

Inhibited Oxidation of Vulcanized Natural Rubber

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Synopsis

Rates of oxidation in oxygen at 140°C. of natural rubber gum vulcanizates containing PBNA as inhibitor have been compared. They are a function of sulfur combined with the rubber, and only slightly affected by curing system for sulfur alone, TMTD sulfurless, and very high-efficiency sulfenamide plus dithiocarbamate-accelerated compositions. Addition of diphenylguanidine to simple sulfur vulcanizates causes much faster oxidation. No conclusions about oxidation mechanism can be drawn from rates of oxidation alone.

The rate of oxidation of sulfur-vulcanized rubber increases directly with the amount of sulfur combined with the hydrocarbon¹⁻⁷; this largely accounts for the reputed superior aging resistance of vulcanizates cured with high efficiency systems. There is a small added contribution to oxidation resistance by residues from vulcanizing agents.⁸ Aging is also affected by vulcanizing systems because of their effects in producing crosslinks of different stabilities. No effects on hydrocarbon stability have been found, except those on oxidation rate, and there has been limited study of this.

This paper reports a comparison of rates of inhibited oxidation of distinctly different vulcanizates of natural rubber. The results confirm earlier work, where comparison is possible, and lead further to the conclusion that effects of structure of the sulfur moiety directly attached to the hydrocarbon on degradation cannot be distinguished simply by measurements of oxidation rates.

Experimental

Recipes are given in Table I. The fully compounded rubber was calendered onto aluminum foil and cured as described previously^{9,10} to give sheets approximately 0.25 mm. thick. Cured samples were peeled from the aluminum foil and submitted to oxidation either as is or after benzene extraction followed by infusion of phenyl- β -naphthylamine (PBNA) from acetone or ethyl acetate solution. For the least highly vulcanized compositions, 20% methanol in benzene was substituted for benzene. Oxidation measurements were made in a static apparatus described previously,¹¹ barium oxide being used as desiccant and acid scavenger. Analysis for combined sulfur was by the procedure of Burger.¹² Compositions and analyses are reported uncorrected for nonrubbers in the pale crepe. Antioxidant

concentrations were checked occasionally by extraction and estimation by ultraviolet spectroscopy; the concentration is not very critical. Rates reported are estimated from the initial slopes of curves of oxygen absorbed as a function of time.

Results and Discussion

Results are collected in Tables II–IV and in Figures 1 and 2.

TABLE I
Formulations Used

Ingredient ^a	Composition, parts ^b				
	S107	S108	S114	S115	S125
Pale crepe	100	100	100	100	100
Zinc oxide	5	5	5	5	3
Stearic acid	0.5	—	0.5	—	—
2,6-MOR	—	—	—	—	5
TMTD	—	<i>x</i>	—	<i>x</i>	—
ZDC	—	(10 - <i>x</i>)	—	—	5
PBNA	1	—	1	—	1
DPG	1/2S	—	—	—	—
S	<i>x</i>	—	<i>x</i>	—	<i>x</i>
Cure: at 130°C., hr.	1,2,4,24	2.5	48	2.5	4

^a 2,6-MOR = 2,6-dimethylmorpholinot hiobenzothiazole; TMTD = tetramethylthiuram disulfide; ZDC = zinc dimethylidithiocarbamate; PBNA = phenyl- β -naphthylamine; DPG = diphenylguanidine.

^b *x* = varied.

TABLE II
Oxidation of DPG/S Vulcanizates at 130°C.

Sulfur used, phr	Cure, hr.	Rate of oxidation, cc./g.-hr.			
		As cured	PBNA infused	Combined sulfur, %	Sulfide sulfur, %
1	1	1.84	2.60	0.52	0.03
	2	2.30	4.10	0.54	0.08
	4	2.45	3.00	0.67	0.13
	24	1.85	1.52	0.62	0.16
2	1	3.11	—	0.88	0.09
	2	4.55	9.00	1.12	0.27
	4	4.30	9.00	1.24	0.45
	24	2.65	6.30	1.17	0.54
3	1	4.65	6.50	1.27	0.22
	2	6.45	13.70	1.66	0.52
	4	6.60	11.10	1.77	0.83
	24	3.45	2.85?	1.64	1.01
4	1	5.90	7.00	1.89	0.26
	2	7.80	12.20	2.53	0.80
	4	9.65	14.00	2.36	1.19
	24	7.10	6.10	2.10	1.45

TABLE III
Oxidation of TMTD Vulcanizates at 140°C.

Compo- sition	TMTD used, phr	Rate of oxidation, cc./g.-hr.			
		As cured	0.5% PBNA ^a	1.0% PBNA ^a	1.0% PBNA, recured ^b
S108	2	0.78	0.58	0.78	0.52
	4	2.00	1.22	1.30	1.50
	6	2.89	1.86	—	1.65
	8	4.36	2.35	2.05	3.15
	10	5.17	2.64	2.25	3.50
S115	2	5.00	—	0.56	0.49
	4	3.35	—	1.25	1.05
	6	2.10	—	1.37	1.60
	8	1.35	—	2.13	2.30
	10	4.65	—	2.90	—

^a Added by infusion from solution.

^b Cure: 8 hr. at 125°C.

TABLE IV
Oxidation of Sulfur Vulcanizates at 140°C.

S114 (simple sulfur)				S125 (high efficiency)				
Sulfur used, phr	Com- bined sulfur, %	Rate, cc./g.-hr.		Sulfur used, phr	Com- bined sulfur, %	Rate, cc./g.-hr.		
		As cured	1% PBNA ^a			As cured	1% PBNA ^a	2% DPG, PBNA ^a
1	0.62	2.18	0.98	0.5	0.55	1.15	1.00	1.10
2	1.34	4.90	2.30	1.0	0.54	1.65	1.30	1.68
3	2.14	6.40	4.10	1.5	1.08	2.20	1.70	2.85
4	2.90	6.40	4.70	3.0	2.40	5.60	5.15	8.00
5	3.56	6.40	5.10					

^a Added by infusion from solution.

As reported,⁷ DPG-accelerated sulfur vulcanizates are oxidized much faster than all the others. Table II shows that except for two aberrant points the rate of oxidation increases with time of cure in early stages, then decreases. Tables III and IV and Figure 1 show that there is a close correlation between rate of oxidation and sulfur content of all the other vulcanizates and the relation is about the same for all. Formulation S125 gives the highest efficiency of vulcanization known; S114 is very inefficient.^{13,14}

Since the structures of the simple rubber/sulfur and the rubber/DPG/sulfur vulcanizates differ much less than those of the rubber/sulfur and the high efficiency vulcanizates, it is obvious that the structures of sulfur moieties directly attached to the hydrocarbon are less important in controlling

oxidative deterioration rates than other factors. The rise and fall in rates of oxidation of the DPG/sulfur vulcanizates may reflect growth and decay of polysulfide as assumed by Parks and Lorenz.⁷ The higher rate of oxidation of the long cures, DPG-accelerated, compared with unaccelerated

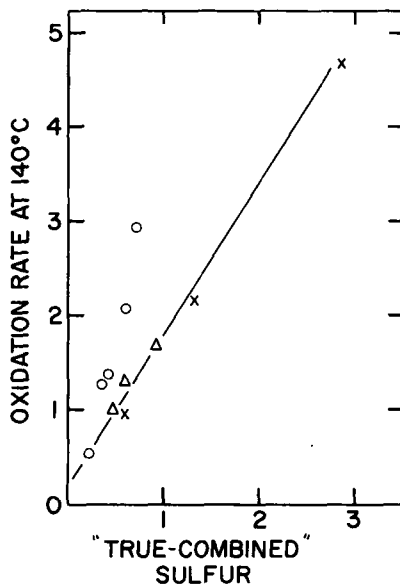


Fig. 1. Rate of oxidation (in cc./g.-hr. at 140°C., pure oxygen) as a function of combined sulfur insoluble in butanone after digestion with HCl: (O) TMTD sulfurless (X) rubber/sulfur, no accelerator; (Δ) highest known efficiency.¹⁶ All specimens contained approximately 1 phr PNBA.

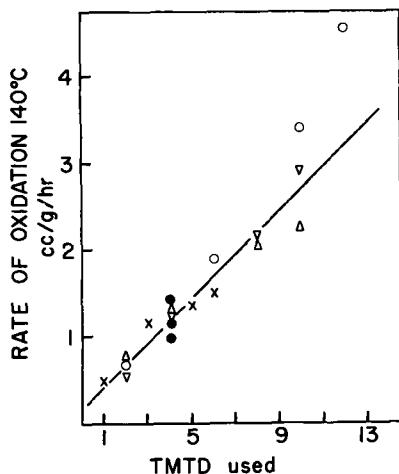


Fig. 2. Rate of oxidation of TMTD vulcanizates after extraction and addition of PBNA. Each symbol represents a separate experiment.

cures must be attributed to a specific effect of the DPG, a strongly basic amine. Two possibilities have been considered: acceleration by reaction of the amine with sulfur-containing groups, and acceleration by rendering trace metals in the rubber more effective as catalysts. Since free DPG should be extracted, the second possibility seems more likely. As shown in Table IV, addition of DPG to an efficiently vulcanized composition does not affect its rate of oxidation much.

Parks and Lorenz⁷ reported that two kinds of vulcanizates were oxidized at rates less dependent on sulfur concentration than simple sulfur vulcanizates. One was vulcanized with TMTD. No data were reported for these vulcanizates, so that it is not possible to compare their results directly with ours. However, they report that rates of oxidation decreased with time in these vulcanizates. This was not true of ours. This suggests that antioxidant was formed in their composition as oxidation proceeded.¹⁵ The data in Table III show that in initially ZDC-free stocks, the more ZDC formed the slower the oxidation, but the factors affecting rate are obviously complex, and this set of data raises some question as to whether it is in fact ZDC which is the active antioxidant in TMTD vulcanizates, or if the form in which it is present is critical. We found free TMTD in some of our vulcanizates after 2.5 hr. at 130°C., which is roughly comparable to the 2 hr. at 135° used by Parks and Lorenz.⁷ To determine effects of incomplete cure some samples were recured *in vacuo* 8 hr. at 125°C. The last column of Table III shows that this had negligible effect on the rate of oxidation. These results have been repeated with several independent preparations. As Figure 1 shows, rate of inhibited oxidation is essentially independent of crosslink structure in these vulcanizates. Although there may be erratic variation in rates of oxidation as cured, after extraction and readdition of PBNA rates are reproducible, as illustrated by Figure 2. Experiments made after those of Table III show that there is a rapid maturation of press-cured TMTD vulcanizates. Oxidizability decreases steadily over several days at room temperature. This was not investigated further.

Reasons for failure of high-zinc, high-fatty-acid, MBT-accelerated vulcanizates to be oxidized at rates not determined by sulfur combined are not obvious, but this may reflect increasing amounts of residues from the vulcanizing system. There is no published information about the fate of MBT in such systems or about whether it is soluble in acetone after cure.

References

1. H. P. Stevens, *J. Soc. Chem. Ind.*, **38**, 192T (1919).
2. W. C. Davey, *Trans. Inst. Rubber Ind.*, **5**, 386 (1930).
3. C. Dufraisse and A. Etienne, *Rubber Chem. Technol.*, **11**, 282 (1938).
4. W. L. Cox and J. R. Shelton, *Ind. Eng. Chem.*, **46**, 2237 (1954).
5. G. J. van Amerongen, *Ind. Eng. Chem.*, **47**, 2565 (1955).
6. A. G. Veith, *Ind. Eng. Chem.*, **49**, 1775 (1957).
7. C. R. Parks and O. Lorenz, *Ind. Eng. Chem. Prod. Res. Develop.*, **2**, 279 (1963).
8. J. Scanlan and J. R. Dunn, in *The Physics and Chemistry of Rubber-Like Substances*, L. Bateman, Ed., Maclaren, London, 1963.

9. E. M. Bevilacqua and E. S. English, *Proc. Rubber Technol. Conf., 4th Conf. London*, **1962**, 607.
10. E. M. Bevilacqua, *J. Appl. Polymer Sci.*, **7**, 789 (1963).
11. E. M. Bevilacqua, *Kautschuk Gummi*, **15**, WT 165 (1962).
12. V. L. Burger, *Rubber Chem. Technol.*, **32**, 1452 (1959).
13. C. G. Moore and B. R. Trego, *J. Appl. Polymer Sci.*, **5**, 299 (1961).
14. C. G. Moore and B. R. Trego, in *The Chemistry and Physics of Rubber-Like Substances*, L. Bateman, Ed., Maclaren, London, 1963, Chap. 15.
15. J. R. Dunn and J. Scanlan, *J. Appl. Polymer Sci.*, **1**, 84 (1959).
16. E. M. Bevilacqua, *J. Polymer Sci. B*, in press.

Résumé

Les vitesses d'oxydation de vulcanisats de gomme de caoutchoucs naturels, contenant du PBNA comme inhibiteur, ont été comparées dans l'oxygène à 140°C. Elles sont fonction du soufre combiné au caoutchouc, et seulement faiblement influencées par la méthode de post-traitement au soufre seul, le TMTD "sans soufre," ou les divers mélanges accélérateurs très efficaces à base de sulfénamide et de dithiocarbamate. L'addition de diphenylguanidine à des vulcanisats de soufre entraîne une oxydation beaucoup plus rapide. Aucune conclusion concernant le mécanisme d'oxydation ne peut être tirée uniquement au départ des vitesses d'oxydation.

Zusammenfassung

Die Geschwindigkeit der Oxydation von ungefüllten Naturkautschukvulkanisaten mit einem Gehalt an PBNA als Inhibitor unter Sauerstoff bei 140°C wurde verglichen. Sie ist eine Funktion des im Kautschuk gebundenen Schwefels und wird nur wenig durch das Vulkanisationssystem für reinen Schwefel, TMTD "schwefelfrei" und hochwirksame, mit Sulfenamid plus Dithiocarbamat beschleunigte Mischungen beeinflusst. Zusatz von Diphenylguanidin zu einfachen Schwefelvulkanisaten führt zu einer viel rascheren Oxydation. Aus der Oxydationsgeschwindigkeit allein kann kein Schluss auf den Oxydationsmechanismus gezogen werden.

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