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The Effects of Some Antioxidants on a Polyurethane Fuel Binder

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The antioxidation effect of *N, N'*-diphenyl-*p*-phenylene diamine and *N, N'*-di-(2-naphthyl)-*p*-phenylene diamine was studied with polyol-cured polyurethane containing an organo-ferric compound as a curing catalyst. These antioxidants, after weathering for one year, were found to be very effective. The same polymer without the antioxidants was degraded and flowed after only three weeks exposure (during the month of May). Although most of the inhibited polymers showed no depression in tensile properties after being exposed for one year, it was noted that the reddish transparent polymers turned dark brown and became opaque. Polyurethane is, in general, strong and resistant to weathering and aging. The degradation mentioned in this study, however, should be attributed to the degradative action of sunlight and the atmospheric conditions. The characteristics of the specimens for tensile strength and elongation at the breaking point have generally been improved without any remarkable change in the tensile modulus, the effect of the "after cure" should be taken into account in addition to the degradative action of sunlight and air.

It is well known that elastomeric polyurethanes are quite resistant to the degradative action of oxygen, ozone and ultraviolet light and more durable in the face of aging and weathering than natural or synthetic diene-type rubbers. Generally, the products catalyzed or cured by amine display excellent resistance. This may be attributed to the fact that polyurethanes have no double bonds in their molecular structure although they are apt to hydrolyse. There are some cases in which a retarder of hydrolysis plays an effective role as a stabilizer.

It has been frequently observed, however, that the polyurethanes produced from toluene diisocyanate, trimethylol propane and diols (such as polyoxybutylene-polyoxypropylene glycol or polyoxypropylene glycol) containing a ferric compound as a catalyst deteriorate and gradually flow from the edge of the surface when exposed to sunlight in a conventional atmosphere. This observation has been restricted only to the case of the polyurethane obtained by the catalytic action of the ferric compound. Direct exposure to sunlight seems to accelerate the deterioration process remarkably.

An amine-catalyzed polyurethane and those elastomers obtained from polyoxypropylene glycol, trimethylol propane and naphthylene diisocyanate using no catalyst are quite stable.

As the deterioration is due to the hydrolysis or to the depolymerization of urethane linkage, it should not be restricted to polymers produced by means of a ferric catalyst.

The following scheme is presumed for the deterioration of polymers¹⁾:

Activation

$$\mathrm{RH} + h\nu \text{ (or thermal energy)} \rightarrow \mathrm{R}\cdot + \mathrm{H}\cdot$$

$$\searrow \mathrm{RH}^* \xrightarrow{\mathrm{O_2}} \mathrm{R}\cdot + \mathrm{HOO}\cdot$$

where RH : polymer molecule

Propagation

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{ROO}\cdot$$

$$\mathrm{RH} + \mathrm{ROO}\cdot \rightarrow \mathrm{R}\cdot + \mathrm{ROOH}$$

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{HO}\cdot$$

$$2\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{ROO}\cdot + \mathrm{H_2O}$$

$$\mathrm{RH} + \mathrm{RO}\cdot \rightarrow \mathrm{R}\cdot + \mathrm{ROH}$$

$$\mathrm{RH} + \mathrm{ROO}\cdot \rightarrow \mathrm{R}\cdot + \mathrm{ROOH}$$

Termination

$$2\mathrm{R}\cdot \rightarrow \mathrm{R{-}R}$$

$$\mathrm{R}\cdot + \mathrm{RO}\cdot \rightarrow \mathrm{R{-}O{-}R}$$

$$2\mathrm{RO}\cdot \rightarrow \mathrm{R{-}O{-}O{-}R}$$

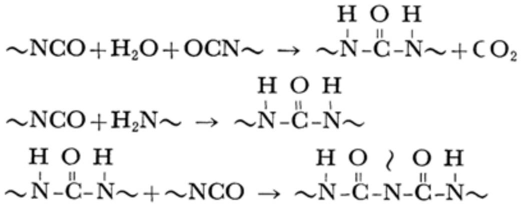
$$2\mathrm{ROO}\cdot \rightarrow \mathrm{R{-}O{-}O{-}R} + \mathrm{O_2}$$

Since ferric and ferrous ions would serve as catalysts to promote the decomposition reactions of the hydroperoxides, the weathering and aging of the polymer might then be accelerated:

$$\mathrm{Fe^{3+}} + \mathrm{ROOH} \rightarrow \mathrm{Fe^{2+}} + \mathrm{H^+} + \mathrm{ROO}\cdot$$

$$\mathrm{Fe^{2+}} + \mathrm{ROOH} \rightarrow \mathrm{Fe^{3+}} + \mathrm{OH^-} + \mathrm{RO}\cdot$$

Tobolsky and his co-workers²⁻⁴⁾ pointed out that the weak bonds in polyurethane elastomers are those of the biuret, disubstituted urea, and allophanate linkages. The urethane linkage is relatively strong, although weaker than that of the polyesters or polyethers which constitute the main chains of the elastomer. Biuret and disubstituted urea are formed by means of the following reactions:



$$\sim\mathrm{NCO} + \mathrm{H_2O} + \mathrm{OCN}\sim \rightarrow \sim\overset{\mathrm{H}}{\mathrm{N}}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\overset{\mathrm{H}}{\mathrm{N}}\sim + \mathrm{CO_2}$$

$$\sim\mathrm{NCO} + \mathrm{H_2N}\sim \rightarrow \sim\overset{\mathrm{H}}{\mathrm{N}}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\overset{\mathrm{H}}{\mathrm{N}}\sim$$

$$\sim\overset{\mathrm{H}}{\mathrm{N}}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\overset{\mathrm{H}}{\mathrm{N}}\sim + \sim\mathrm{NCO} \rightarrow \sim\overset{\mathrm{H}}{\mathrm{N}}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\overset{\wr}{\mathrm{N}}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\overset{\mathrm{H}}{\mathrm{N}}\sim$$

While aging, amine-catalyzed and cured polymers were quite stable. Deterioration, however, occurred with polyol-cured products. Accordingly, it may be reasonable to assume that the mechanism for aging (described above) in conjunction with the accelerating effect of ferric ions.

Schollenberger and his co-workers⁵⁾ studied the aging of the polyurethane, produced from the diphenylmethane diisocyanate and polyester derived from adipic acid and butanediol-1, 4. According to their theory, the incident radiant energy initiates free radical chains in the elastomer; the surface radicals in contact with air form hydroperoxides, which then decompose and produce an extensively cross-linked surface and cause hardened deterioration. This is in accordance with the mechanism mentioned above. Consequently, an ultraviolet light accepter and conventional antioxidants would be effective, since they improved the resistance against weathering of the polyurethane by the addition of carbon blacks, *N, N'*-diphenyl-*p*-phenylene diamine or *N, N'*-di-(2-naphthyl)-*p*-phenylene diamine.

The effect of the last two diamines as antioxidants was studied in order to improve the resistivity of the polyurethane against weathering or aging. In this work, however, the hardening as a result of cross-linking reaction did not occur, but the flowing due to the chain scission of the polymer was observed.

Polyoxybutylene-polyoxypropylene glycol was used as one of the starting materials for the polyurethane. Madorsky and Straus⁶⁾ reported, however, that introduction of oxygen in the skeleton of an aliphatic hydrocarbon lowered the stability of the chain, and that the C–C bond strength in the skeleton decreased with the substitution of alkyl groups for hydrogen atoms. Therefore, the polyurethanes employed in this work might be unstable against aging as compared with hydrocarbon polymers having C–C bond skeleton or polyethers containing no side alkyl groups (such as polyoxybutylene glycol or polyoxyethylene glycol).

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1) T. Matsuda et. al., "Degradation of High Molecular Materials (Kobunshi-Zairyo no Rekka)," Corona Pub., Tokyo (1958).

2) J. A. Offenbach and A. V. Tobolsky, *J. Colloid Sci.*, **11**, 39 (1956).

3) P. C. Colodny and A. V. Tobolsky, *J. Am. Chem. Soc.*, **79**, 4320 (1957).

4) A. V. Tobolsky, V. Johnson and W. J. MacKnight, *J. Phy. Chem.*, **69**, 476 (1965).

5) C. S. Schollenberger, H. Scott and G. R. Moore, *Rubber World*, **137**, 547 (1958).

6) S. L. Madorsky and S. Straus, *J. Polymer Sci.*, **36**, 183 (1959).

Raw Materials

Polyoxybutylene-polyoxypropylene Glycol (*Sanyo Chem. Co.*).—A random copolymer of oxybutylene and oxypropylene units containing 25 mol. % of the latter. The hydroxyl number was 58.7.

Toluene Diisocyanate (*Mitsui Chem. Co.*).—A 80/20 mixture of 2, 4- and 2, 6- isomers.

Antioxidants (*Ouchi Shinko Co.*).—*N, N'*-Diphenyl-*p*-phenylene diamine and *N, N'*-di(2-naphthyl)-*p*-phenylene diamine sold under the trade names Nocrac DP and Nocrac White respectively.

Commercial materials were used without any further treatment.

Curing Catalyst.—An organo-ferric compound was synthesized.

Experimental

Polyurethane was synthesized by means of the one-shot method. A round flask is equipped with a gas outlet and a mechanical stirrer. Polyether, trimethylol propane, the curing catalyst and the antioxidant were mixed together in the flask; the mixture was heated to 80°C in an oil bath for one hour under a vacuum of 3—4 mmHg. In the course of the heating, the catalyst and trimethylol propane were dissolved, and the impregnated water was removed. After the mixture had then been cooled to 20°C, toluene diisocyanate

TABLE I. CHANGES IN PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS ON WEATHERING

No.	Anti-oxidant added*	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
1	Nocrac DP 0.25	Before	11.9	1490	—	3.4	20.6	Turned dark brown, lozenge patterned crack
		After	22.3	1930	2.3	3.6	22.6	
2	Nocrac DP 0.50	Before	14.2	1710	—	3.6	20.2	Turned dark brown, no appreciable change
		After	17.4	1530	2.7	4.2	24.1	
3	Nocrac DP 0.75	Before	12.2	720	—	6.1	21.8	Turned dark brown
		After	14.5	810	3.6	6.2	28.8	
4	Nocrac DP 1.00	Before	14.8	1750	—	3.5	16.6	Turned dark brown
		After	18.5	1730	2.2	3.7	22.3	
5	Nocrac DP 1.50	Before	16.9	1630	—	3.6	20.0	Turned dark brown
		After	16.6	1500	2.3	3.8	22.6	
6	Nocrac DP 2.00	Before	17.5	2580	—	2.3	16.8	Turned dark brown
		After	—	>2000	1.9	2.7	15.7	
7	Nocrac DP 3.00	Before	—	>2500	—	—	11.2	Turned dark brown
		After	—	>2000	1.2	1.6	11.3	
8	NONE	Before	15.0	1390	3.0	5.1	24.4	Deteriorated, flown on exposure of only three weeks
		After	—	—	—	—	—	
9	Nocrac White 0.25	Before	19.4	1540	—	4.6	19.0	Turned dark brown, lozenge patterned crack
		After	22.9	1950	2.3	3.7	25.5	
10	Nocrac White 0.50	Before	13.6	980	3.1	5.1	18.1	Turned dark brown, lozenge patterned crack
		After	17.4	1230	2.9	5.0	26.6	
11	Nocrac White 0.75	Before	13.4	1220	2.6	4.3	20.0	Turned dark brown
		After	19.8	1610	2.8	4.6	24.8	
12	Nocrac White 1.00	Before	13.6	1080	—	4.9	23.2	Turned dark brown
		After	20.5	1500	3.2	5.1	26.2	
13	Nocrac White 1.50	Before	17.1	1340	—	4.5	25.2	Turned dark brown
		After	15.3	1370	2.8	4.5	24.8	
14	Nocrac White 2.00	Before	18.5	1570	—	4.3	19.0	Turned dark brown
		After	21.1	1810	2.8	4.3	25.0	
15	Nocrac White 3.00	Before	12.0	830	3.2	5.5	22.6	Turned dark brown
		After	15.8	1180	3.5	5.5	28.3	

* Parts per hundred parts of polyether.

was added, and stirred again for 15 min. While the stirring, the pressure in the flask was held in vacuum. The reaction mixture was then poured into a cavity (2—3 mm. thick) formed by two parallel surface-lubricated glass plates, and cured at 50°C in an electric oven for 48 hr.

The ratio of the equivalents of isocyanates to hydroxyl groups, $R=1.10$, and the fraction of -OH from triol, $\rho_t=0.25$ were set as the composition of the polyurethane.[7] While R and ρ_t were kept constant, the amount of the antioxidants added were varied from 0 to 3%.

The tensile properties of the elastomers were determined on the basis of the JIS-K-6301 (Physical Testing Methods for Vulcanized Rubber); No. 3 dumbbell-shaped specimens were used, and the strain rate was 500 mm./min. The hardness was measured using an Asker Durometer J.

The weathering process was carried out as follows: Dumbbell-shaped specimens were fixed on the plates of the polyethylene-lined plywood and exposed on the roof of the Central Research Laboratory of the Daicel Ltd. (171 Ohi-mura Tsuruoka, Iruma-gun, Saitama Pref., Japan; longitude 139°30′ E; latitude 35°53′ N). The plates stood at a 30° angle to the floor and faced south. The exposure test was carried out from May 4, 1964 to May 6, 1965.

Results and Discussion

The results of the weathering test are tabulated in Table I.

Figures 1 and 2 show the changes in the tensile properties with the amounts of the antioxidants before and after exposure.

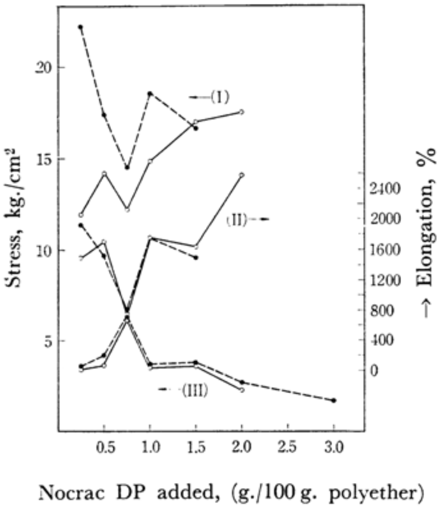

Fig. 1. Tensile properties of polyurethane containing Nocrac DP.
(I) Tensile strength
(II) Elongation at break point
(III) Stress at 300% elongation
—— before exposure ---- after exposure

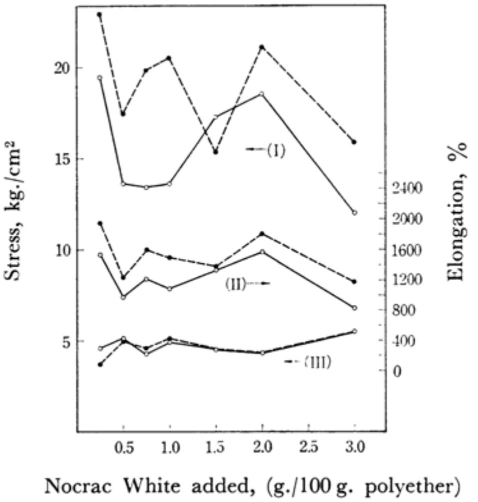

Fig. 2. Tensile properties of polyurethane containing Nocrac White.
(I) Tensile strength
(II) Elongation at break point
(III) Stress at 300% elongation
—— before exposure ---- after exposure

Since Nocrac DP was soluble to the reaction mixture, the produced elastomers were transparent, while Nocrac White was insoluble and the produced elastomers were less clear. After being exposed for one year, the reddish transparent elastomers turned dark brown and became opaque.

Die-cut specimens containing small amounts of the antioxidants (Nos. 1, 9 and 10) were attacked on exposure, and lozenge-patterned cracks developed on the surfaces from the edge. Figure 3 shows the appearance of the exposed surface of Specimen No. 9. (The back surface remained unchanged.)

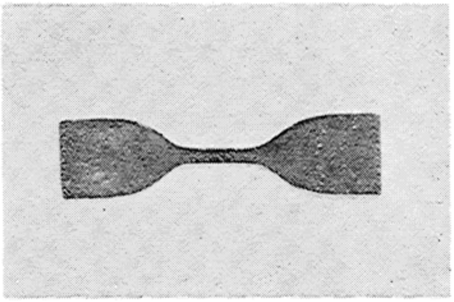

Fig. 3. View of the deteriorated surface of a specimen.
(No. 9, after exposure for one year)

Apparently, the tested antioxidants were very effective, for the uninhibited polymer deteriorated and showed a flow upon exposure for only three weeks in May. The quantities of the antioxidants, 0.5—1.0 parts per hundred parts of polyether, would be sufficient to inhibit the flow of the elastomer for at least one year.

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7) H. E. Marsh, Jr., *Ind. Eng. Chem.*, **52**, 768 (1960).

Since amino groups would react faster than hydroxyl groups do with isocyanate, the *R* values and the degree of cross-linking changed from the predetermined values; then the physical properties of the elastomers changed irregularly with the amounts of the antioxidants. For this reason, the lines in Figs. 1 and 2 have little meaning; they make it easy, however, to look over the figures.

After being exposed, the stress at 300% elongation was slightly increased; the tensile strength, however, was increased remarkably. In the case of the specimens containing Nocrac White, moreover, the values of elongation at the breaking point also increased. Some polybutadiene rubbers were tested similarly. In this case, the tensile modulus was increased, while the tensile strength and elongation at the breaking point decreased and became very brittle. Since the polyurethanes did not show any decrease in tensile properties, these changes may be attributed to be the effect of the "after cure." The change in physical properties would be partly due to the aging by the mechanism mentioned above, and the slight increase in stress at 300% elongation might be the result of the cross-linking reaction caused by sunlight and air. The degrees of augmentation in tensile strength and elongation, however, were too large to attribute to the action of sunlight and air alone. In addition, the exposed specimens did not become brittle.

An effort was made to explain the effect of the "after cure" of polyurethane in connection with the residual quantity of isocyanate groups in the elastomer.(8) In the case of polyurethane containing Nocrac DP, the degree of augmentation in tensile strength after exposure decreased as the quantity of the antioxidant increased. Since, in all cases, toluene diisocyanate was used in excess; the more the quantity of the antioxidant, the less the quantity of unreacted isocyanate, and then the possibility of the succeeding reaction would be decreased. Nocrac White was insoluble to the reaction mixture; therefore, the reaction rate of isocyanate with an amino group could not be so fast as to influence the degree of the "after cure". Therefore, the amount of augmentation in tensile strength was almost the same as far as the data in Fig. 2 was concerned.

All of the specimens except Nos. 1, 8, 9 and 10 showed no depression in physical properties or any remarkable change in their appearance.

There still remain problems to solve for practical processing; for example, the unaimed side reactions as well as the reduction of pot life as a result of the catalytic effect of the antioxidants should be controlled, since these compounds may serve as a kind of amino compounds. The polyurethane used in this study was developed as a fuel binder for composite propellants; since ammonium perchlorate is widely used as an oxidizer for solid fuel, however, it may liberate ammonia and react with isocyanate.(9)

$$RNH_2 + NH_4^+ \rightarrow RNH_3^+ + NH_3$$

Phenolic antioxidants seems to be preferable to use in solving the problems cited above; it has been shown, however, that the propellant grain containing such a compound as an antioxidant is generally inferior to amino derivatives against aging.(10)

The authors wish to express their thanks to Mr. Toshimitsu Iwase for his assistance for the experiment.

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8) Y. Komaki, K. Murai and Y. Fukuda, *Synthesized Resin (Gosei Jushi)*, **10**, 36 (1964).

9) B. Siegel and L. Schieler, "Energetics of Propellant Chemistry," Wiley, New York (1964).

10) K. Yamazaki and K. Kishi, unpublished.