

Studies of Tetrazoles as Rubber Chemicals. II.

Reactivities and Antioxidation Activities of Reactive Antioxidants Based on Tetrazoles

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Synopsis

The chemical reactivities of novel reactive antioxidants based on tetrazoles for carbon-carbon double bonds of liquid polybutadiene and their antioxidation activities toward isoprene rubber were evaluated. These antioxidants, i.e., 2-substituted phenyl-5-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)tetrazoles (PHPT), were pyrolyzed in liquid polybutadiene at 160–170°C for 30 min to attach to rubber in extents of 61–85% of the nitrileimines formed from PHPT by 1,3-dipolar addition reaction. The reactivities of PHPT followed the order $p\text{-Cl} > m\text{-Cl} > \text{H} > p\text{-CH}_3 > m\text{-CH}_3, p\text{-OC}_2\text{H}_5$, suggesting that PHPT reacts with diene rubber in electrophilic reaction and *p*-derivatives exhibit higher contents of binding than *m*-derivatives due to steric hindrance. From oxygen absorption data, the antioxidation activities of PHPT for isoprene rubber vulcanizates followed the order $m\text{-Cl}, m\text{-CH}_3 > \text{H}, p\text{-Cl}, p\text{-CH}_3 > p\text{-OC}_2\text{H}_5$. Isoprene rubber vulcanizates, obtained after pretreatment with PHPT by heating, were extracted with acetone, followed by aging to show that there was good retention and appreciable antioxidation activities of PHPT, especially, *p*-CH₃ and *p*-Cl substituted PHPT.

INTRODUCTION

Conventional antioxidants compounded in polymers are extracted by solvents and evaporated by heating since they are mixed physically with the polymers.¹ To prevent this phenomenon, antioxidants containing polymerizable or reactive groups have been developed.² Especially, the latter are favorable for handling. Thus, the antioxidants with such reactive groups as mercaptan,³ nitrene,⁴ nitroso group,⁵ carbene,⁶ etc., were reported to show antioxidation activities after solvent extraction.

Huisgen et al. reported that thermolysis of 2,5-diphenyl tetrazole in dicyclopentadiene afforded 1,3-dipolar addition product with dicyclopentadiene.⁷ Similarly, it was expected that tetrazoles react with diene rubbers by 1,3-dipolar addition mechanism. We have reported the preparation of the reactive antioxidants based on tetrazoles, i.e., 2-substituted phenyl-5-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)tetrazoles (PHPT) and the reaction of *m*-chloro derivative of PHPT towards styrene.²

In this paper, we report the reaction of PHPT with liquid polybutadiene as a model experiment and the evaluation of the antioxidation activities of PHPT for isoprene rubber vulcanizates before and after Soxhlet extraction by acetone.

EXPERIMENTAL

Reagents. The preparation of PHPT was reported in the preceding paper.² Isoprene rubber (Cariflex IR-307, Shell Nederland Chemie, New York) with a *cis* content of 92% was used without further purification. The liquid polybutadiene (LPBd), used without further purification, was Poly bd R-45HT supplied by the ARCO Chemical Co., Ltd., (hydroxy equivalent, 8.3×10^{-4} mol/g; molecular weight, about 2700; iodine value, 398; microstructure: *trans*-1,4-, 60 mol %, *cis*-1,4-, 20 mol %, 1,2-addition, 20 mol %). 3,5-Di-*tert*-butyl-4-hydroxytoluene (BHT; Nocrac 200, Ouchi Shinko, Ltd.), tetramethylthiuramdisulfide (TMTD; Nocceler TT, Ouchi Shinko, Ltd.), and zinc oxide (Mitsui Metal Mining Co.) were used without further purification as well as other chemicals obtained from Tokyo Kasei Kogyo Co., Ltd.

Measurements. Infrared spectra (IR) were recorded with a Hitachi EPI-G₃ type on a nujol mull in a rock salt plate cell. ¹H-NMR spectra were recorded with a Hitachi Perkin-Elmer R-24B type using tetramethylsilane as the internal standard. Thin-layer chromatographies (TLC) were measured using a silica gel as the absorbent, a mixed solvent of benzene and ethyl acetate (4:1 by volume) as the developer, and 2,6-dichloroquinone-4-chloroimide (CQCI) as the color former.

Compounding, Curing, and Oxidation. The base formulation (wt pts) of rubber compounds used was: Isoprene rubber 100, TMTD 4, ZnO 5, antioxidant 0.01 mol. The optimum curing times for all compounds were measured with a JSR type curelometer NoII. The vulcanizates with 0.057–0.073 cm in thickness were oxidized before and after Soxhlet extraction by acetone for 22 h and their oxygen absorption curves were recorded with a Polymer Degradation Measurement Apparatus made by Shibayama Scientific Instrument Factory.

Model Reaction of PHPT with LPBd. A mixture of LPBd 10.8 g (0.2 mol), xylene 3 mL, and antioxidant 0.05 mol was stirred at 160–170°C for 30 min. After dilution with xylene 30 mL, the reaction mixture was poured into 500 mL of methanol with vigorous stirring to separate the rubber. The reprecipitation was repeated more than two times using benzene and methanol, followed by condensation at 100–110°C under reduced pressure up to 5 mm Hg to yield the viscous liquid. Qualitative and quantitative analyses of the products were carried out by TLC, IR, and ¹H-NMR.

RESULTS AND DISCUSSION

Model Reaction of PHPT with LPBd

Evolution of nitrogen, from a mixture of PHPT and LPBd heated with stirring, demonstrated the formation of the nitrileimine in the thermal breakdown of PHPT. The reaction products were identified by TLC, IR, and ¹H-NMR spectra. TLC of the reaction product of unsubstituted PHPT with LPBd is shown in Figure 1. Although LPBd was not colored by CQCI, the reaction product of PHPT with LPBd produced a tailing colored spot, indicating the 1,3-dipolar addition reaction of the nitrileimine formed from PHPT for LPBd. Moreover, both spots of unreacted PHPT and other byproducts were not ob-

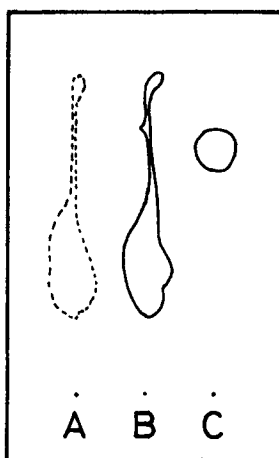


Fig. 1. TLC of the reaction product of unsubstituted PHPT with LPBd: (A) LPBd; (B) reaction product; (C) unsubstituted PHPT.

served in the reaction product. Hence, IR and $^1\text{H-NMR}$ spectra indicate the absorptions of the chemical reaction product of PHPT with LPBd alone. IR spectrum of the reaction product is shown in Figure 2. Besides the absorptions at 3400 and 1645 cm^{-1} assigned to the alcoholic—OH group and vinyl group of the LPBd, respectively, two absorptions were observed at 3630 and 1600 cm^{-1} in the range of $1600\text{--}4000\text{ cm}^{-1}$ assigned to the hindered phenolic—OH group and to the $>\text{C}=\text{N}$ — group, respectively. $^1\text{H-NMR}$ spectrum of the reaction product is shown in Figure 3. Besides the absorptions at 2.04 , 5.03 , and 5.37 ppm assigned to protons of the saturated methylene and methine groups, those of vinyl methylene groups and those of vinyl methine groups in the LPBd, respectively, three absorptions were observed at 1.48 ppm as a singlet, at $6.60\text{--}7.75\text{ ppm}$ as a broad band, and at 2.30 ppm as a small broad band overlapping at the base of the absorption at 2.04 ppm . The absorptions at 1.48 ppm , 6.60 ppm , and 2.30 ppm can be assigned to the protons of the *tert*-butyl group, to those of the aryl group, and to those of the methylene and methine groups of the 2-pyridazoline ring, respectively. The intensity ratio of the $^1\text{H-NMR}$ absorption at 1.48 ppm

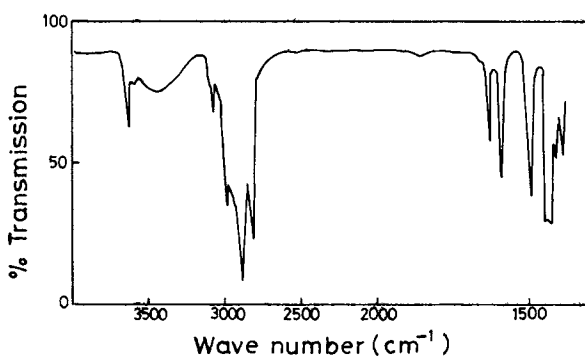


Fig. 2. IR spectrum of the reaction product of unsubstituted PHPT with LPBd.

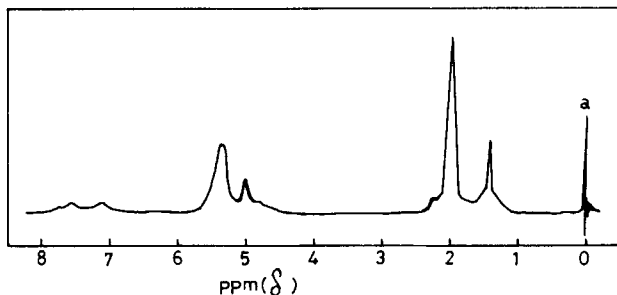
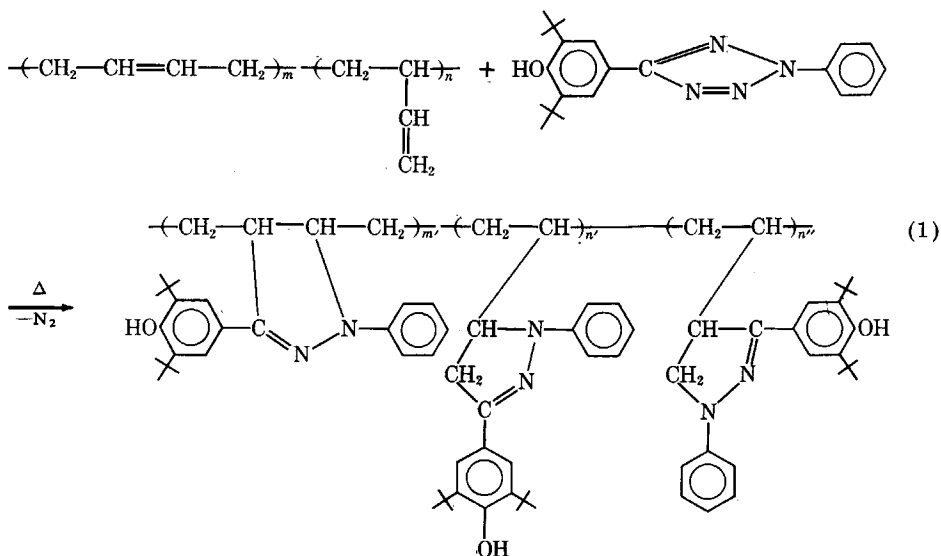


Fig. 3. $^1\text{H-NMR}$ spectrum of the reaction product of unsubstituted PHPT with LPBd: (a) $\text{Si}(\text{CH}_3)_4$.

to that at 6.60–7.75 ppm was 18:7.09, to agree very closely with the calculated ratio 18:7.00 of the nitrileimine from unsubstituted PHPT. These results and the formation of 2-pyridazoline derivatives from tetrazoles with dicyclopentadiene⁷ or styrene² lead to the conclusion that the product has the following structure:

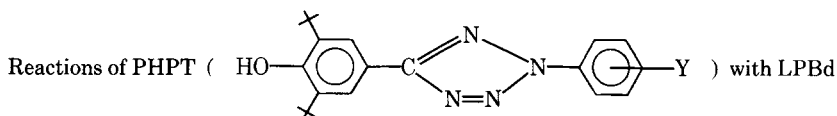


Results of other derivatives of PHPT are shown in Table I.

Assuming that the nitrileimines formed from PHPT add to either 1,2-structure or 1,4-structure equally, the contents (y) of PHPT attached to rubber were determined by measurement of the intensity ratio (A) of the $^1\text{H-NMR}$ absorption at 6.60–7.75 ppm (protons of aryl group) to the sum of that at 2.04 ppm (protons of the saturated methylene and methine groups in the LPBd) and that at 2.30 ppm (protons of 2-pyridazoline ring). The intensity ratio (A) described above is represented in

$$\begin{aligned}
 A = a/b &= 0.05 \times B \times y / (3.8 + 0.05 \times y \times 0.2 \times 3 + 0.05 \times y \times 0.8 \times 2) \\
 &= 5 \times B \times y / (380 + 11y) \quad (2)
 \end{aligned}$$

TABLE I



Tetrazole —Y	Content of binding (%)	IR(Nujol mull) ^a (cm ⁻¹)			¹ H-NMR in CDCl ₃ ^{a,b} (ppm)		
—H	74.3	1500	1600	3630	1.48	2.30	6.60–7.75
(<i>p</i>)—CH ₃	70.0	1520	1620	3640	1.49	2.26	2.38 6.65–7.70
(<i>p</i>)—OC ₂ H ₅	61.3	1520	1620	3640	1.26	1.47	2.37 4.06 6.50–7.74
(<i>p</i>)—Cl	85.2	1505	1600	3635	1.48	2.41	6.70–7.72
(<i>m</i>)—CH ₃	61.6	1495	1605	3630	1.49	2.30	2.45 6.67–7.71
(<i>m</i>)—Cl	78.3	1490	1595	3625	1.48	2.50	6.51–7.72

^a A few absorptions of IR and ¹H-NMR spectra at 1645 and 3400 cm⁻¹ and 2.04, 5.03, 5.37 ppm assigned to that of LPBd, respectively, are not designated.

^b All absorptions were observed as broad bands, except for the absorption of the protons of the *tert*-butyl groups which appeared as a singlet.

Equation (2) can be converted into

$$y = 380A/(5B - 11A) \quad (3)$$

where *a* and *b* indicate the intensity of ¹H-NMR absorption at 6.60–7.75 ppm and the sum of the intensities at 2.04 and 2.30 ppm, respectively. *B* is 7 for unsubstituted PHPT or 6 for others. The contents of PHPT attached to rubber are calculated, therefore, from the observed values of *A*. The results are shown in Table I.

Figure 4 indicates a linear relationship between the Hammett σ values and the contents of PHPT attached to rubber (Table I). These results demonstrate that the 1,3-dipolar addition reaction of nitrileimines toward LPBd is an electrophilic reaction. Furthermore, Figure 4 shows that *m*-CH₃ or *m*-Cl derivatives exhibit lower contents of PHPT attached to rubber than the *p*-derivatives due to steric hindrance.

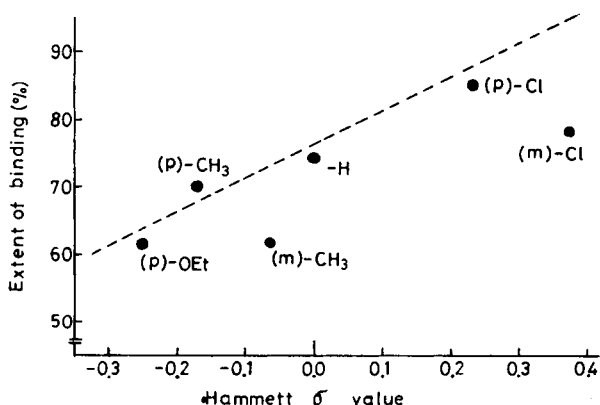


Fig. 4. Effects of substituents of PHPT on reactivity for LPBd.

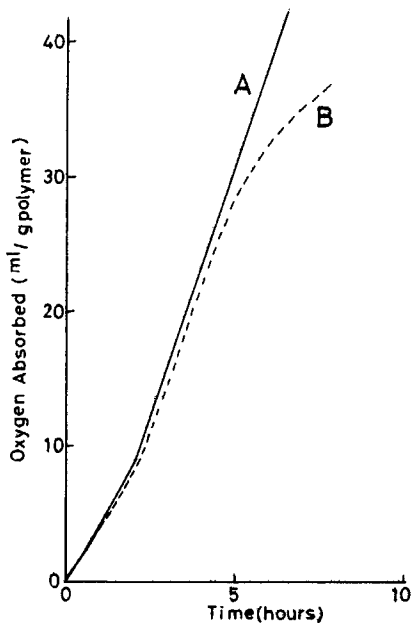


Fig. 5. Oxygen absorption curves at 110°C of extracted isoprene rubber vulcanizates cured at 120°C for 1 hour: (A) control (no antioxidant); (B) isoprene rubber vulcanizate compounded with unsubstituted PHPT.

Antioxidation Activities of PHPT

Antioxidation activities of PHPT for TMTD sulfurless isoprene rubber vulcanizates were evaluated by oxygen absorption data.

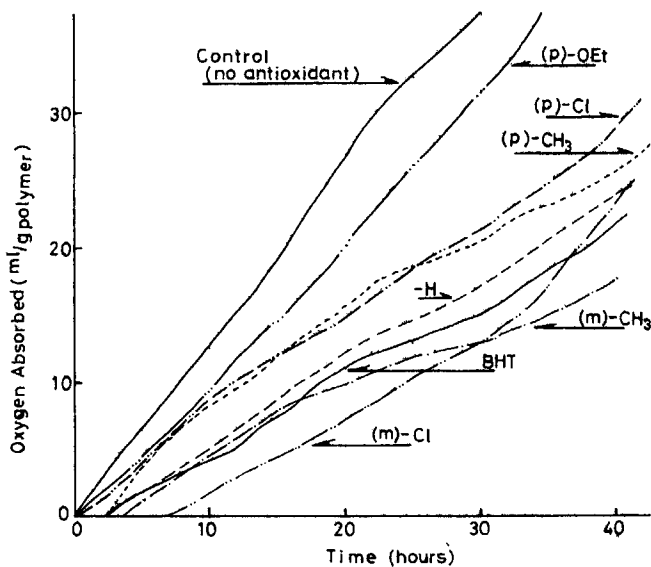


Fig. 6. Effects of PHPT on the oxidation at 120°C of unextracted and unpretreated isoprene rubber vulcanizates.

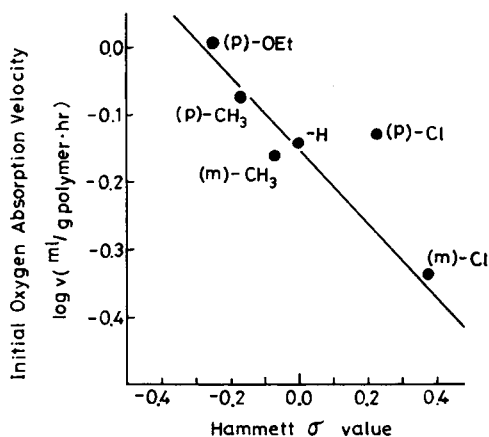


Fig. 7. Relation between the Hammett σ values of substituents of PHPT and the initial oxygen absorption rate on the oxidation at 120°C of unextracted and unpretreated isoprene rubber vulcanizates.

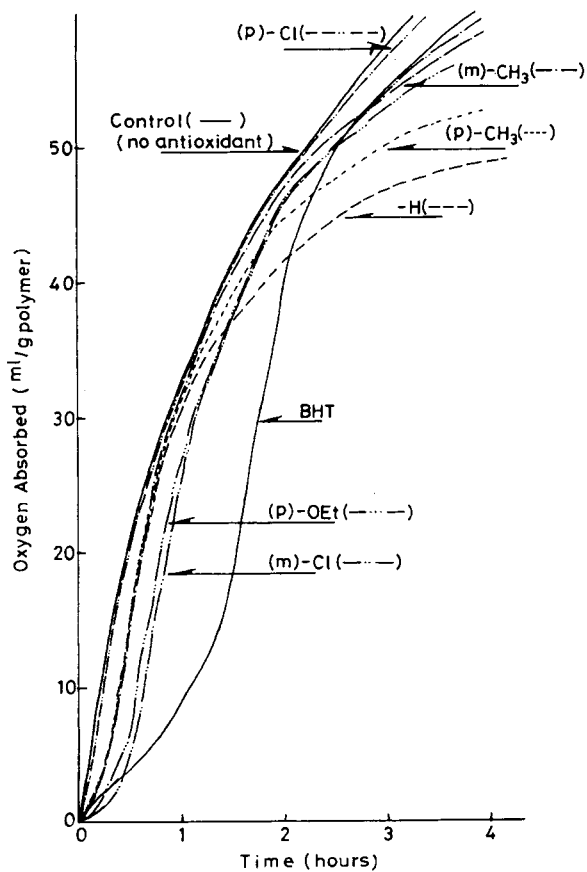


Fig. 8. Effects of PHPT on the oxidation at 120°C of extracted and unpretreated isoprene rubber vulcanizates.

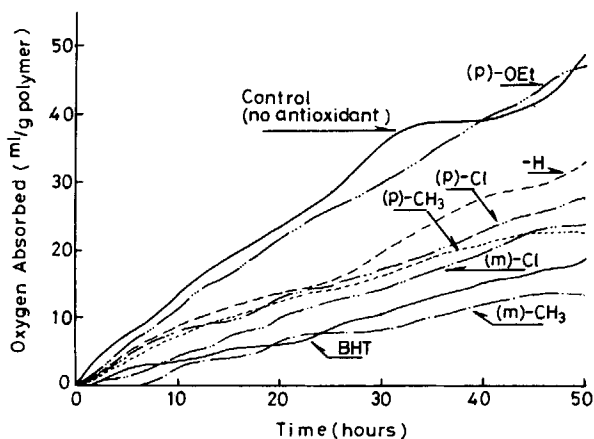


Fig. 9. Effects of PHPT on the oxidation at 110°C of unextracted and preheated isoprene rubber vulcanizates.

Determination of Extraction Condition. To evaluate the antioxidation activities of PHPT attached to rubber, isoprene rubber vulcanizates were oxidized after Soxhlet extraction by acetone for 22 h. The isoprene rubber vulcanizate compounded with unsubstituted PHPT as antioxidant and cured at 120°C for 1 h was oxidized after Soxhlet extraction. Thermogravimetric analysis showed that unsubstituted PHPT didn't pyrolyze at 120°C.² The result is shown in Figure 5. The isoprene rubber vulcanizate compounded with unsubstituted PHPT exhibited the oxygen absorption curve similar to the vulcanizate without antioxidant, indicating that the antioxidant not attached to rubber was extracted under the condition described above.

Oxidation of Isoprene Rubber Vulcanizates. Isoprene rubber vulcanizates cured at 170°C for 20 min were oxidized at 120°C before Soxhlet extraction. Figure 6 shows the oxygen absorption curves, indicating that the antioxidation activities of PHPT follow the order $m\text{-Cl} > m\text{-CH}_3 > \text{H} > p\text{-CH}_3, p\text{-Cl} > p\text{-OC}_2\text{H}_5$. Figure 7 shows the correlation between the initial oxygen absorption

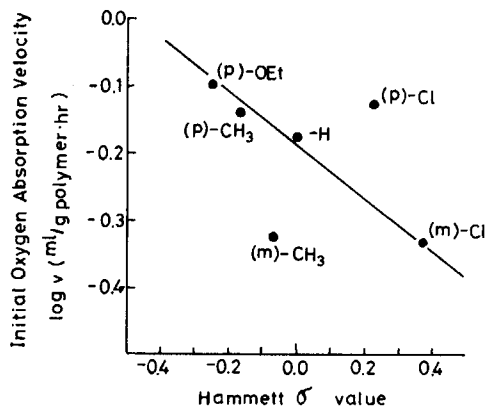


Fig. 10. Relation between the Hammett σ values of substituents of PHPT and the initial oxygen absorption rate on the oxidation at 110°C of unextracted and preheated isoprene rubber vulcanizates.

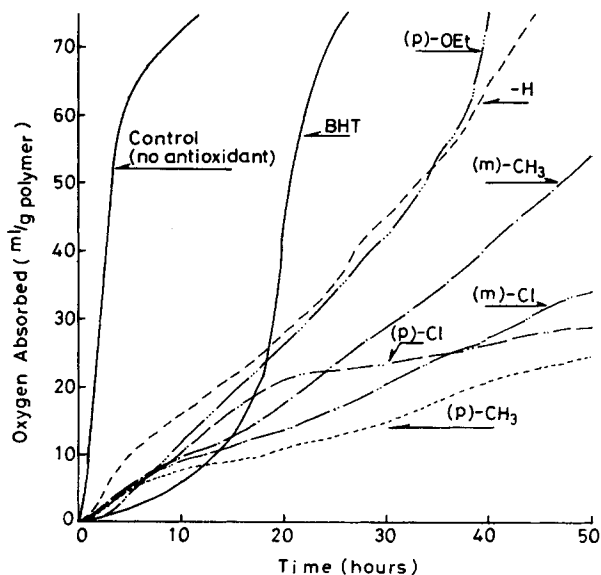


Fig. 11. Effects of PHPT on the oxidation at 110°C of extracted and preheated isoprene rubber vulcanizates.

rate and the Hammett σ values of substituents, indicating that antioxidation activities increased linearly with increasing Hammett σ values of substituents. The electron density of the nitrogen at the 2-position appeared to be an important factor. Especially, *m*-Cl and *m*-CH₃ derivatives of PHPT exhibited antioxidation activities superior to BHT.

Figure 8 shows oxygen absorption curves of isoprene rubber vulcanizates after Soxhlet extraction. Retention of antioxidation activity was negligible in the case of PHPT since PHPT scarcely formed nitrileimine during the thermal breakdown due to suppression of nitrogen evolution by the closed system of press cure. Small retention of the antioxidation activity observed in BHBT is derived from the chemical reaction with rubber on heating in the presence of free radical.⁴

Chemical Attachment of PHPT to Rubber by Pretreatment with Heating. In order to attach PHPT to rubber via the formation of nitrileimines in the thermal decomposition of PHPT, isoprene rubbers compounded with PHPT alone by milling were preheated in a mold at 170°C for 20 min under a pressure of 25 kg/cm², followed by degassing several times during the pretreatment. Both isoprene rubber and isoprene rubber compounded with BHBT were similarly preheated for comparison. Figure 9 shows the oxygen absorption curves for isoprene rubber vulcanizates cured at 170°C for 6 min after preheating as described above, indicating that the antioxidation activities of PHPT follow the order *m*-CH₃ > *p*-CH₃, *p*-Cl, *m*-Cl > H > *p*-OC₂H₅. Figure 10 shows the relationship between the initial oxygen absorption rate and the Hammett σ values⁸ of substituents, indicating that the correlation was complicated more or less without preheating, and *m*-CH₃, *p*-CH₃, and *m*-Cl derivatives of PHPT exhibited the equivalent antioxidation activities compared to BHT.

The isoprene rubber vulcanizates obtained after preheating were oxidized after Soxhlet extraction. The results are shown in Figure 11. Isoprene rubber vul-

canizates compounded with or without BHT exhibited steep oxygen absorption curves. Isoprene rubber vulcanizates compounded with PHPT, especially *p*-CH₃ and *p*-Cl derivatives, exhibited oxygen absorption curves resembling those before Soxhlet extraction, indicating that there was appreciable retention of antioxidant activities after Soxhlet extraction. These results agreed with those of model reaction of PHPT with LPBd and demonstrate that PHPT attached effectively to rubber by 1,3-dipolar addition reaction via nitrileimines.

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