Effect of Curing System on Rubber Oxidation and Physical Degradation

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The rubber industry has long been interested in protecting rubber articles from factors such as ozone, oxygen, heat, and light, which can cause serious physical property deterioration. Recently, there has been much discussion on curing systems to improve the aging properties of rubber vulcanizates. Studies (*11, 17–19*) have shown that certain curing recipes containing no elemental sulfur—e.g., tetramethylthiuram disulfide or dicumyl peroxide—yield vulcanizates with age resistance superior to stocks containing elemental sulfur. Low-sulfur stocks exhibit better aging resistance than high-sulfur stocks, and a change in the nature of the accelerator may affect both the rate of oxidation and the change in properties brought about by a given absorption of oxygen (*5*).

This work presents data on the volumetric oxygen absorption and physical degradation of natural and styrene-butadiene rubber (SBR-1500) which were cured by ten different formulations, including the major types of accelerators used in industry today. The purposes of this study were to examine the relative age resistance of a variety of curing systems and to correlate this age resistance with possible differences in the types of cross links formed.

PROCEDURE

The volumetric oxygen-absorption method (*4, 21*) was used to follow the degradation of the vulcanizates. This method has an advantage over other aging tests of giving an accurate measure of oxygen uptake with time and a measure of physical deterioration with oxygen uptake.

Commercial pale crepe and SBR-1500 were compounded on a 6-inch rubber mill according to ASTM procedures. The compounded stocks were stored at constant temperature from the time of mixing until they were cured in a steam press at 50 p.s.i. steam (298° F.). Cure times were selected on the basis of physical properties obtained at various times of vulcanization in a preliminary investigation of each curing system. In a typical case, the initial samples were cured 10, 20, 40, and 80 minutes and quadruplicate samples pulled to determine tensile strength, modulus (or stress) at 300% elongation, and ultimate elongation. Slower cures were heated for proportionately longer times. Cure times were selected a little beyond the usual optimum cure to avoid the complicating effects of undercure upon aging. In the case of SBR vulcanizates, a moderate overcure has no significant effect upon either oxygen absorption or rate of change in properties during aging. The situation is more critical with natural rubber vulcanizates because reversion occurs with longer cures. In no case was the cure selected for further study in the range of definite reversion.

Stock compositions and curing times selected are listed in Table I. Styrene-butadiene gum stocks were not tested due to their extremely poor tensile properties. Dumbbell test specimens (ASTM tensile die C) were approximately 0.040 inch thick to minimize the rate limitation of oxygen absorption due to diffusion and were aged in triplicate in the oxygen-absorption apparatus at 90° C. under 1 atm. of oxygen. Samples were removed at appropriate times, and the tensile strength, stress at 200 and 300% elongation, and ultimate elongation were measured on a Scott tensile tester.

RESULTS AND DISCUSSION

Effect on Oxygen Absorption. Each curing recipe was tested for its effect on the rate of oxygen uptake and physical degradation in four substrates: styrene-butadiene black stock, uninhibited Hevea gum stock, uninhibited Hevea black stock, and inhibited Hevea black stock. The volumes of oxygen absorbed by the vulcanizates at 90° C. were calculated as milliliters of oxygen absorbed per gram of actual polymer, corrected to 25° C. and 760 mm. of mercury, and were plotted graphically against the elapsed time. These data are presented in Figures 1 to 4. The suffix designation B—e.g., 4B—indicates that the stock also contains 50 phr Philblack O, an HAF black; A—e.g., 11B-A—in the Hevea black stocks indicates

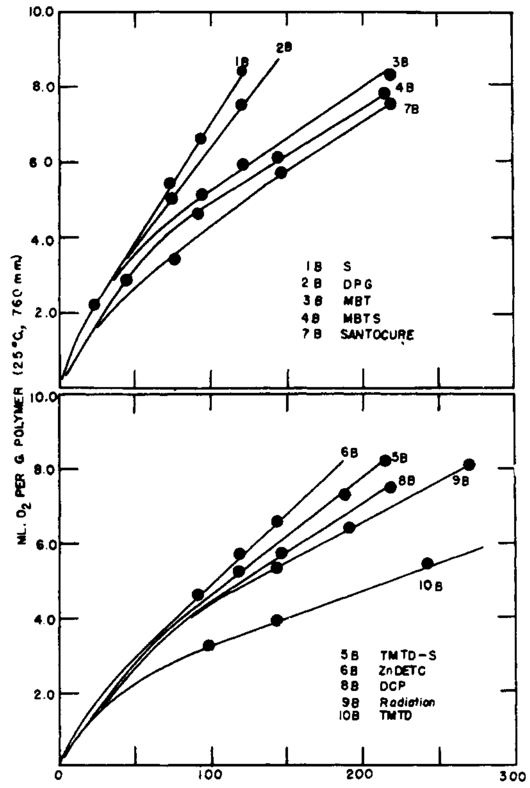


Figure 1. Oxidation rates of styrene-butadiene black stocks at 1 atm. O_2

that 1 phr *N*-phenyl-2-naphthylamine (PBNA) has been added.

In general, for a given curing system the rate of oxygen uptake is lowest in the SBR-1500 vulcanizates. The uninhibited natural rubber black stocks exhibit the fastest oxygen absorption, even more rapid than the corresponding gum vulcanizates. This accelerating effect of carbon black on rubber oxidation has been studied (*19*). The oxidation rates of the inhibited Hevea black stocks are intermediate between the uninhibited Hevea and the SBR-1500 vulcanizates.

Of particular interest are the differences in oxygen absorption for different types of cures in the same polymer. In the SBR-1500 black stock the sulfur (1B) and the diphenylguanidine (2B) cures have the most rapid oxidation rates. The mercaptobenzothiazole (3B), benzothiazolyl disulfide (4B), *N*-cyclohexyl-2-benzothiazolyl sulfenamide (7B), and dicumyl peroxide (8B) stocks have, in the constant rate portion, almost identical slopes which are significantly lower than 1 B. The tetramethylthiuram disulfide–sulfur (5B) and zinc diethyldithiocarbamate (6B) stocks have oxidation rates slightly higher than 3B but significantly lower than 1B or 2B. This is in accord with Scott (*18*), who found that substitution of TMTD for MBT without changing the proportion of sulfur was often detrimental to age resistance. The radiation-cured stock (9B) has a slightly lower oxidation rate than 3B, and the tetramethylthiuram disulfide cure (10B) has a much lower rate than all other vulcanizates.

In the uninhibited natural rubber black stocks, the sulfur (11B) and DPG (12B) cures again show the highest oxidation rates, with 12B being slightly lower than 11B. Stocks 13B, 14B, 15B, and 16B have approximately the same rate of oxygen uptake which is lower than 11B. Stock 17B has a slightly lower rate than 13B which is possibly due to the slight inhibitory effect of this accelerator (Santocure). Stocks 18B, 19B, and 20B (cured with peroxide, radiation, and with TMTD) show a much lower oxygen uptake than the other stocks, with 20B having the lowest rate.

The oxidation rates of the natural rubber black stocks inhibited with one part per hundred PBNA show 11B-A to have the highest relative rate. This, however, is only slightly greater than the rates of 12B-A, 15B-A, and 16B-A which are approximately the same. Stocks 13B-A, 14B-A, and 17B-A have approximately the same rates, which are slower than the above stocks. The slopes of oxygen absorption for the peroxide cures, 18B-A, and the TMTD cure, 20B-A, are equal and much lower than the other cures.

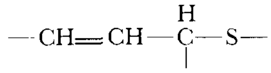
Graphs of uninhibited natural rubber gum stocks show much the same relative rates as the uninhibited Hevea black stocks, the stocks rapidly reaching autocatalytic rates. Stock 17 shows a high oxidation rate but slower than for the other accelerated vulcanizates. Again this is probably due to the slight antioxidant effect of the Santocure accelerator which seems to become apparent when not masked by stronger antioxidants. Stocks cured without free sulfur (18, 19, and 20) oxidized significantly slower than the previous stocks and at approximately the same rate.

From the relative oxidizability of different curing systems in the various substrates several generalizations become apparent. The presence of elemental sulfur as a curing agent causes an increase in the rate of oxygen absorption. Addition of vulcanization accelerators to the elemental sulfur lowers this oxygen uptake, slightly with diphenylguanidine, somewhat more with the dithiocarbamates and thiuram disulfides, and most with the thiazole accelerators. The three formulations containing no free sulfur, dicumyl peroxide, TMTD, and radiation cures, all oxidize at significantly lower rates than stocks containing free sulfur. In the uninhibited natural rubber, the radiation cures show the lowest initial oxidation rates. This might be due to some catalytic activity on the part of the dicumyl peroxide or tetramethylthiuram disulfide, but is more likely to be due to the fact that the natural antioxidants present in Hevea are not destroyed by radiation as they are in thermal vulcanization. On the other hand, it seems possible that TMTD or its reaction products might impart some protection to a vulcanizate because 10B has a lower oxidation rate than either 8B or 9B. Also, the curve for the uninhibited gum stock 20 (cured with TMTD) remains in the constant-rate stage long after 19 has begun to move into the autocatalytic region.

The evidence that cures made with elemental sulfur have higher oxidation rates than cures prepared without free sulfur is in accord with other workers (*11*, *17*, *18*). This is in contrast to reports by Kuzminskiĭ (*13*) that free sulfur in uninhibited sodium butadiene rubber exerts a weak but definite inhibitory effect on oxidation and disappears, causing "after vulcanization" on aging. Fletcher and Fogg (*9*) report that acetone extraction of a TMTD vulcanizate, which is known to remove the zinc dimethyldithiocarbamate, leads to a reduction in heat aging resistance. This indicates that acetone-extractable material in the vulcanizate plays a major role in protecting thiuram disulfide stocks. The beneficial effect of zinc dimethyldithiocarbamate has recently been confirmed by Ossefort (*17*).

This difference in age resistance due to the curing recipe probably includes at least two factors: (1) The bonds formed by a given curing system may be more stable to oxygen attack than those formed by a different system; (2) the ingredients of a given curing system or their decomposition products may contribute to an antioxidant action in the vulcanizate. Haehl (*10*) lends support to the second possibility by showing that mercaptobenzothiazole with zinc mercaptobenzimidazole exhibits a synergetic deactivating effect on aging, while diphenylguanidine has a slight or negligible effect on age resistance. Evidence also indicates that *N*-cyclohexyl-2-benzothiazolyl sulfenamide has antioxidant properties (*5*).

The type of bond formation seems to be important to age resistance. British workers (*1*) report that allylic acyclic monosulfides react initially with oxygen much more rapidly than comparable unsaturated hydrocarbons, while saturated sulfides are inert. *tert*-Butyl disulfide is not oxidized under conditions which cause oxidation of *n*-butyl sulfide (*12*). The autoxidation of organic sulfides, such as cyclohex-2-enyl methyl sulfide, yield keto-sulfides and secondary reaction products in addition to the sulfoxides expected (*2*, *3*). These findings indicate that the increased oxidizability associated with higher sulfur content could result from reaction of adjacent C—H linkages rather than from direct oxidation at the sulfur-carbon bond because there is no strong tendency for C—S bonds to be broken by oxidation. This is seemingly due to the double activation of the alpha hydrogen in such a structure as



$—CH{=}CH—\overset{H}{\underset{|}{C}}—S—$. If this were the case, it would be logical to expect vulcanizates with a high proportion of carbon-carbon cross links to have a lower oxidation rate than those with sulfur cross links.

The relative oxidation rates of the various curing formulations in this study show three general classes: (1) rapid oxidation (elemental sulfur or sulfur plus diphenylguanidine), (2) intermediate oxidation rates (sulfur plus accelerators such as the thiazoles), (3) relatively slow oxidation (non free-sulfur cures). These findings give the relative order for oxygen absorption: diphenylguanidine > mercaptobenzothiazole > thiuram disulfide or dicumyl peroxide. An interesting correlation may be made with the type of cross link. Tikhomirova and Kuzminskiĭ (*22*) report the same order for the mobility of sulfur cross links in vulcanizates: diphenylguanidine > mercaptobenzothiazole > tetramethylthiuram disulfide. Dogadkin and Tarasova (*8*) report that elemental sulfur, alone or with diphenylguanidine yields mainly poly- and disulfide bonds, while thiuram vulcanizates give chiefly carbon-carbon and monosulfide links with no polysulfide bonds. The mercaptobenzothiazole cure is thought to consist mainly of mono- and disulfide cross links with a low proportion of polysulfide bonds. They have established that thermal resistance of vulcanizates depends on the total quantity of cross links and on the relative proportions of

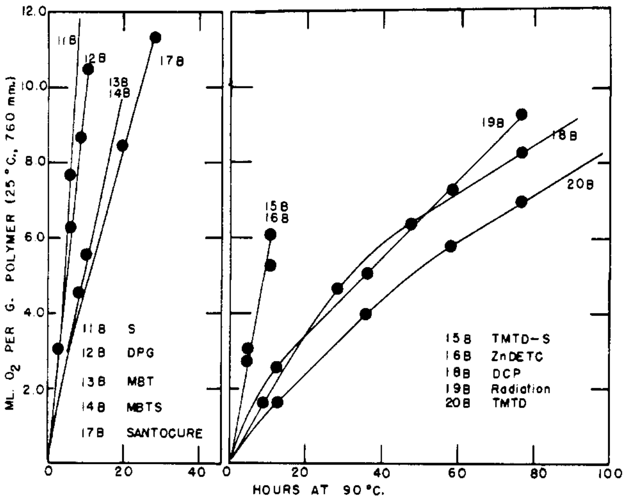


Figure 2. Oxidation rates of uninhibited natural rubber black stocks at 1 atm. O_2

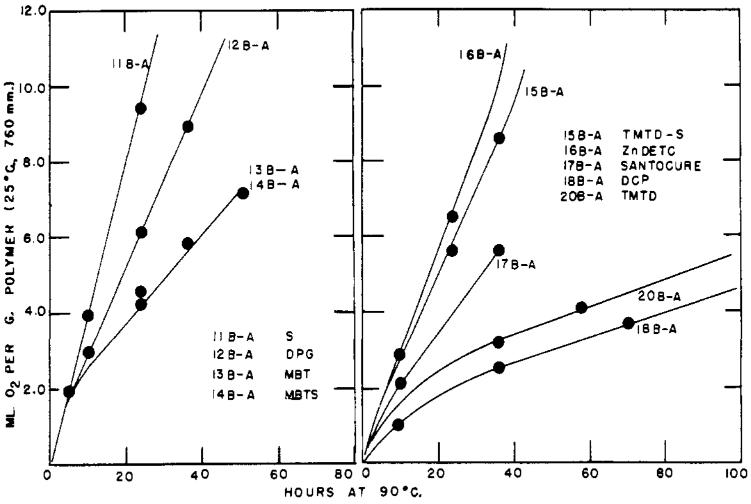


Figure 3. Oxidation rates of inhibited natural rubber black stocks at 1 atm. O_2

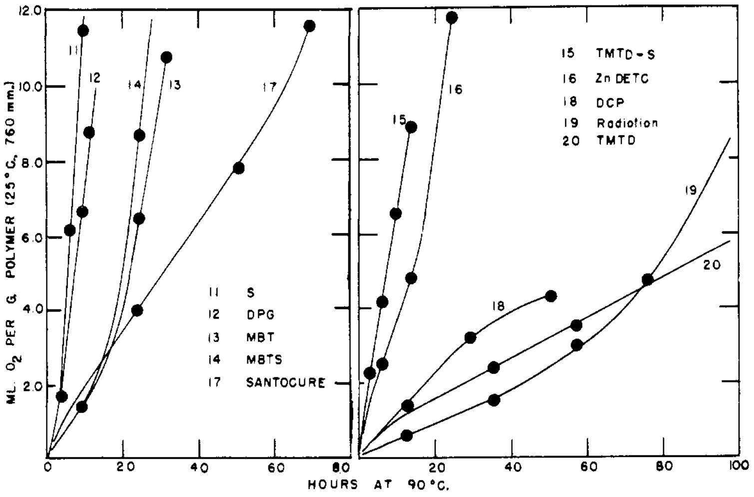


Figure 4. Oxidation rates of uninhibited natural rubber gum stocks at 1 atm. O_2

Table I. Composition of Stocks

Stock Number		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ingredient	Code Name																				
SBR 1500[a]		100	100	100	100	100	100	100	100	100	100										
Hevea pale crepe												100	100	100	100	100	100	100	100	100	100
Zinc oxide		3	3	3	3	3	3	3			3	3	3	3	3	3	3	3			3
Stearic acid		2	2	2	2	2	2	2			2	2	2	2	2	2	2	2			2
Sulfur	S	4.0	2.0	2.0	2.0	2.0	2.0	2.0				4.0	2.0	2.0	2.0	2.0	2.0	2.0			
Diphenylguanidine	DPG		1.2										1.2								
Mercaptobenzothiazole	MBT			1.2										1.2							
Benzothiazolyl disulfide	MBTS				1.2										1.2						
Tetramethylthiuram disulfide	TMTD					0.4					3.0					0.4					3.0
Zinc diethyldithiocarbamate	Zn DETC						0.4										0.4				
Santocure[b]								1.0										1.0			
Di Cup 40 C[c]	DCP								2.5										2.5		
Cure time at 298° F., min.		550	200	40	80	35	30	70	40	[d]	20	330	80	45	70	10	10	20	80	[d]	20
B Stock[e]		550	200	80	75	30	30	70	60		30	270	55	35	30	12	10	20	80		30

[a] Commercial bale, polymerized at 41° F., contains 1.25 phr N-phenyl-2-naphthylamine.

[b] N-Cyclohexyl-2-benzothiazylsulfenamide, Monsanto Chemical Co.

[c] 40% dicumyl peroxide, 60% calcium carbonate, Hercules Powder Co.

[d] Cured with cobalt-60 source, exposure 30 × 10^6 R.

[e] Also contains 50 phr Philblack O, an HAF black.

carbon-carbon, mono-, di-, and polysulfide linkages. Kuzminskiĭ (*14*) concludes that the presence of polysulfide bonds lowers vulcanizate resistance to oxygen, but reports that the fatigue life of vulcanizates is in the following order: polysulfide > monosulfide > carbon-carbon (*15*). These findings coupled with evidence from this laboratory show that the rate of oxidation in vulcanizates exhibits a direct correlation with the type of cross link believed to be formed.

Effect on Physical Properties. Absorption of oxygen by rubber vulcanizates can cause changes, sometimes drastic, in their physical properties. Tables II to V list for the various curing formulations the changes of physical properties with aging in oxygen at 1 atm. and 90° C.

Two major competing effects occur with oxygen attack on rubber polymers—chain scission and chain cross linking. The change in modulus, and to a lesser degree the change in tensile strength, reflects the degree to which chain scission or cross linking predominates. Figure 5 shows the changes in 300% modulus and tensile strength for representative SBR-1500 black stocks.

Table II. Oxidation and Aging Data for Styrene–Butadiene Black Stocks, at 90° C. and 1 Atm. O_2

Stock	Time Hr.	O_2 Absorbed, Ml./G. Polymer, 25° C., 760 Mm.	Shore A Hardness	200% Modulus, P.S.I.	300% Modulus, P.S.I.	Tensile Strength, P.S.I.	Ultimate Elongation, %
1B	0	0	60	600	1900	3400	390
	21.75	2.3	62	800	2525	3475	350
	73.0	5.4	66	1050	3000	3100	300
	93.0	6.6	66	1150	3300	3300	300
	120.0	8.4	66	1300	. . .	2300	250
2B	0	0	54	320	920	3300	525
	21.75	2.1	56	400	1280	3150	525
	73.0	5.0	59	600	1650	3100	425
	105.0	6.6	63	650	1950	3200	400
	145.5	8.8	62	750	2250	2450	310
3B	0	0	56	300	900	3350	550
	21.75	2.0	58	400	1200	3800	525
	73.0	4.3	59	600	1725	3500	425
	120.0	5.9	60	650	1950	3325	400
	216.5	8.3	63	800	2400	3050	350
4B	0	0	54	300	1050	4125	600
	44.5	2.9	57	500	1675	3800	500
	71.25	4.1	59	550	1700	3575	450
	143.25	6.1	61	700	2025	3550	400
	214.5	7.8	63	800	2425	3500	375
5B	0	0	58	425	1650	4000	475
	44.5	2.5	60	700	2400	3800	400
	91.0	4.2	61	750	2450	3725	375
	143.25	6.4	64	850	2800	2950	310
	214.5	8.1	65	900	. . .	2700	275
6B	0	0	53	300	900	3975	625
	44.5	2.6	58	500	1650	3900	475
	91.0	4.6	59	600	1900	3850	450
	143.25	6.8	60	700	2100	3550	400
	187.5	8.2	61	750	2300	2800	325
7B	0	0	57	575	1400	3900	475
	48.0	2.8	60	600	2100	3725	400
	121.5	4.8	62	825	2600	3350	350
	217.75	7.6	64	875	2775	3300	325
8B	0	0	54	375	1400	2800	400
	48.0	2.0	57	400	1600	3300	400
	104.75	4.4	58	400	1675	2850	385
	146.75	6.1	57	525	1775	2775	375
	190.75	8.4	58	500	1825	2550	350
9B	0	0	47	300	850	2875	575
	36.0	2.1	45	350	1000	2775	500
	99.4	4.4	47	325	1000	2600	450
	191.75	6.3	47	375	1200	2350	400
	270.0	8.1	50	400	1400	2200	350
10B	0	0	54	325	1100	2700	425
	36.0	1.9	52	350	1225	2900	425
	119.5	3.6	54	475	1550	3600	425
	311.0	6.2	59	650	2000	3625	400

Table III. Oxidation and Aging Data for Uninhibited Natural Rubber Black Stocks, at 90° C. and 1 Atm. O_2

Stock	Time Hr.	O_2 Absorbed, Ml./G. Polymer, 25° C., 760 Mm.	Shore A Hardness	200% Modulus, P.S.I.	300% Modulus, P.S.I.	Tensile Strength, P.S.I.	Ultimate Elongation, %
11B	0	0	51	250	750	1650	425
	3.25	2.9	50	250	750	1400	400
	6.0	7.3	49	250	725	1275	375
	8.75	12.3	47	250	700	975	350
	10.75	16.0	48	250	725	875	325
12B	0	0	52	400	1150	3375	525
	3.25	3.1	48	250	900	2100	425
	6.0	6.2	46	225	750	1500	400
	8.75	8.7	45	200	675	1325	400
	22.75	18.6	38	150	400	. . .	375
13B	0	0	54	400	1100	3200	500
	6.0	3.3	53	325	900	2250	475
	10.75	5.5	51	300	800	1700	425
	22.75	11.1	47	200	600	1100	425
	31.0	14.2	47	175	500	900	400
14B	0	0	53	350	1100	3425	525
	4.5	3.0	51	300	900	2550	450
	9.75	5.6	49	250	825	1800	425
	21.25	10.6	46	200	650	1350	425
15B	0	0	54	425	1400	3775	500
	4.5	2.8	54	400	1275	3100	425
	9.75	5.3	51	350	1100	2350	400
	21.25	. . .	46	250	800	1150	350
16B	0	0	54	400	1200	3550	500
	4.5	3.0	51	350	1150	2275	425
	9.75	6.1	49	300	950	1825	400
	21.75	. . .	44	200	575	875	375
17B	0	0	54	400	1300	4150	525
	4.5	2.7	54	400	1400	3300	475
	8.25	4.4	52	400	1200	3100	465
	19.75	8.6	49	375	1125	2000	400
	28.0	11.3	47	300	925	1650	385
18B	0	0	46	200	925	2950	475
	8.25	1.8	43	200	800	2300	450
	28.0	4.9	36	125	400	1450	475
	51.25	6.8	34	100	300	1025	475
	91.5	9.2	31	75	200	. . .	475
19B	0	0	40	200	900	1900	400
	23.75	2.7	35	175	800	1350	387
	36.0	4.0	32	100	650	1125	375
	58.0	6.2	29	100	475	925	375
	99.5	8.1	27	75	400	800	400
20B	0	0	52	375	1275	3300	475
	12.0	2.6	50	300	1125	2600	450
	36.0	5.1	47	300	1000	1850	375
	57.75	7.5	45	250	900	1575	375
	76.5	9.3	45	250	875	1450	375

These and the following figures show changes in the physical properties with the amount of oxygen absorbed rather than as a function of time. Consequently, differences shown here are over and above the differences already pointed out with respect to the effect of the curing system and polymer type upon the rate of oxygen uptake.

The stress at 300% elongation shows an increase on aging which is characteristic of most styrene-butadiene stocks. Other workers (*6, 7*) explain that this increase in modulus is the result of a structurizing effect by the oxygen in which cross linking predominates over chain scission. The effect of the oxygen is attributed to the increase of intermolecular forces, due to the formation of polar groups, to oxygen bridges, and to polymerization processes occurring during oxidation. The rate of modulus increase is approximately the same for all stocks except the peroxide cure (8B) and the radiation cure (9B) which undergo a much smaller increase. Generally speaking, the ultimate elongation and moduli of the SBR black stocks exhibit a linear change with oxygen uptake except for some early variations. However, the relative change in tensile strength seems to be less simple. In most cases the tensile strength shows a fairly linear decrease on aging only in the latter stages of the measurements. The notable exception to this is the TMTD cure (10B) whose tensile strength increases on aging.

Figure 6 shows the changes in 300% modulus and tensile strength with aging for representative uninhibited natural rubber black stocks. The 300% modulus shows a general decrease with oxygen uptake which is linear in the latter stages of oxidation. The rate of modulus decrease is approximately the same for all stocks but 11B, whose modulus shows only slight change over the oxidation range. The over-all decrease of modulus shows the predominance of chain scission over cross linking at this temperature. The tensile strengths show a fairly linear decrease during the initial oxidation stages with a noticeable decrease in slope during the latter stages. The stocks show approximately the same rate of tensile decrease except for 11B, whose slope is much smaller than the rest. The relative decrease of tensile strength is greater for the natural rubber vulcanizates than for the corresponding SBR vulcanizates. This is probably due to differences in the relative ratios of chain scission and cross linking.

Figure 7 shows the changes in 300% modulus and tensile strength with aging for selected inhibited natural rubber black stocks which illustrate the variations observed. These stocks differ in formulation from the above stocks only in that they contain one part PBNA per hundred of rubber. All of the inhibited vulcanizates show an increase in initial physical prop-

Table IV. Oxidation and Aging Data for Inhibited Natural Rubber Black Stocks, at 90° C. and 1 Atm. O_2

Stock	Time Hr.	O_2 Absorbed, Ml./G. Polymer, 25° C., 760 Mm.	Shore A Hardness	200% Modulus, P.S.I.	300% Modulus, P.S.I.	Tensile Strength, P.S.I.	Ultimate Elongation, %
11B-A	0	0	51	300	850	1900	425
	4.5	1.9	53	300	900	1850	400
	6.25	2.5	53	350	950	1700	390
	23.25	9.3	54	390	975	1350	350
	35.75	16.9	55	420	950	1050	300
12B-A	0	0	54	400	1200	3600	490
	9.75	2.9	52	360	1175	2525	450
	23.25	6.1	51	350	1100	2100	425
	35.75	8.9	50	350	1000	1675	375
	50.75	12.6	49	275	950	1200	325
13B-A	0	0	55	400	1200	3400	500
	9.75	2.4	55	460	1350	3125	460
	23.25	4.2	56	440	1250	2825	440
	35.75	5.5	54	440	1230	2700	440
	50.75	7.1	54	450	1265	2425	425
14B-A	0	0	53	365	1175	3975	550
	10.0	2.5	54	465	1350	3325	485
	24.0	4.6	55	590	1300	3075	465
	36.5	5.6	54	410	1300	2900	435
	51.25	7.3	54	400	1275	2750	450
15B-A	0	0	57	450	1525	3100	410
	10.0	2.8	56	510	1625	3450	435
	24.0	5.6	55	500	1575	2550	375
	36.5	8.6	54	425	1400	1700	310
	51.25	13.4	53	400	1200	1275	305
16B-A	0	0	53	400	1450	4200	550
	10.0	2.8	53	400	1250	3400	500
	24.0	6.4	52	325	1100	2350	425
	36.5	11.0	50	300	950	1475	375
	51.25	18.2	47	250	750	875	310
17B-A	0	0	55	440	1550	4400	525
	9.5	2.0	56	490	1600	4125	500
	23.25	4.0	56	500	1600	3850	475
	35.5	6.0	55	500	1575	3200	450
	50.5	7.0	55	500	1525	2850	400
18B-A	0	0	47	200	850	2525	450
	35.5	2.6	42	150	650	1900	475
	94.5	4.3	40	125	575	1425	450
	173.0	6.4	40	100	410	1125	425
20B-A	0	0	52	375	1275	3275	475
	23.5	2.9	50	400	1300	3050	450
	76.5	4.8	52	425	1400	2825	400
	143.5	6.9	54	400	1475	2800	400
	242.25	10.1	56	425	1450	2300	350

Table V. Oxidation and Aging Data for Uninhibited Natural Rubber Gum Stocks, at 90° C. and 1 Atm. O_2

Stock	Time Hr.	O_2 Absorbed, Ml./G. Polymer, 25° C., 760 Mm.	Shore A Hardness	500% Modulus, P.S.I.	700% Modulus, P.S.I.	Tensile Strength, P.S.I.	Ultimate Elongation, %
11	0	0	19	150	300	550	900
	6.25	6.0	16	...	350	....	750
	9.0	11.5	15	150	....	....	525
	10.75	14.3	13	...	....	100	475
	13.50	17.8	12	...	....	100	450
12	0	0	23	200	....	2650	925
	6.25	3.4	20	175	....	2600	900
	9.0	7.7	15	...	500	500	700
	10.75	8.8	15	...	500	500	700
	13.50	10.0	14	...	400	....	750
13	0	0	24	200	650	2950	925
	13.50	2.2	21	200	600	2300	900
	24.75	7.5	14	125	400	850	800
	30.75	10.2	12	125	....	....	550
14	0	0	25	200	700	2900	900
	10.0	1.6	22	200	600	2300	850
	13.0	2.3	22	200	600	2200	875
	24.25	8.9	14	150	400	....	775
	30.25	13.4	12	125	....	200	600
15	0	0	27	300	900	4000	900
	2.5	2.2	25	275	1100	2700	825
	6.0	4.2	23	300	1000	3100	825
	10.0	6.7	21	200	850	2225	850
	13.0	8.9	19	200	800	1150	750
16	0	0	24	200	650	3250	925
	6.0	2.6	22	200	750	2350	850
	13.0	5.1	20	200	600	2400	900
	24.25	11.6	14	150	450	850	800
	30.25	16.3	11	125	....	200	650
17	0	0	29	350	1600	4150	900
	12.0	2.4	28	450	1900	4500	850
	29.0	4.8	26	400	1800	3100	800
	50.5	7.9	23	400	1650	2700	800
	69.5	11.6	20	150	....	900	625
18	0	0	20	150	1000	1950	875
	23.25	2.9	16	125	350	1050	850
	29.0	4.1	15	...	350	350	700
	50.5	4.3	13	...	350	....	775
	69.5	5.4	11	...	250	....	725
20	0	0	22	190	675	2300	900
	34.75	2.5	19	190	575	1925	875
	75.5	4.5	16	175	500	1300	850
	118.0	6.9	14	150	400	....	750
	142.0	8.5	13	125	400	400	700
20A	0	0	22	400	800	2500	850
	75.5	1.9	24	450	1100	2700	850
	240.75	4.0	23	475	1200	2300	800
	334.0	6.1	23	500	1100	1925	775

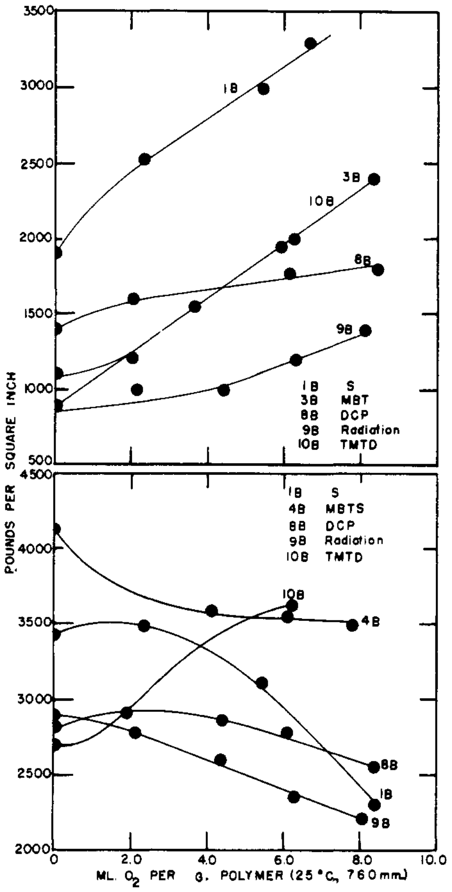


Figure 5. Styrene-butadiene black stocks at 90° C. and 1 atm. O_2

Top, change of 300% modulus
Bottom, change of tensile strength

erties over the uninhibited stocks except for 18B-A (dicumyl peroxide cure), whose physical properties are lowered by the addition of PBNA no doubt due to interference with the free-radical vulcanization. The PBNA evidently inhibits degradative processes during the vulcanization itself in the other cases.

The change of 300% modulus in the inhibited stocks involves only relatively small increases or decreases. This indicates a fairly even balance between cross linking and scission processes at this temperature. The tensile strengths again exhibit a fairly linear decrease. The rate of change of tensile strength in the inhibited black stocks is generally lower when compared to that of the uninhibited black stocks.

Figure 8 shows the changes in the 700% modulus and tensile strength with aging for representative uninhibited natural rubber gum stocks. The 700% moduli show relatively small linear decreases with aging except for 18, which has a relatively large initial decrease, and 11 which increased slightly. The tensile strengths have a fairly linear decrease on oxygen absorption with 17 exhibiting some aftercure. Stock 18 had very poor age resistance, becoming soft and sticky. The radiation-cured gum stock gave physical properties too poor to measure.

In comparing the physical properties of vulcanizing systems and their resistance to oxidation, the original properties and the change of these properties with aging must be considered. In the natural rubber stocks, the elemental sulfur cures gave lower changes in modulus and tensile strength than other cures, but the initial physical properties were very poor. The radiation cures and dicumyl peroxide vulcanizates show a higher proportion of chain scission to cross linking in the polymer systems. This effect is not harmful in the SBR stocks where the structurizing process predominates, but it causes a fairly high degradation in the natural rubber stocks. The increased amount of cross linking, over the radiation and peroxide cures, by the accelerated sulfur stocks could well be due to a slow cross-linking process during aging brought about by continued reaction of sulfur in the presence of residual accelerator. This is the interpretation which LeBras (*16*) now gives for what he originally called the "deactivating effect."

CONCLUSIONS

Elemental sulfur as a curing agent for natural rubber or SBR polymer increases the oxidation rate of the vulcanizate.

The relative oxidation rate of different curing systems can be correlated qualitatively with the type of cross link believed to be formed in the vulcanization process. However, by-products of the vulcanization reaction also affect the rate of oxidation and thus may obscure the observed relationships.

The relative rates of chain scission and cross linking on aging depend, not only upon the aging temperature, oxygen pressure, and type of polymer, but also upon the vulcanizing system. The proportion of cross linking to chain scission influences the physical properties, particularly the modulus and tensile strength.

ACKNOWLEDGMENT

This work is a part of a study sponsored by the Office of Ordnance Research, U. S. Army on some factors involved in the deterioration of rubber polymers and vulcanizates. The radiation cures were prepared through the courtesy of the Rubber Laboratory of the Rock Island Arsenal.

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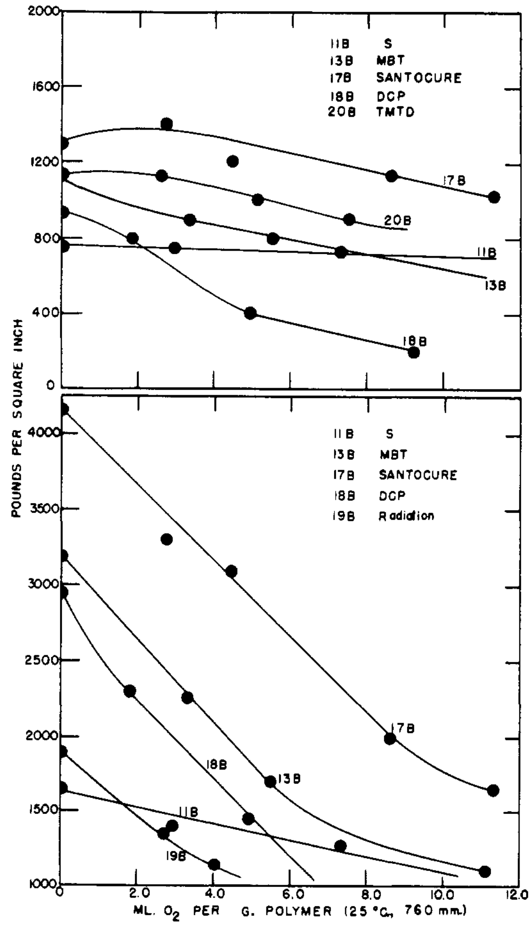

Figure 6. Natural rubber uninhibited black stocks at 90° C. and 1 atm. O_2

Top, change of 300% modulus
Bottom, change of tensile strength

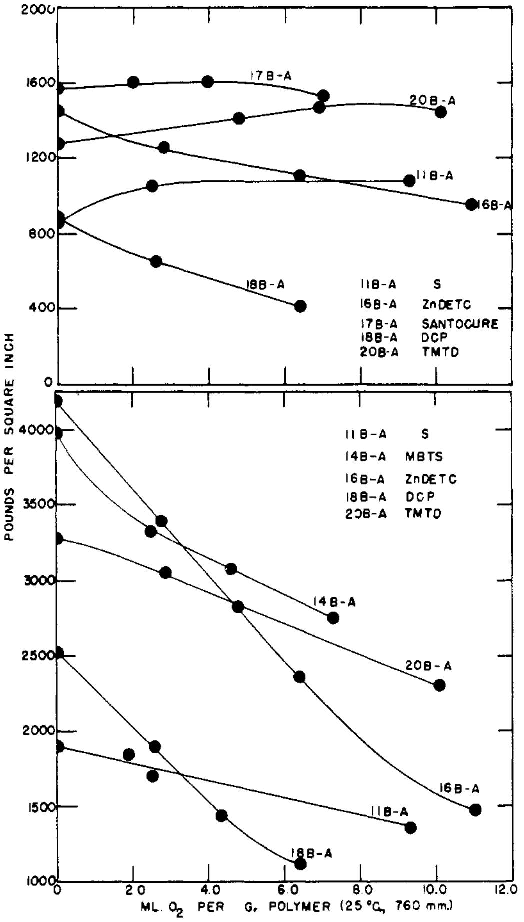

Figure 7. Inhibited natural rubber black stocks at 90° C. and 1 atm. O_2

Top, change of 300% modulus

Bottom, change of tensile strength

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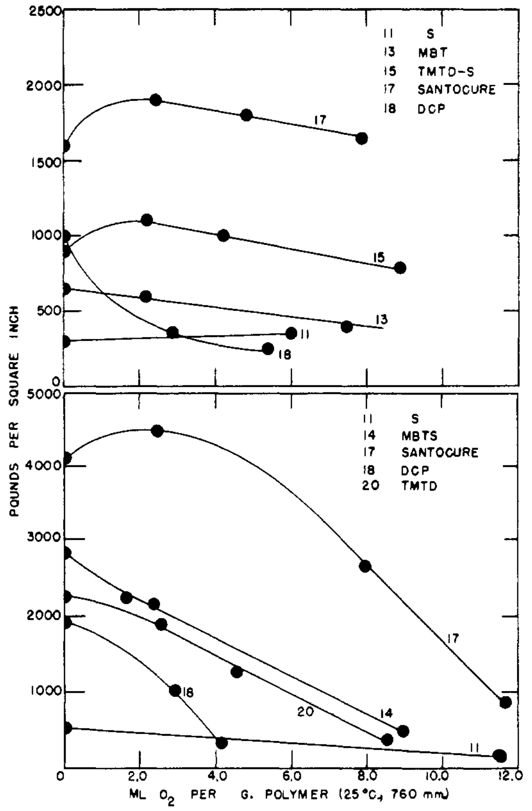

Figure 8. Natural rubber gum stocks at 90° C. and 1 atm. O_2

Top, change of 700% modulus

Bottom, change of tensile strength

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CORRECTION

In "Effect of Molecular Structure on Burning Velocity" [G. J. Gibbs and H. F. Calcote, *J. Chem. Eng. Data* **4,** 227 1959)] Equation 3 should be two equations,

$$C_1 = 4/\pi D^2$$

and

$$C_2 = 2/\pi D^4$$