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The Effects of Some Antioxidants on the Elastomers Derived from Carboxy-terminated Polybutadiene

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The capability of several sorts of conventional antioxidants was studied by means of the tensile and the swelling tests of the elastomers derived from the carboxy-terminated polybutadiene prepolymer. When exposed for one year, the elastomers containing no antioxidants deteriorated remarkably; they became brittle and, without exception, no longer looked like the so-called "elastomers." Many kinds of the antioxidants worked out and were found to be effective; their capabilities were evaluated as almost the same as far as the tensile properties of the exposed material were concerned. The changes in the reciprocal value of the average chain length between cross-links, $1/M_c$, in the course of the exposure, however, would be a convenient semi-quantitative measure of the induced cross-linking reaction. With this assumption, the swelling test might prove that, among the additives covered, the amine-type antioxidants were most effective in preventing the deterioration induced by the over-cross-linking reaction of the elastomer. The relationship between the amount of the sol-fraction and the cross-linking density for the exposed specimens was fitted to that of the random cross-linking and the scission of the polymer with a random distribution of chain lengths.

The conventional composite propellants are composed of an inorganic oxidizing material, several sorts of additives, and a polymeric resin fuel. The fuel resin also acts as a binder; a lot of solid materials are finely dispersed therein. It should give the grain of good mechanical properties as well as of high energy. It is quite difficult, however, to combine good mechanical properties with the conventional resinous materials, since the required quantities of solid ingredients usually amount to 75—85% or more of the grain.

On the other hand, from the point of view of energy, fuel binders of a low heat of formation, and the low molecular weight of the burnt gas are plausible.

The starting materials should be liquid at an ambient temperature; they should be able to be cured after the solid components are dispersed therein. From these standpoint, the synthesized elastomeric materials (such as polysulfide, polyurethane and polybutadiene rubbers) are at present preferred as fuel binders for composite propellants.

Work on the cross-linking reactions of carboxy-terminated polybutadiene, which is believed to be an excellent fuel binders, has been reported by the present authors.[1] It may deteriorate easily on aging, and then cause physical or chemical changes which would offer serious problems, especially for storability, since it is a kind of diene-type rubber.

The changes in tensile properties and the values of the equilibrium swelling in the course of the one-year exposure were determined in order to evaluate the capability of the antioxidants.

The effect of some conventional antioxidants will also be described.

Materials

The following antioxidants were tested:

	Commercial name	Maker*
(Amine Type)		
N, *N'*-Diphenyl-*p*-phenylenediamine	Nocrac DP	O
N, *N'*-Di-(2-naphthyl)-*p*-phenylenediamine	Nocrac White	O
Phenyl-α-naphthylamine	Nocrac PA	O
Phenyl-β-naphthylamine	Nocrac D	O
Blend of phenyl-β-naphthylamine and diphenyl-*p*-phenylenediamine	Nocrac HP	O
Blend of phenyl-α-naphthylamine and diphenyl-*p*-phenylenediamine	Nocrac 500	O
Octyl diphenylamine	D. D. A.	Bayer

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[1] K. Yamazaki and H. Tokui, This Bulletin, **38**, 2172 (1965).

(Phenol Type)		
2, 6-Di-*t*-butyl-*p*-cresol	Ionol	Shell
1, 1′-Bis-(4-hydroxy-phenyl)cyclohexane	Antigene W	S
4, 4′-Thiobis-(6-*t*-butyl-3-methylphenol)	Antigene WX	S
Derivative of 6-*t*-butyl-3-methylphenol	Antigene WL	S
Styrenated phenol	Antigene S	S
(Reaction Products of Amine and Aldehyde)		
Aldol-α-naphthylamine	Nocrac C	O
(Reaction Products of Amine and Ketone)		
6-Ethoxy-2, 2, 4-trimethyl-1, 2-dihydroquinoline	Nocrac AW	O
Reaction product of diphenylamine and acetone	Nocrac B	O
(Benzimidazoles)		
2-Mercapto-benzimidazole	Antigene MB	S
Zinc salt of 2-mercapto-benzimidazole	Antigene MBZ	S
(Others)		
Tri-(nonyl phenyl) phosphite	Antigene TNP	S
Di-lauryl-thiodipropionate	Antigene TPL	S
Nickel dibutyl dithiocarbamate	Antigene NBC	S
——	Polygard C	N
——	Flexzone	N

* O: Ouchi Shinko Chem. Co., Ltd.
S : Sumitomo Chem. Co., Ltd.
N: Naugatuck Chem. Div., U. S. Rubber Co.

The antioxidants, the carboxy-terminated prepolymers, HC-434 (Thiokol Chem.) and Butarez CTL (Phillips Petr. Co.), and the cross-linking agent, tris[1-(2-methyl)aziridinyl]phosphine oxide [MAPO] (Interchemical Co.), were used as received.

Experimental

The polybutadiene prepolymer, MAPO, an accelerator, and the antioxidant were mixed thoroughly and then cured as an elastomer sheet 2 mm. thick. While the quantities of the prepolymer, the curing agent and the accelerator were kept constant, the quantity of the antioxidant recommended by the maker was added.

Dumbbell-shaped specimens (JIS-K-6301, No. 3-type) were die-cut from the sheet and used for both the tensile and the exposure tests.

The details of the elastomer preparation, the tensile test, and the process of the equilibrium swelling have already been described.[1]

The specimens were fixed on polyethylene-lined plywood plates which faced south and which were inclined at a 30° angle. They were then exposed on the roof of the Central Research Laboratory of Daicel, Ltd. (171 Ohi-mura Tsuruoka, Iruma-gun, Saitama Pref., Japan; longitude 139°30′ E; latitude 35°52′ N). The weathering test was carried out from Oct. 29, 1964, to Oct. 30, 1965. After the samples had been exposed, both the tensile and the swelling tests were performed again with the aged specimens.

Results and Discussion

Table I illustrates the changes in the tensile properties upon exposure. Obviously, the specimens containing no antioxidant deteriorated most. They were no longer the so-called "elastomeric material" after the exposure; they turned very brittle, and showed an extremely poor elongation. The elastomers with the antioxidant still retained the elongation values of 100—150% at the breaking point for the exposed specimens; they thus proved the capability of the antioxidant.

It is an interesting fact that the former faded from brown to light yellow and increased in transparency, while the latter did not, but became rather opaque and turned dark brown upon exposure.

After the specimens had been exposed for one year, their tensile moduli were increased remarkably. This seems undoutedly due to the cross-linking reaction caused by sunlight and air. It could not be a measure of the deterioration of the material, however, because almost all of the exposed specimens produced small cracks upon being stretched. These cracks should cause a local concentration of the stress and so induce failure.

From the results of the tensile tests, it may be concluded roughly that the effectiveness of these additives against aging are all nearly the same.

The swelling data are compiled in Table II.

The content of the sol in the elastomer, and the average molecular weight of the chain between cross-links, M_c, decreased after exposure, while the density of the polymer increased slightly. Indeed, some of the specimens were warped concave to the exposed surface in the course of the exposure.

These results show that the cross-linking reaction of the chains of the network structure, and that of the residual impregnated sol fraction, took place.

Assuming that the density of the elastomer is unity, and that $1/M_c$ equals the moles of the effective chain of the network per unit mass; then the change of $1/M_c$ caused by the exposure would be proportional to the number of sites where the cross-linking reaction has occurred.

Charlesby[2] defined the cross-linking density, q, as in Eq. 1:

$$q = k\,M_o/M_c \qquad (1)$$

where M_o is the molecular weight of the monomer unit.

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[2] A. Charlesby and S. H. Pinner, *Proc. Royal Soc.*, **A249**, 367 (1959).

TABLE I. CHANGES IN TENSILE PROPERTIES OF THE ELASTOMERS CAUSED BY THE EXPOSURE

No.	Composition*	Before or after exposure	Tensile strength kg./cm^2	Elongation at break point %	Stress at 100% elongation kg./cm^2	Stress at 300% elongation kg./cm^2	Hardness	Appearances after exposure
1	Nocrac DP 1.00	before	8.7	400	3.5	7.2	24.8	turned dark brown
		after	10.0	150	8.7	—	46.2	
2	Nocrac White 1.00	before	9.5	350	4.1	8.4	30.5	turned dark brown
		after	10.2	110	10.1	—	51.0	
3	Nocrac White 2.00	before	8.9	380	3.7	7.4	23.8	turned dark brown
		after	9.1	120	8.6	—	48.5	
4	Nocrac PA 2.00	before	11.1	500	3.8	7.3	26.0	turned dark brown
		after	8.9	220	6.5	—	41.8	
5	Nocrac D 1.00	before	11.9	450	4.3	8.5	29.9	turned dark brown
		after	8.2	150	7.4	—	44.3	
6	Nocrac HP 1.00	before	9.8	390	4.1	8.0	28.7	turned dark brown
		after	7.4	170	6.4	—	44.3	
7	Nocrac 500 1.00	before	11.5	320	5.6	11.1	35.5	turned dark brown
		after	10.6	150	8.8	—	50.4	
8	D.D.A. 2.00	before	9.2	420	3.8	7.4	29.1	turned dark brown
		after	8.1	120	7.8	—	47.9	
9	Ionol 2.00	before	11.2	370	4.8	9.5	31.0	turned dark brown
		after	8.6	100	8.5	—	50.8	
10	Antigene W 1.00	before	10.1	290	5.3	—	34.0	turned dark brown
		after	9.8	90	—	—	52.6	
11	Antigene WX 2.00	before	12.5	370	5.6	10.6	34.5	turned dark brown
		after	9.3	110	9.1	—	52.2	
12	Antigene WL 2.00	before	10.1	400	4.3	8.2	30.0	turned dark brown
		after	8.8	120	8.7	—	50.0	
13	Antigene S 2.00	before	8.7	330	4.1	8.1	29.1	turned dark brown
		after	8.6	90	—	—	50.8	
14	Nocrac C 2.00	before	10.7	480	4.0	7.6	29.2	turned dark brown
		after	7.7	120	7.5	—	44.9	
15	Nocrac AW 2.00	before	10.2	480	3.6	7.0	26.5	turned dark brown
		after	7.6	160	6.9	—	42.0	
16	Nocrac B 1.00	before	12.0	410	4.6	9.1	30.0	turned dark brown
		after	8.7	110	8.5	—	49.8	
17	Nocrac-White 1.00 Antigene MB 1.00	before	11.8	450	4.5	8.7	30.9	turned dark brown
		after	6.9	160	6.5	—	43.1	
18	Nocrac-White 1.00 Antigene MBZ 1.00	before	11.7	450	4.4	8.5	30.4	turned dark brown
		after	8.0	130	7.7	—	50.2	
19	Antigene TNP 2.00	before	11.4	420	4.5	8.7	30.6	turned dark brown
		after	7.7	120	7.5	—	46.5	
20	Antigene TPL 2.00	before	10.6	420	4.1	8.0	28.5	turned dark brown
		after	7.8	120	7.5	—	45.5	

Table I (Continued)

No.	Composition*	Before or after exposure	Tensile strength kg./cm²	Elongation at break point %	Stress at 100% elongation kg./cm²	Stress at 300% elongation kg./cm²	Hardness	Appearances after exposure
21	Antigene NBC	before	10.6	360	4.5	9.0	34.1	turned dark brown, bloomed remarkably
	2.00	after	9.5	110	9.4	—	53.3	
22	Polygard C	before	10.9	370	4.8	9.4	33.1	turned dark brown
	2.00	after	7.0	110	6.9	—	46.4	
23	Flexzone	before	9.6	500	3.5	6.5	25.8	turned dark brown
	2.00	after	7.8	150	7.1	—	46.7	
24	No Anti-	before	10.1	420	4.2	8.0	26.3	faded to light yellow, became brittle
	oxidant	after	5.8	8	—	—	55.9	
25	No Anti-	before	10.5	490	3.8	7.1	27.8	turned dark brown
	oxidant	after	7.5	110	7.3	—	47.7	
26	No Anti-	before	9.2	420	3.7	7.2	25.5	faded to light yellow, became brittle
	oxidant	after	6.5	14	—	—	53.3	
27	No Anti-	before	6.3	440	2.4	4.6	17.3	faded to light yellow, became brittle
	oxidant	after	6.2	25	—	—	52.3	

* No. 1—24: HC-434 100, MAPO 9.8, Accelerator 5 (parts)
No. 25 : Butarez CTL 100, MAPO 5.3, Accelerator 5
No. 26 : Butarez CTL 100, MAPO 7.9, Accelerator 5
No. 27 : Butarez CTL 100, MAPO 10.5, Accelerator 5

Table II. Changes in swelling data of the elastomers caused by the exposure

No.	ρ*	ρ'	S**	S'	M_c	M_c'	$(1/M_c'-1/M_c)$
1	0.947	0.954	11.14	4.70	10100	6390	0.5748×10^{-4}
2	0.947	0.954	—	—	—	—	—
3	0.975	0.953	—	—	—	—	—
4	0.946	0.956	19.96	6.56	17860	8060	0.6808
5	0.946	0.955	15.30	5.50	13580	7580	0.5829
6	0.943	0.954	11.85	5.99	12490	8040	0.4432
7	0.943	0.952	9.83	4.78	10640	6480	0.6034
8	0.947	0.957	9.36	4.84	10500	6230	0.6527
9	0.942	0.957	13.60	3.11	13680	5270	1.1665
10	0.944	0.956	12.05	2.27	13340	4560	1.4434
11	0.945	0.958	10.20	2.68	12550	4990	1.2072
12	0.943	0.955	8.49	2.71	9610	4870	1.0127
13	0.942	0.955	9.01	3.38	9805	4670	1.1214
14	0.939	0.960	14.15	4.83	14480	6440	0.8622
15	0.945	0.954	15.29	5.06	17720	7690	0.7361
16	0.945	0.958	12.59	3.57	14350	5580	1.0952
17	0.947	0.959	13.66	5.06	16690	7320	0.7669
18	0.946	0.959	14.81	3.96	18300	6470	1.0088
19	0.943	0.958	7.78	3.97	9560	5540	0.7595
20	0.940	0.959	16.34	3.49	18050	5710	1.1973
21	0.944	0.963	13.18	2.22	13720	5340	1.1438
22	0.945	0.959	8.13	5.19	9550	6320	0.5353
23	0.945	0.954	15.50	3.86	18590	6620	0.9727
24	0.942	0.968	7.21	—	9040	3650	1.6337
25	0.936	0.956	10.07	3.14	14540	6110	0.9489
26	0.939	0.966	—	—	—	—	—
27	0.940	0.970	14.67	4.03	14130	4600	1.4662

* Density of the polymer
** Solfraction of the polymer
(Dashed notation means the states of the postexposure)

k means the average number of cross-links per effective chain. When two functional carboxy-terminated polybutadienes are cured with a trifunctional compound, MAPO, in such a manner that no terminal sections result, the k-value should be 2/3, while in the case of conventionally-cured rubbers with sulfur or peroxides, that value should be 1.0. In this study, the degree of the cross-linking reaction during the exposure is defined as $(q'-q)$. (The dashed notation means the state of the post-exposure.)

Since the quantity of the cross-linked sol fraction caused by the exposure is relatively small, it might be assumed that k' is nearly equal to k. On this assumption, $(q'-q)$ is represented by Eq. 2:

$$(q' - q) = k M_o (1/M_c' - 1/M_c) \tag{2}$$

The values of $(1/M_c-1/M_c')$, tabulated in Table II, is proportional to the degree of the cross-linking reaction; the smaller the value, the lower the degree of cross-linking. This should be a semi-quantitative measure of the effectiveness of the antioxidants in preventing the cross-linking reaction.

Apparently, the amine-type antioxidants are the most effective. It should be noticed, however, that the capability of the antioxidants can not be evaluated only from the effect in preventing the cross-linking reaction.

Antigene NBC was not compatible in the precured medium, and it bloomed remarkably on the elastomer surface.

The relationship between the quantity of the sol fraction, S, and the cross-linking density, q, has been studied by Charlesby(2) and by Bristow(3,4). For the random cross-linking and the scission of a polymer having a random distribution of chain lengths, they deduced the following Eq. 3:

$$S + S^{1/2} = p/q + 1/q\overline{Y}_n \tag{3}$$

where p: the density of the main fracture of the chain.

$\overline{Y}_n$: the number average chain length of the polymer.

Assuming that the k-value in Eq. 1 is 2/3, the quantity of $(S+S^{1/2})$ is plotted versus $1/q$ in Fig. 1. A good linearity was observed for the exposed elastomers. The cross-linking and scission processes occurred at random in the system, so that the initial polymer should have a random distribution of chain lengths; this connection, however, is not very stringent, because the cross-linking reaction can occur optionally at any site of the network structure.

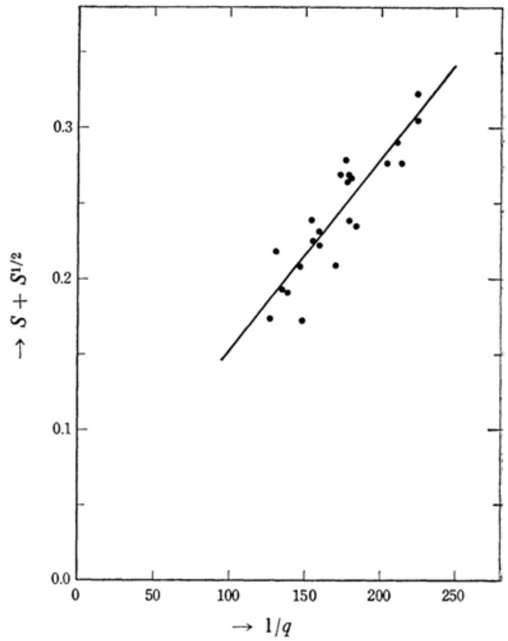

Fig. 1. Plot of $S+S^{1/2}$ versus $1/q$ for exposed elastomers.

The plot of $(S+S^{1/2})$ versus $1/q$ for the unexposed elastomer deviated from the line remarkably, since the cross-linking took place only at aboth ends of the prepolymer chain. From these facts, it may be assumed that the cross-linking reaction caused by the exposure was so effective that it randomized the relatively regular distribution of the initial cross-linking sites.

Conclusions

The elastomer derived from the carboxy-terminated polybutadiene prepolymer (cured with MAPO) showed a fatal deterioration tendency in the course of a one-year exposure test. Several sorts of antioxidants were tested; it was found that they were all effective as far as the experiments showed.

From the tensile data, it was roughly observed that all these antioxidants were almost equally effective; the swelling test, however, proved that the amine-type compounds were most effective among the antioxidants tested in preventing the cross-linking reaction caused by the exposure.

The plot of $(S+S^{1/2})$ versus $1/q$ for the exposed elastomers showed a good linearity, proving that the random crosslinking and scission of the polymer resulted from the exposure.

The authors offer their deep thanks to Mr. Toshimitsu Iwase for his assistance in the experiment.

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3) G. M. Bristow, *J. Appl. Pol. Sci.*, **7**, 1023 (1963).
4) G. M. Bristow, ibid., **8**, 1696 (1964).