Carbon black	0 or 5	N-cyclohexyl benzothiazole sulfenamide	1
		Zinc oxide	3
		Stearic acid	2
		Disproportionated rosin acid	2
		Carbon black	0 or 5

[a] 40% dicumyl peroxide on calcium carbonate (Hercules Powder Co., Di-Cup 40C.).

The samples were mixed on a 6 × 2 in. laboratory roll mill at a temperature of approximately 25°C. and press-cured in stainless steel molds for 45 min. at 307°F. for the peroxide vulcanizates and 60 min. at 307°F. for the sulfur vulcanizates. Final thickness of the cured slabs was approximately 0.020 in.

The number of network chains per unit volume was calculated from the Flory-Rehner theory of swelling.[13,14] Measurements were made in n-heptane by the method of Kraus.[14] The amount of peroxide used was varied to obtain stocks of approximately equal crosslink density.

In preparation for stress-relaxation measurements all samples were extracted to remove antioxidants added to the polymer at the time of its production* and also, in the case of sulfur vulcanizates, antioxidants formed as by-products of vulcanization. Samples were extracted 72 hr. in nitrogen-purged acetone (acetone changed after 24 and 48 hr.) under an inert atmosphere and dried in a room temperature vacuum oven.

* Stress-relaxation measurements made with vulcanizates which had never contained antioxidant were identical with those made with the extracted vulcanizates, indicating that complete extraction was achieved.

B. Stress-Relaxation Measurements

Continuous Relaxation. Stress-relaxometers were patterned after the spring relaxometer of Berry,[15] with the exception that each relaxometer was equipped with a micrometer screw for ease of reading. The relaxometers were fitted into individual chambers of a thermostatically controlled aluminum aging block. In conducting the stress-relaxation measurements rubber strips 0.020 in. in thickness were clamped into the relaxometer at the extension (50%) of the oxidative relaxation experiment and allowed to relax for 16 hr. at room temperature *in vacuo*. The relaxometers were then quickly inserted into the preheated block (100°C.), the block was evacuated and filled with oxygen. Oxygen was leaked into the block during the experiment to maintain atmospheric pressure. The prerelaxation was necessary to minimize physical relaxations during the course of the test. Upon insertion of the sample into the heated block, the tension in the rubber strip rose initially in seeking its new equilibrium value. The maximum stress attained was taken as initial tension and time reckoned from this point on. This maximum occurred within 5–10 min. after insertion.

When the stress relaxations were carried out in nitrogen at 100°C., very little relaxation occurred in the time of the oxidative experiments with either gum or black stocks. This shows that these measurements are not significantly complicated by nondegradative relaxations.

Intermittent Relaxation. Samples for intermittent stress-relaxation measurements were aged in an all-glass, oxygen-filled system contained in a thermostatted electric oven maintained at 100°C. The oxygen pressure was so adjusted as to equal atmospheric at all times. At intervals the samples were removed and the stress at an extension of 50% was measured at room temperature by means of an Instron Tester. A period of 5 min. was allowed for approaching elastic equilibrium, but a true equilibrium was not attained in this time.

C. Oxygen Absorption

The oxygen absorption measurements were conducted in a system similar to that described by Hawkins et al.[9] Samples were placed in tubes which were situated in an air-circulating oven at 100°C. The tubes were flushed, then filled with oxygen and, after temperature equilibrium was reached, the gas system was adjusted to atmospheric pressure and the initial readings made. Oxygen uptake was followed by subsequent measurements made at atmospheric pressure.

D. Carbon Blacks

Table II lists the carbon blacks used in these experiments and the results of the various analytical tests made on the blacks. A brief description of these tests follows.

Surface Area. Surface area measurements were made by the nitrogen adsorption method of Brunauer, Emmett, and Teller.[16]

TABLE II

Physical Characteristics of Carbon Black

Black	Trade name	Nitrogen surface area, m.²/g.	Oxygen, %	pH	DPG adsorption meq./g.[a]	Strong acids meq./g.[b]	Weak acids, meq./g.[c]	H₂ uptake (NaBH₄ red.), %[d]	Effect on peroxide decomp.[e]
HAF	Philblack O	78	0.93	8.2	0.020	0.006	0.31	0.014	FR
ISAF	Philblack I	114	0.90	8.6	0.022	0.005	0.32	0.015	FR
Graphitized MPC	Graphon	94	0.12	10.5	0.004	0.00	0.04	0.00	FR
Acetylene	Shawinigan	65	0.23	5.7	0.007	0.01	0.03	0.011	FR
EPC	Wyex	114	4.0	4.7	0.041	0.07	0.59	0.038	I/FR
FEF, attrited[f]	—	69	1.3	6.5	0.050	0.07	0.38	0.022	I/FR
Experimental No. 1	—	198	4.2	3.9	0.038	0.12	0.27	0.049	I/FR
Experimental No. 2	—	121	1.6	4.2	0.067	0.06	0.54	0.035	I/FR
MCC	Monarch 74	333	2.3	5.8	0.072	0.08	0.73	0.037	I/FR
MCC, modified No. 1[g]	—	—	—	7.0	0.028	0.01	0.61	0.040	FR
MCC, modified No. 2[h]	—	—	—	6.0	0.362	0.07	0.66	0.026	FR
MCC, modified No. 3[i]	—	—	—	6.9	0.041	0.02	0.62	0.026	FR

[a] Diphenylguanidine adsorption.
[b] Carboxyl type oxygen.[17]
[c] Phenolic type oxygen.[17]
[d] Quinone type oxygen.[18]
[e] I = ionic, FR = free radical.[19]
[f] Prepared by method of Gessler.[20]
[g] Modified with diazomethane.
[h] Modified with LiAlH₄.
[i] Modified first with LiAlH₄, then diazomethane.

Oxygen Content. Oxygen content was measured by a modified Unter-zäucher method. An *in situ* drying step, flushing the system with dry nitrogen for 1 hr. at 150°C., was included to remove traces of moisture.

Slurry pH. The pH measurements were done according to ASTM D1512-60.

Diphenylguanidine Adsorption. Carbon black (1 g.) was agitated 30 min. with 100 cc. of 0.001N diphenylguanidine in toluene, centrifuged, and an aliquot of the clear solution was titrated to a tetrabromophenyl-sulphonephthalein endpoint with 0.002N HCl in methanol. The DPG number is given in microequivalents of diphenylguanidine absorbed per gram of black.

Strong and Weak Surface Acids. These measurements were made without significant modification by the method of Rivin.[17] The strong acidity is believed to be due to carboxy groups. The weakly acidic groups are regarded as phenolic hydroxyls.

Hydrogen Uptake on NaBH₄ Reduction. This determination, which is a measure of quinone oxygen, was carried out by the method of Studebaker and co-workers.[18]

Effect of Carbon Black on Peroxide Decomposition. These experiments were conducted by a procedure patterned after Dannenburg, Jordan, and Cole.[19] Dry, degassed, 1-g. samples of black in thin-walled glass ampules placed in 10 cc. of mineral oil, 0.1M in dicumyl peroxide, in a sample tube. The solution was degassed and sealed off under vacuum. The ampule was broken by shaking and the sample tube was placed in a 135°C. oil bath for sufficient time to completely decompose the peroxide. The carbon black was separated by centrifuging and the decomposition products were analyzed by their infrared absorptions, obtained with a Perkin-Elmer Infracord.

E. Chemical Treatment of Carbon Black

The reduction of MCC (medium color channel) black with lithium aluminum hydride was done by the technique of Rivin.[17]

Diazomethane for the methylation of MCC was prepared by a literature method.[21] The diazomethane was distilled over a period of 2 hr. into an agitated slurry of carbon black in ether at 0°C. An amount of diazomethane about ten times in excess of the active hydrogen content of the black was used.

III. RESULTS

A. Carbon Black Characterization

The results of the various analyses to characterize the carbon blacks are shown in Table II.

Graphitized channel black shows little, if any, surface chemical activity. All tests for acidity are nil within the experimental accuracy of the tests.

This, combined with the low oxygen content, indicates a very inert black. The same is true for acetylene black except that an appreciable amount of the oxygen present is of the quinone type.

The furnace blacks are characterized by basic pH values, low oxygen content (about 1%), and low adsorptive capacities for organic bases (DPG). Strongly acidic sites are absent. The weak acid and quinone concentration is one-half to one-third of that of channel blacks. The decomposition of dicumyl peroxide in the presence of furnace blacks occurs entirely by the free radical mechanism.[19]

Channel blacks exhibit acidic pH values, high oxygen content (and therefore high volatile content since the volatiles removed on calcination are mainly CO and CO_2, along with H_2) and a high concentration of both strong and weak acids, as well as quinones. The DPG adsorption is two to three times that of furnace blacks. When dicumyl peroxide is decomposed in the presence of channel blacks, products of the ionic mechanism of decomposition are detected. The results of this test with typical blacks are given in Table III. It can be seen that the channel black does not entirely exclude the free radical mechanism and the ionic entries in the last column of Table II indicate only the main route of decomposition. It should also be noted that this test is only semi-quantitative due to the difficulty of entirely separating the products in the presence of a highly adsorbing material such as carbon black, and due to the likely presence of side reactions.

The experimental blacks and the attrited FEF black are, in general, similar to the channel blacks.

When the MCC black was methylated (MCC, modified no. 1), a black of neutral pH and low assays for DPG adsorption and strong acids re-

TABLE III
Results of Peroxide Decomposition at 135°C.[a]

	Product, moles/mole dicumyl peroxide					
Black	Aceto-phe-none	Dimethyl-phenyl carbinol	α-Methyl-styrene	Acetone	Phenol	Total products
—	0.45	1.35	—	—	—	1.80
HAF	0.48	1.14	0.17	—	—	1.79
MCC	0.12	—	0.80	0.30	0.30	1.52
MCC, modified no. 1	0.37	0.95	0.21	—	—	1.53
MCC, modified no. 2	0.47	0.10	0.67	—	—	1.24
MCC, modified no. 3	0.30	0.77	0.26	—	—	1.33
Experimental no. 2	0.20	—	0.52	0.31	0.25	1.28

[a] Acetophenone and dimethylphenyl carbinol result from the free radical mechanism and acetone and phenol from an ionic mechanism. α-Methylstyrene results from both processes in the presence of black.

sulted.   The quinone concentration was unchanged and only a small change in weak acid concentration was found.   The effect on peroxide decomposition was to change the route from mainly ionic to entirely free radical. When the MCC black (MCC, modified no. 2) was reduced with lithium aluminum hydride, the only significant change in any of the assays was a one-third decrease in quinone concentration.   There was an analogous result, however, in that this treatment changed the peroxide decomposition route from ionic to free radical which was unexpected.   When the reduction was followed by methylation (MCC, modified no. 3), the combined effect of the two treatments was observed.

To the extent that the above analytical techniques lead to valid esti- mates of the concentration of surface groups, certain correlations with antioxidant properties might be expected.   First, hindered phenols are well known antioxidants, so that phenolic OH groups may play a part in anti- oxidant properties of carbon blacks.   It also seems likely that quinones, which are good inhibitors of free radical reactions, would contribute to antioxidant activity.   Since the decomposition of peroxides is an important step in hydrocarbon oxidation reactions, the presence of acidic groups ca- pable of decomposing peroxides by the ionic mechanism would be expected to influence the oxidative degradation of the polymer.

B. Stress Relaxation and Oxygen Absorption

The results of the stress-relaxation measurements are shown in Figures 1–5.   The open circles are from continuous measurements and the closed circles show data obtained in the intermittent tests.   The data are plotted as log (f/f_0) versus t, where f_0 is initial tension and f is the tension at time
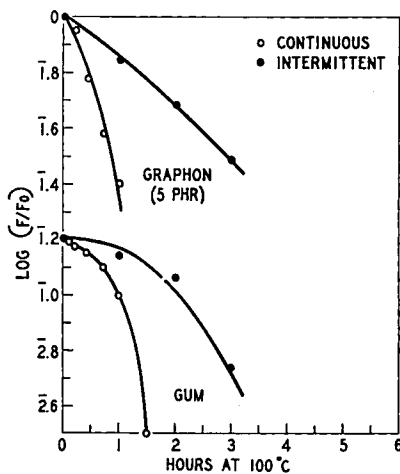

Fig. 1. Stress relaxation in oxygen. (Curves for gum have been displaced on or- dinate to avoid crowding.   This was done on all subsequent figures showing stress relaxations.)
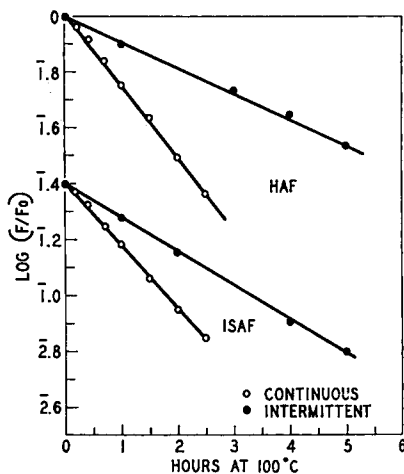
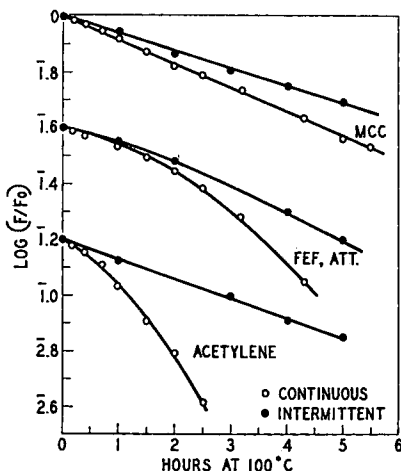Fig. 2. Stress relaxation in oxygen (5 phr black).

Fig. 3. Stress relaxation in oxygen (5 phr black).

t. Figure 6 shows the results of oxygen absorption measurements plotted as oxygen uptake per gram of polymer versus time.

The effect on stress relaxation of introducing a filler (carbon black) into the network requires further comment. Recently Maisey and Scanlan[3] have shown that fillers contribute no additional relaxations in chemical stress-relaxation measurements at loadings as high as 50 phr. These authors conclude, therefore, that carbon black does not interfere with the observation of network changes by means of stress relaxation. From consideration of these findings and the very low loadings (only 2.5 vol.-%) used in the present work, along with careful nonoxidative prerelaxation,
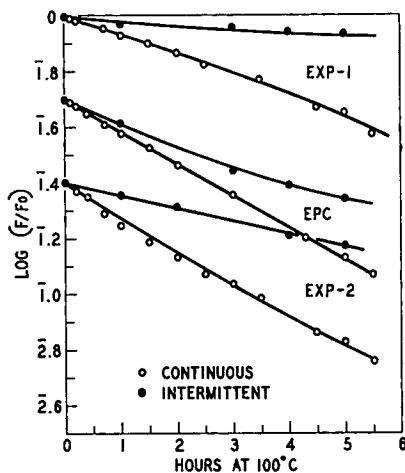
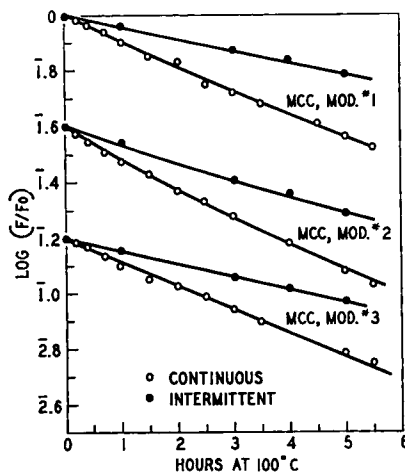Fig. 4. Stress relaxation in oxygen (5 phr black).

Fig. 5. Stress relaxation in oxygen (5 phr black).

it seems safe to conclude that no relaxations due to filler need to be considered in the present experiments.

Correlation with Carbon Black Properties.   At first glance an obvious correlation exists between the antioxidant behavior of the various blacks and their acidity as measured either by pH, diphenylguanidine adsorption, or concentration of strong acids.   However, when these properties are considerably altered by methylation (MCC, modified nos. 1 and 3), there is little difference in the stress-relaxation or oxygen absorption measurements between stocks containing treated and untreated blacks.   Also, the treated blacks have lost their ability to decompose peroxides via the ionic route (Table III).   If the ability of a black to decompose peroxides to
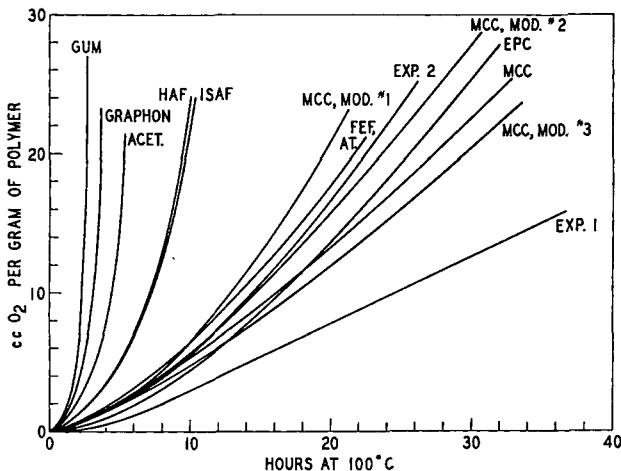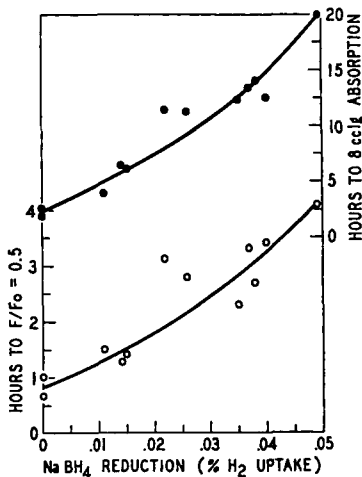
Fig. 6.   Oxygen absorption.

Fig. 7. Antioxidant activity as function of quinone oxygen.

nonradical products were important in antioxidant behavior, these treated blacks should be less effective.

Figure 7 shows the time to 50% relaxation and time to an oxygen absorption of 8 cc./g. of polymer plotted against hydrogen uptake on sodium borohydride reduction, i.e., a measure of quinone-type oxygen. The correlation here appears to be fairly good.

Similar correlations were attempted with weak acid concentration (phenolic OH) and strong acids.   No clear-cut trend could be established.

Behavior of Sulfur-Cured Stocks.   In unextracted sulfur-cured stocks the protective action of black is masked and partially cancelled (Fig. 8). However, in stocks free of other antioxidants no evidence has been obtained
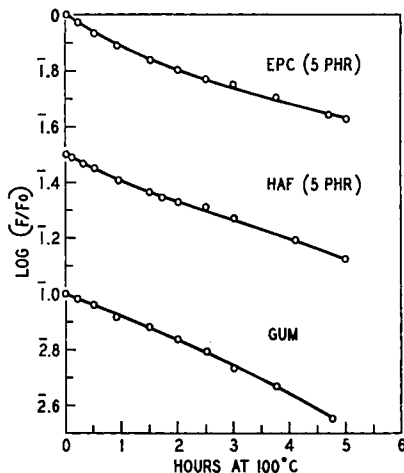
Fig. 8.   Continuous stress relaxation in oxygen of unextracted sulfur vulcanizates
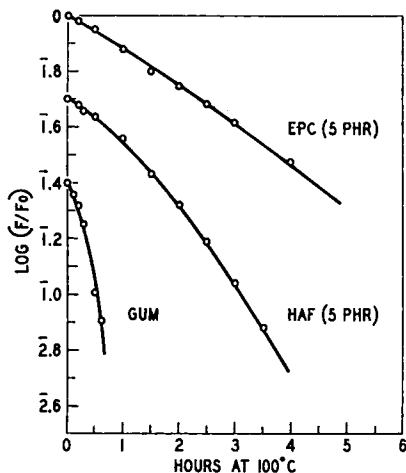

Fig. 9.   Continuous stress relaxation in oxygen of extracted sulfur vulcanizates.

of the black actually being deleterious to the aging of the vulcanizate, and the results with extracted stocks show that stress-relaxation occurs at about the same rate as in a similar peroxide vulcanizate (Fig. 9).

   Synergistic Antioxidant Effects.   It has been reported[9,22] that carbon black interferes with the antioxidant ability of the usual phenolic and amine antioxidants, with acid blacks being more harmful than basic blacks. On the other hand, Hawkins et al.[10] have reported a large number of sulfur-organo compounds which are synergistic in their antioxidant behavior with carbon black.   Two of these compounds (2-naphthalenethiol and 2-benzo-thiazyl disulfide) were selected and incorporated into several gum and black vulcanizates by impregnation.   The concentration of the additive was

0.2%. The results are shown in Table IV. As with the polyolefins, the sulfur compounds themselves were relatively poor antioxidants for *cis*-polybutadiene but in conjunction with carbon black improved protection was obtained, especially with the naphthalenethiol.

TABLE IV
Effect of Synergistic Antioxidants

Compound	Time to $(f/f_0) = 0.50$ hr.			
	Gum	HAF	EPC	MCC
None	1.2	1.2	2.6	3.5
2-Benzothiazyl disulfide	1.8	2.0	4.9	4.2
2-Naphthalenethiol	2.0	3.8	6.8	7.0

IV. DISCUSSION

The results of these investigations show clearly that carbon blacks are mild thermal antioxidants for an unsaturated elastomer. However, this antioxidant behavior varies considerably from black to black and depends on the surface chemistry of the blacks. A carbon black from which nearly all surface groups have been removed by graphitization, such as Graphon, is nearly inert as an antioxidant. As the oxygen (and volatile) content of carbon blacks increases, the acid character of the blacks increases. In general, these blacks tend to be the best antioxidants. Our results, however, prove that the antioxidant character of a carbon black is not related to its acidity. Removal of strong acid sites by methylation results in a black whose antioxidant ability is unchanged. The best correlation of antioxidant behavior appears to be with quinone-type oxygen (Fig. 7) as determined by sodium borohydride reduction. The mechanism by which quinone groups would act as antioxidants is most likely through interruption of the free radical chain carrying step. It has been shown[23] that the quinone concentration of a carbon black correlates with its ability to inhibit free radical polymerization of styrene. The retardation effect was considerably decreased by removing quinone-type oxygen by reduction. Attempts to remove quinone-type oxygen completely were unsuccessful in the present work, probably due to the ease of reoxidation of the reduced quinone sites.

Although the phenolic type oxygen content of the blacks, as estimated by the method of Rivin,[17] does not seem to correlate with antioxidant properties, the function of such groups as antioxidants is not excluded. Unfortunately, it has not been possible to prepare carbon blacks containing either quinones or phenolic hydroxyl groups alone. Hallum and Drushel[24] have proposed a model for the surface of carbon black in which there is a co-occurrence of quinone and phenolic groups to form hydrogen bonded structure, such as:
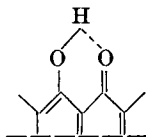
If this picture is correct, the antioxidant behavior might well be related to such groupings.

It has been suggested by Szwarc[25] that the presence of unpaired electrons in carbon black contributes to its behavior in retarding thermal oxidation. In view of the work of Kraus[23,26] and Spackman and Charlesby[27] on the reactivity of unpaired electrons in carbon blacks, we do not feel there is any strong evidence for this. On the other hand, this mechanism cannot be discounted entirely from the available data, particularly since the highest concentrations of unpaired electrons are often found in blacks of high quinone concentration.

In considering the data on intermittent stress relaxation the interesting observation is that, in general, the presence of blacks tends to suppress the oxidative crosslinking reaction. There is, however, no correlation between any of the chemical properties of the blacks determined in this study and the degree to which this reaction takes place. It appears that further work is needed in this area to elucidate what mechanism is involved between the polymer radicals which result from peroxide decomposition and the carbon black surface.

In vulcanizates prepared in a sulfenamide-accelerated sulfur crosslinking system the antioxidant effects of the carbon blacks are not observed in unextracted stocks; but in the extracted sulfur-cured stocks, the antioxidant behavior is similar to that in the peroxide cures. It appears, therefore, that the mechanism of protection against oxidative degradation by carbon black in rubber vulcanizates is independent of the manner in which the polymer is crosslinked, but is dependent on interaction with antioxidants formed as by-products of the vulcanization.

In the end uses of rubber vulcanizates, the antioxidant properties of carbon black are obscured by other antioxidants employed and by-products of vulcanization. However, a large volume of black masterbatch (preblended rubber and carbon black) is being sold commercially at this time. The antioxidant ability of carbon black in many cases affects the storage stability of such compositions.

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Résumé

On a étudié le comportement d'antioxydant thermique du noir de carbone dans des polybutadiène-*cis* vulcanisés en rapport avec la chimie de surface du noir de carbone. On a utilisé des mesures de traction-relaxation continue et intermittente pour détermines la propriété antioxydante des noirs de carbone. Les noirs sont caractérisés par des concentrations en surface de groupements fonctionnels contenant de l'oxygène, en utilisant des méthodes décrites dans la littérature. On trouve que l'activité antioxydante est supérieure dans les carbones contenant des quantités relativement élevées en liaisons oxygènes. Ces carbones sont également acides et décomposent les peroxydes par un mécanisme ionique. On a démontré ceci au moyen peroxyde de dicumyle. De toute façon même si l'acidité et la tendance à décomposer le peroxyde de dicumyle en phénol et acétone peut être détruite par méthylation, ce traitement ne diminue pas beaucoup l'activité antioxydante de telle façon que le rôle des groupements acide semble être mineur. Ces résultats suggèrent fortement que le comportement antioxydant des noirs de carbone est dû aux surfaces quinoniques et aux liens hydrogènes possibles avec les groupements hydroxyles adjacents. De mesures faites sur des échantillons vulcanisés par des peroxides et des systèmes sulfurés indiquent que le comportement antioxydant est indépendant de la méthode de vulcanisation en l'absence d'autres antioxydants. Une caractéristique marquante de l'action antioxydante des noirs de carbone est leur tendance

à diminuer les réactions de pontage par oxydation, la quantité relative de compensation, des ruptures de chaînes par pontage étant inférieure à celles des gommes vulcanisées.

Zusammenfassung

Das Verhalten von Russ als thermisches Antioxydans in vulkanisiertem *cis*-Polybutadien wurde untersucht und zur chemischen Beschaffenheit der Oberfläche des Russes in Beziehung gesetzt. Zur Bestimmung der Antioxydanswirkung von Russen wurden kontinuierliche und intermittierende Spannungsrelaxationsmessungen und Sauerstoffabsorptionsmessungen herangezogen. Die Russproben wurden durch die Oberflächenkonzentration der sauerstoffhältigen funktionellen Gruppen unter Verwendung der in der Literatur beschriebenen Methoden charakterisiert. Die oxydationshemmende Wirking ist bei Russen mit relativ grossen Mengen gebundenen Sauerstoffs am grössen. Diese Russe sind sauer und zersetzen Peroxyde nach dem ionischen Mechanismus. Dies wurde an Dicumylperoxyd nachgewiesen. Während jedoch die saure Natur und die Fähigkeit zur Zersetzung von Dicumylperoxyd zu Phenol und Aceton bei der Methylierung verloren ging, wurde die oxydationshemmende Wirkung durch diese Behandlung nicht ernstlich vermindert. Daraus geht hervor, dass die sauren Gruppen anscheinend von untergeordneter Bedeutung sind. Es konnte nachgewiesen werden, dass die oxydationshemmende Wirkung von Russ sehr wahrscheinlich auf an der Oberfläche vorhandene Chinone zurückgeht, die möglicherweise durch Wasserstoffbrückenbindungen mit benachbarten Hydroxylgruppen verbunden sind. Aus Messungen an mit Peroxyd- und Schwefelsystemen vulkanisierten Proben geht hervor, dass das Antioxydansverhalten von Russ in Abwesenheit anderer Antioxydantien von der Vulkanisationsmethode unabhängig ist. Ein Charakteristikum der oxydationshemmenden Wirkung von Russ ist dessen Tendenz, oxydative Vernetzungsreaktionen zu unterdrücken, so dass das relative Ausmass der Kompensation der Kettenspaltung durch Vernetzung kleiner ist als in ungefüllten Vulkanisaten.