

Study on Triazine Thiols. IV. Action of Triazine Thiols and Their Metal Salts to Peroxide

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Synopsis

Decomposition of *t*-butylhydroperoxide was retarded by triazine thiols and their zinc salts, but accelerated by the copper salts of triazine thiols as well as sulfur compounds such as dithiocarbamates and mercaptobenzothiazolates. Triazine thiols and their zinc salts are effective antioxidants for polyethylene crosslinked with peroxide and containing copper, and for protecting epichlorohydrin vulcanizates against attack by "sour" or hydroperoxide-containing gasoline.

INTRODUCTION

Sulfur compounds such as dithiocarbamates,¹ dithiophosphates,² mercaptobenzothiazolates,³ and mercaptobenzimidazolates⁴ have been used as an antioxidant in elastomers. These sulfur compounds have in common the ability to destroy hydroperoxides generated in elastomers.

On the other hand, when the hydroperoxides are stabilized to inhibit their decomposition, polymers may then exhibit a high fatigue resistance. However, little is known about sulfur compounds which retard the decomposition of peroxides. In this paper, the retarding action of triazine thiols and their zinc salts on the decomposition of *t*-butylhydroperoxide is reported. Moreover, the stabilization of polymers containing peroxides or copper, which catalyzes the generation of peroxides, by using triazine thiols and their zinc salts were investigated.

EXPERIMENTAL

Reagents

t-Butylhydroperoxide (70% in water) and isopropanol were commercial reagents of extra-pure grade of JIS standards.

Triazine thiols such as triazine trithiol (Zisnet F), 6-anilino-1,3,5-triazine-2,4-dithiol (Zisnet AF), and 6-dibutylamino-1,3,5-triazine-2,4-dithiol (Zisnet DB) were obtained from Sankyo kasei Co., Ltd (Dojima, Osaka, Japan). Their metal salts were prepared by a procedure described in our previous paper.⁵ Dibutylidithiocarbamates were used in commercial grade. Copper powder was used in reagent grade.

Decomposition of *t*-Butylhydroperoxide

A 100-mL, four-necked flask was equipped with a stirrer, air or nitrogen inlet tube, a thermometer, and a condenser. In the flask were placed isopropanol (50

mL) and stabilizers or accelerators (0.01–0.2 g). After the mixture was regulated at temperature of 80°C, the isopropanol solution (1 mL) of *t*-butylhydroperoxide (0.05 g) was added with a micropipette. The concentration of *t*-butylhydroperoxide was determined by an iodine method.⁶

Sample

Crosslinked polyethylene sheets were obtained as follows: polyethylene (Mitsubishi yuka Co., Ltd., LK-30) (100 g); dicumene peroxide (2 g); 4,4'-thio-bis(6-*t*-butyl-cresol) (0.5 g); and stabilizer (0.5 g) were blended at 170°C for 10 min, sheeted and crosslinked at 180°C for 45 min. These sheets contained a small amount of undecomposed peroxides.

Polyethylene sheets (0.5 mm) containing copper powder were prepared by blending for 10 min at 160°C a mixture of polyethylene (100 g), copper powder (1 g), and stabilizers (0.5 g). These sheets were compression molded for 10 min at 170°C with an uncured sheet of the above peroxide-containing blend.

Epichlorohydrin vulcanizates were prepared⁷ by curing for 30 min at 160°C in a compression mold a blend of epichlorohydrin rubber (Zeon 3100, 100 g), FEF black (40 g), Zisnet F (1 g), MgO (3 g), CaCO₃ (5 g), and stabilizers (1 g).

Aging Test

Samples of the polyethylene sheets were aged in a test tube at 180°C for various period of time and tested for tensile properties. The degree of aging was expressed by the retention of elongation at break. All samples had tensile strengths of 180–220 kgf/cm² and elongations of 350–450% at break. The measurement of oxygen uptake was carried out by the apparatus described in our previous paper.⁸

Sour Gasoline Aging Test

Sour gasoline aging test of epichlorohydrin vulcanizates is as follows. Samples (JIS C-type dumbbell, about 1 g) were immersed in 20 mL of model sour gasoline (toluene, 60 mL, isooctane, 40 mL, *t*-butylhydroperoxide, 0.5 g) at 30°C. To simulate the fuel injection recycle system, the tubes were emptied every 2 days and recharged with 20 mL of fresh model gasoline. Samples were removed after various periods of immersion and observed for crazing.

RESULTS AND DISCUSSION

Effect of Triazine Thiols and Their Metal Salts on the Decomposition of *t*-Butylhydroperoxide

A wide variety of sulfur compounds had in common the ability to destroy hydroperoxide through the formation of an acidic product in a radical generating reaction involving the hydroperoxides. They are used as antioxidants in rubbers. The similar antioxidant effect for triazine thiols and their metal salts was therefore expected to occur.

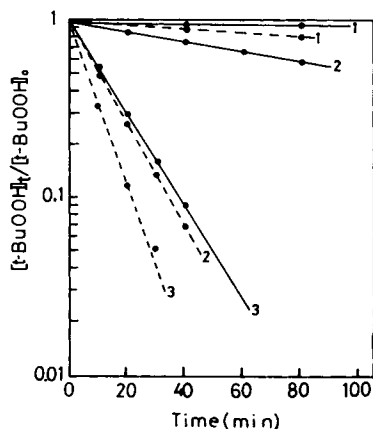


Fig. 1. Effect of stabilizers or accelerators on the decomposition of *t*-butylhydroperoxide (*t*-BuOOH) in isopropanol (50 mL) using air (---) and nitrogen (—) atmospheres at 80°C. Stabilizer or accelerator: (1) triazine trithiol, 0.1 g; (2) control; (3) copper salt of triazine trithiol, 0.1 g.

Decomposition of *t*-butylhydroperoxide in the presence of triazine thiols and their metal salts in isopropanol at 80°C was investigated. Figure 1 shows that the decomposition of *t*-butylhydroperoxide is of first order reaction in the presence and in the absence of triazine thiols and their metal salts. Triazine trithiol retarded the rate of decomposition of *t*-butylhydroperoxide both in air and nitrogen atmospheres. In this reaction system, the trithiol is only slightly soluble in isopropanol and is present mainly as a suspension. The rate constant of the decomposition was constant at the concentration over 0.04 g/dL (Fig. 2). A very small amount of triazine trithiol proved to retard the rate of the decomposition markedly. A variety of triazine thiols and their metal salts also retarded the decomposition of *t*-butylhydroperoxide as shown in Table I. In air atmosphere, triazine thiols had a higher retarding action for the decomposition of *t*-butylhydroperoxide than their zinc salts. However, in the decomposition in a nitrogen atmosphere, the zinc salts showed a higher retarding action than triazine thiols. The structure of 6-substituted-(*R*)-1,3,5-triazine-2,4-dithiol had a significant effect on the decomposition. The rate constant differed with *R* and decreased in the order; $-SR_1 > -NHR_1 > -NR_1R_2$, where R_1 and R_2 are H, alkyl,

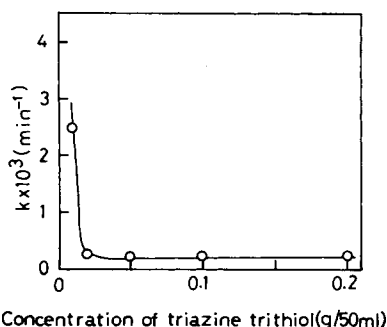


Fig. 2. Effect of triazine trithiol concentration on the decomposition of *t*-butylhydroperoxide in isopropanol (50 mL) using air atmosphere at 80°C.

TABLE I
Effect of Triazine Thiols and Their Metal Salts on the Rate (k) of Decomposition of *t*-Butylhydroperoxide at 80°C

Stabilizer or accelerator	$k \times 10^3$ (min ⁻¹)	
	Air	Nitrogen
Triazine trithiol	0.25	1.80
Zinc salt of triazine trithiol	0.81	0.29
6-Anilino-1,3,5-triazine-2,4-dithiol	1.36	5.60
Zinc salt of 6-anilino-1,3,5-triazine-2,4-dithiol	2.53	1.00
6-Dibutylamino-1,3,5-triazine-2,4-dithiol	4.50	13.2
Control	5.40	43.0
Copper salt of triazine trithiol	36.8	65.0
Copper salt of 6-anilino-1,3,5-triazine-2,4-dithiol	69.5	48.1
Copper salt of 6-dibutylamino-1,3,5-triazine-2,4-dithiol	78.2	143
Copper dibutylthiocarbamate	62.4	153

and aryl groups. This order agrees with that of increase of pK_{a1} for triazine thiols.⁹ The result suggests that triazine thiols with low reactive thiol groups for the reaction with peroxides retard the decomposition. A part of the thiol groups in the triazine thiols and in their zinc salts changed to disulfide groups after the decomposition. These results show that thiol groups in triazine thiols play an important role in inhibiting the induced decomposition of *t*-butylhydroperoxide by capturing radicals.

On the other hand, the copper salts of triazine thiols as well as many sulfur compounds^{1,4} had the ability to destroy *t*-butylhydroperoxide. These copper salts seem to act as catalytic peroxide decomposers.

Thermal Antioxidant and Copper Inhibition Effects on Polyethylene

It is known that polyethylene crosslinked by peroxides easily deteriorates at high temperature, to give low elongations. Triazine trithiol, 6-anilino-1,3,5-triazine-2,4-dithiol, and 6-dibutylamino-1,3,5-triazine-2,4-dithiol and their zinc salts were effective in preventing the oxidative deterioration of peroxide cured

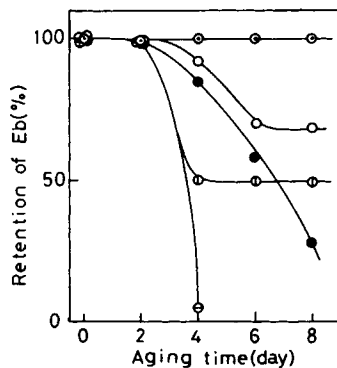


Fig. 3. Effect of stabilizers on the relation between the retention of elongation at break (Eb) and aging time at 160°C for polyethylene crosslinked with dicumylperoxide. Stabilizer: (⊙) Zinc salt of triazine trithiol; (O) triazine trithiol; (⊕) 6-anilino-1,3,5-triazine-2,4-dithiol; (⊖) 6-dibutylamino-1,3,5-triazine-2,4-dithiol; (●) control.

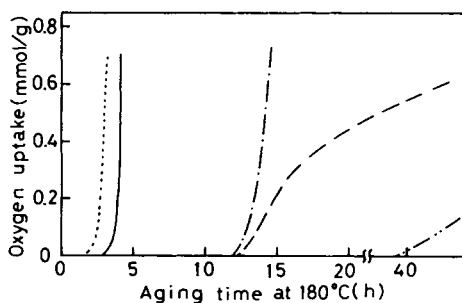


Fig. 4. Effect of stabilizers on the oxygen uptake at 180°C for polyethylene crosslinked with dicumylperoxide. Stabilizer: (---) triazine trithiol; (--) 6-anilino-1,3,5-triazine-2,4-dithiol; (-.-) zinc salt of triazine trithiol; (-.-.-) 6-dibutylamino-1,3,5-triazine-2,4-dithiol; (—) control.

polyethylene, as shown in Figures 3 and 4. In particular, the zinc salts showed higher stabilizing effects than triazine thiols. This effect is similar to the retardation of the decomposition of *t*-butylhydroperoxide in a nitrogen atmosphere. However, 6-dibutylamino-1,3,5-triazine-2,4-dithiol and the copper salts of triazine thiols hardly prevented the deterioration of polyethylene.

The very effective triazine trithiols and their zinc salt showed low oxygen uptake at 180°C. These results suggest that triazine thiols and their zinc salts retarded the decomposition of residual peroxides present in polyethylene sheets. This retardation inhibited oxygen uptake and prevented the deterioration (decrease of elongation) of the sheets.

On the other hand, polyethylene is known to deteriorate in the presence of copper or copper ion. Triazine thiols have been reported to react with copper or copper ion to give inactive copper salts.^{10,11} As shown in Figure 5, triazine thiols were effective in preventing the copper activated deterioration of polyethylene. Polyethylene involving 1 part of triazine trithiol showed very excellent thermal stability even in the presence of 5 parts of copper powder. Although the copper and zinc salts of triazine thiols had no high copper inhibition effect, they showed a little accelerating effect on the deterioration of polyethylene.

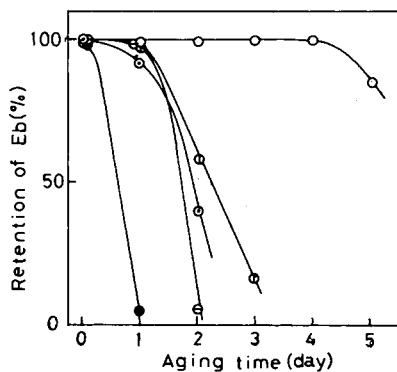


Fig. 5. Effect of stabilizers on the relation between the retention of elongation at break (Eb) and aging time at 180°C for polyethylene containing copper powder. Stabilizer: (O) triazine trithiol; (⊕) copper salt of triazine trithiol; (⊙) 6-anilino-1,3,5-triazine-2,4-dithiol; (⊖) CDA-1 (copper inhibitor, Mark CDA-1, Adeka Argus in Japan); (●) control.

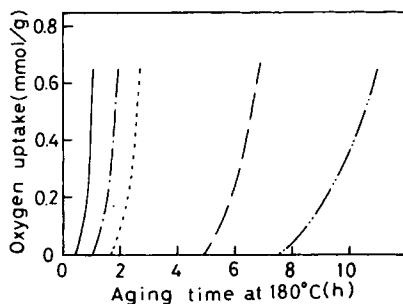


Fig. 6. Effect of stabilizers on the oxygen uptake of polyethylene containing copper powder. Stabilizer: (----) triazine trithiol; (---) 6-anilino-1,3,5-triazine-2,4-trithiol; (· · ·) copper salt of triazine trithiol; (- · -) CDA-1 (copper inhibitor, Mark CDA-1, Adeka Argus in Japan); (—) control.

Figure 6 shows that the copper inhibition effect of triazine thiols is due to the retarding action of oxygen uptake by them. Their results can be explained by the formation of a protective film of triazine thiols-copper salt which is formed by the reaction of copper surface with triazine thiols. Triazine trithiol seems to be effective as a stabilizer for polymers containing peroxide and containing catalyst (copper) which brings about the generation of peroxide.

Sour Gasoline Resistance of Epichlorohydrin Vulcanizates

The failure of rubber fuel hoses is well known to occur frequently in gasoline-containing hydroperoxides ("sour gasoline"), generated in cars equipped with electronic fuel injection systems.¹² Few effective stabilizers for sour gasoline have been reported.¹³ Table II shows sour gasoline resistance of epichlorohydrin vulcanizates. Because triazine thiols crosslink epichlorohydrin rubber, they did not exhibit high resistance to sour gasoline. The zinc salts of triazine thiols gave high sour gasoline resistance because they are ineffective crosslinkers and inhibit the decomposition of *t*-butylhydroperoxide. However, the copper salts were ineffective for sour gasoline resistance of the vulcanizates. Excellent sour gasoline resistance is exhibited by the inhibition effect for decomposition of *t*-butylhydroperoxide in the presence the zinc salts.

TABLE II
Sour Gasoline Resistance of CHC Vulcanizates Containing Triazine Thiol Stabilizers

Stabilizer	Aging time at 30°C. (days) ^a			
	2	4	6	8
Nickel dibutyl dithiocarbamate	NC	SNC	SC	BC
Copper dibutyl dithiocarbamate	SNC	SNC	SC	BC
Zinc salt of triazine trithiol	NC	NC	NC	NC
Nickel salt of triazine trithiol	NC	SNC	SC	BC
Copper salt of triazine trithiol	SNC	BC	B	
Zinc salt of 6-anilino-1,3,5-triazine-2,4-dithiol	NC	NC	SNC	SNC

^a NC: no crazing; SNC: soft no crazing; SC: soft, craze; BC: bad craze; B: break.

References

1. R. O. R. Ranaweera and G. Scott, *Eur. Polym. J.*, **12**, 825 (1976).
2. G. Scott, G. J. Pimblott, and J. E. Stuckey, *J. Appl. Polym. Sci.*, **19**, 865 (1975).
3. F. A. A. Ingham and G. Scott, *Eur. Polym. J.*, **11**, 783 (1975).
4. G. Scott, *Developments in Polymer Stabilization*, Applied Science Publishers, London, 1981, p. 15.
5. Y. Nakamura, K. Mori, K. Hasegawa, and T. Saito, *Nippon Gomu Kyokaishi*, **48**, 716 (1975).
6. N. D. Cheronis, *Functional Group Analysis*, Wiley, New York, 1964, p. 206.
7. Y. Nakamura, K. Mori, and S. Oka, *Nippon Gomu Kyokaishi*, **46**, 514 (1973).
8. Y. Nakamura, K. Mori, *Nippon Gomu Kyokaishi*, **47**, 48 (1974).
9. K. Mori and Y. Nakamura, *J. Appl. Polym. Sci.*, **16**, 1981 (1978).
10. K. Mori and Y. Nakamura, *Nippon Kagakukaishi*, 780 (1977).
11. K. Mori and Y. Nakamura, *KagakuKojo*, **19**, 81 (1975).
12. A. Nersasian, SAE Paper 790659, 1979.
13. M. L. Zwickert, SAE Paper 790660, 1979.

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