

Commercial Antioxidants as Photostabilizers for Butadiene Rubber

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Synopsis

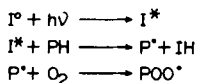
In this work we have studied the stabilizing effect of several commercially available antioxidants on the free-radical photooxidation of butadiene rubber. Two kinds of stabilizers were investigated; hindered phenols: 2,4-di-*t*-butyl-*p*-hydroxytoluene, octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate and 2,4-bis(octylthio)-6-(4-hydroxy-3,5-di-*t*-butylanilino)-1,3,5-triazine; and amine stabilizers: *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine and *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine. Their stabilizing effect is mostly produced by scavenging the peroxy radicals formed during the initial steps of the photodegradation process. We also tested tri(nonylphenyl)phosphite associated with the phenoltriazine stabilizer. Of the additives studied in this work, octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate was the most effective photostabilizer for butadiene rubber.

INTRODUCTION

Although an enormous amount of research has been dedicated to the photodegradation and photostabilization of unsaturated elastomers, many unsolved problems still persist.¹⁻³ Much research effort still remains to be done in order to obtain a polybutadiene-containing rubber which could be classified as a "light-stable rubber". For many applications, the introduction of carbon black as a filler prevents photodegradation. However, black-free rubbers are also widely used, making stabilizers necessary. Also, the severe environmental conditions of a tropical country make stabilization agents even more necessary. In view of this, we carried out a study comparing the photostabilizing activity of several nonstaining commercially available stabilizers. In this paper we concentrated in this study on using the butadiene rubber (BR) produced by Coperbo.

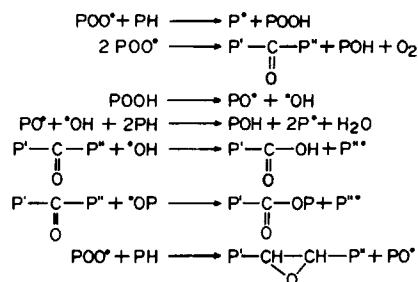
It has been demonstrated that singlet oxygen is susceptible to react with BR.^{4,5} Nevertheless, it has been recently shown that this reaction is not responsible for the environmental degradation of this polymer.⁶ More recently,⁷ in a detailed study of the photodegradation of BR, it was shown that the initial step in the photooxidation is the formation of alkyl radicals:

INITIATION

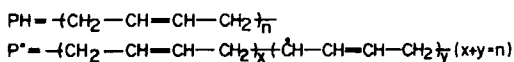
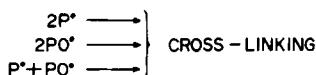


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PROPAGATION



TERMINATION



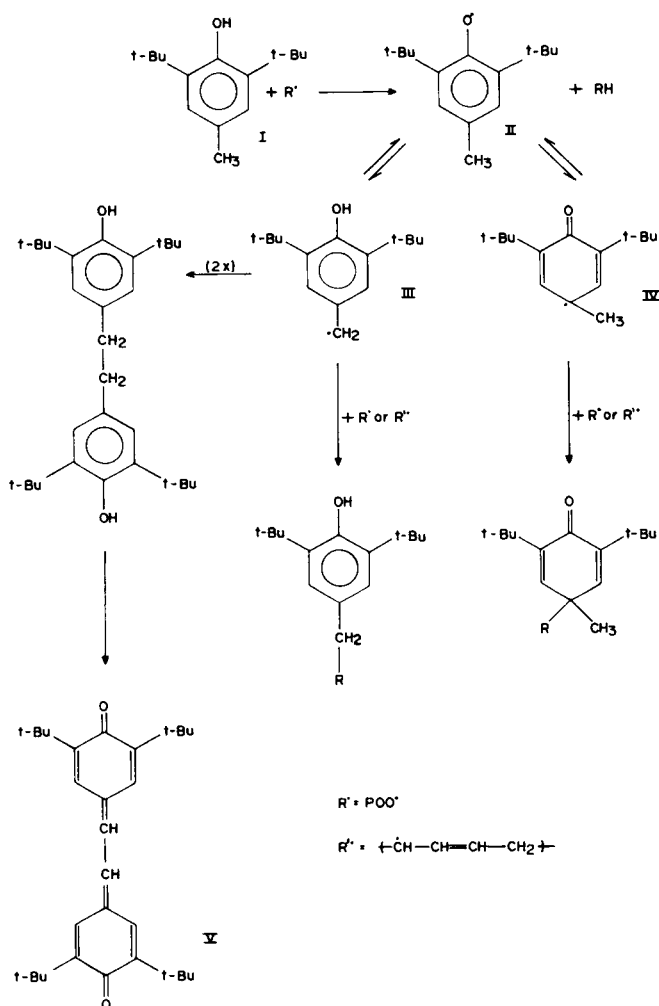
Scheme 1

Depending on the light intensity, these radicals produce crosslinks or react with oxygen, forming peroxy radicals, with the consequent formation of hydroperoxides. These decompose photochemically producing alcohols, ketones, esters, and carboxylic acids. Peroxy radicals may also form epoxides.

There are several possibilities for photostabilizing polymers.⁸ The most obvious one is the introduction of an ultraviolet filter in the polymer, in order to preclude the physical process of light absorption. With the exception of triazoles and 2-hydroxybenzophenones, most of the colorless compounds with high extinction coefficients in the 300–400 nm range are photoactive. In addition, efficient excited state quenchers normally also suffer undesirable side reactions which sensitize the degradation of the polymer. It is thus preferable to use a stabilizer that will act on the initial chemical products of the oxidation, as, for example, a free-radical scavenger. In this case, peroxy radical scavengers used as heat stabilizers will also increase the lifetime of a polymer subjected to ultraviolet (UV) irradiation. In fact, the problem is more complex and a decision can be made only after testing the performance of each additive.

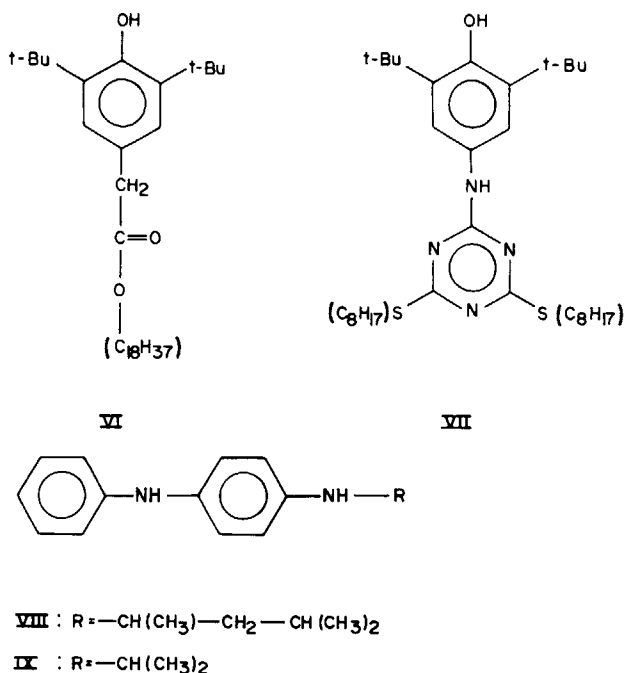
Hindered phenol antioxidants, such as 2,4-di-*t*-butyl-*p*-hydroxytoluene (I), have been studied by several authors. Its reactions are shown in Scheme 2.⁹⁻¹¹

Polymeric peroxy radicals easily abstract the hydroxylic proton of the phenol, forming a phenoxy radical (II) and polymeric hydroperoxides. By tautomerism this radical may form a benzyl (III)⁹ or a *p*-cyclohexadienonyl radical (IV).¹⁰ Depending on the diffusability and on the concentration of the additive in the polymer, the benzyl radical can dimerize and further oxidize, forming a stilbenoquinone (V). A second possibility is a radical-radical interaction of a benzyl radical with a polymeric methylenic radical. In this case, it is assumed that a polymer-bound antioxidant is more efficient as a heat stabilizer than a free antioxidant.¹¹ Radical IV may also react with other radicals with similar results.¹⁰ The inclusion of a long chain



Scheme 2

substituent in the *para* position of the phenolic additive reduces by steric hindrance the possibility of dimerization. This effect, associated with reduced loss by volatilization caused by lower mobility in the polymer matrix, may increase the efficiency of the additive. This could be the case with octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate (VI). In this case the same kind of oxidation products as with BHT are formed.¹² Also, other groups in the *para* position may improve the performance of the additive by stabilizing the intermediate compound formed during the oxidation reaction, as with 2,4-bis(*n*-octylthio)-6-(4-hydroxy-3,5-di-*t*-butylanilino)-1,3,5-triazine (VII). In this case the thiosubstituted triazine group also acts as a UV-light absorber. It has been reported that *N*-alkyl-*N*-phenyl-*p*-phenylenediamine stabilizers, like VIII and IX, form nitroxyl radicals upon degradation and that the nitroxyl concentration increases rapidly after the induction period of the reaction.¹³ This product may be formed by the re-



Scheme 3

action of the amine with the peroxy radical, thus interrupting the auto-catalytic oxidation cycle.

In this work, we compared the photostabilizing activity of the above-mentioned antioxidants with samples of unstabilized BR and BR containing compound I associated with *N,N*-bis-(1-ethyl-3-methylpentyl)-*p*-phenylenediamine (NPD). In order to reproduce the conditions of the polymer in the solid state, we studied our samples in the form of solid films and the oxidation reactions were followed by means of transmission infrared spectra.

EXPERIMENTAL

Samples of BR were furnished by Coperbo. Unstabilized BR was sampled in the plant reactor prior to addition of stabilizer, and coagulated with water. BR stabilized with I (0.62%) and NPD (0.007%) was also sampled in the plant and coagulated with water. This material was characterized by its infrared spectrum¹⁴ as a copolymer containing 33%, 56%, and 12% of *cis*-1,4-, *trans*-1,4-, and 1,2-vinyl units, respectively.

Compounds VI and VII are commercially produced by Ciba-Geigy Química S.A. and were supplied by this manufacturer, VIII and IX were furnished by Industrias Monsanto Ltda.

Films of ca. 40 μm thickness were obtained by casting of 3 mL of a chloroform solution of the polymer (24 g/L), containing the desired amount of stabilizer, onto 5 \times 5 cm Teflon plates. After evaporation of the solvent, the films were removed from the Teflon and fixed in stainless steel frames of 3.0 cm internal diameter. All these operations were carried at 20°C with protection from light.

A tohwalite TB 20 BLB lamp was used for the irradiations. This lamp emits a broad band (half-width = 40 nm) centered at 350 nm with an average intensity of $1.2 \times 10^3 \mu\text{W}/\text{cm}^2$. The light intensity was measured with a Black-Ray UV Meter Model J 221. The temperature of the irradiation chamber was $20 \pm 2^\circ\text{C}$. The kinetics of photooxidation were followed by means of infrared spectra (IR) measured in a Jasco Model A-202 spectrophotometer, together with measurement of the absorbance of the films at 350 nm. The absorbance was measured in a single beam Micronal B-280 Spectrophotometer.

RESULTS AND DISCUSSION

After photooxidation, the changes observed in the IR spectra of films of BR-containing additives are the same as for the unstabilized sample independent of the irradiation time (Fig. 1). Upon irradiation, new strong absorptions are observed at 3400 cm^{-1} and 1720 cm^{-1} , followed by an overall increase of absorption between 1450 and 600 cm^{-1} . According to our previous studies the absorption at 3400 cm^{-1} is assigned to the O—H stretching mode of the hydroperoxides formed in the first step of the photooxidation reaction, and those centered at 1720 cm^{-1} are due to the C=O stretching mode of ketones, carboxylic acids, and esters, formed upon the decomposition of the hydroperoxides.⁷ From this, we decided to center our attention on the 3400 cm^{-1} region of the IR spectra. In this case brittle failure corresponds to the point of maximum absorption.

Samples of BR containing 1% (by weight) of the additives VI, VII/TNPP, VII, VIII, and IX were prepared in order to study their stabilising effect. The formation of hydroperoxides in these samples, compared to an unstabilized sample and to BR containing the stabilizer mixture I/NPD (0.6%), is shown in Figure 2. In Table I we show the calculated induction period (IP) and the maximum kinetic rate for this reaction. Initially we compared the photostability of the two samples of BR containing the mixture I/NPD added at different steps. In sample A the stabilizer was added after the

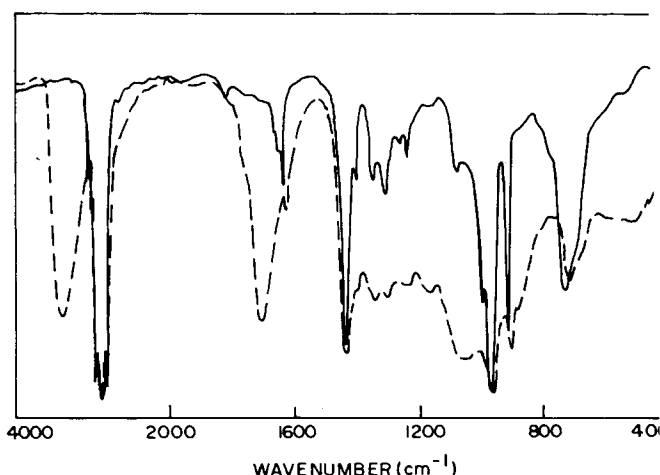


Fig. 1. Infrared spectrum of butadiene rubber films: (—) non-irradiated; (---) irradiated for 20 h.

termination step of the polymerization, and in sample B the stabilizer was added before the termination step. Although the rate of formation of hydroperoxides does not change, the IP shows an increase in case of sample B. This indicates that the reaction of the termination step may produce radicals which initiate the formation of hydroperoxides.

Comparing the two hindered phenol stabilizers, I and VI, we observed that the introduction of a long chain ester in the additive molecule increases the IP by a factor of 3.3. This is probably associated with the lower possibility of dimerization of VI in comparison with I, caused by lower mobility of VI in the polymer matrix in comparison with I and steric hindrance of the bulky ester group. This is corroborated by the results of Scott et al., who showed that polymer-bound hindered phenols are better stabilizers than the free molecules.¹¹ Comparing the above-mentioned stabilizers with the phenol-triazine compound, VII, we observed that this additive has an intermediate performance between I/NPD and VI. Apparently, the filtering effect of the triazine group of compound VII is not enough to counterbalance the steric effect of the long ester chain of compound VI. Comparing the reaction rates, we observed that with I/NPD there is no change in relation to the unstabilized sample, but, when we used the other hindered phenol stabilizers, compounds VI and VII, there is a lowering of the rate, thus indicating a slower photodegradation process. This effect may be due to the light absorption by the chromophores present in the stabilizers VI and VII (absorbance of the films at 350 nm are: unstabilized 0.160, VII 1% 0.308 and VI 1% 0.320). Association of VII with tri(*p*-nonylphenyl)phosphite (TNPP), in the formulation VII:TNPP:solvent 7:83:10 does not change the IP but produces a small decrease in the reaction rate.

Both diamine stabilizers studied in this work (VIII and IX) showed almost the same performance (Fig. 2 and Table I). This indicates that, in this case, the introduction of a higher molecular weight substituent does not markedly change the performance of this type of additive towards the photostabilization of BR. Although they produce some staining of the polymer films, both diamine stabilizers showed a better performance than the mixture I/NPD in sample B.

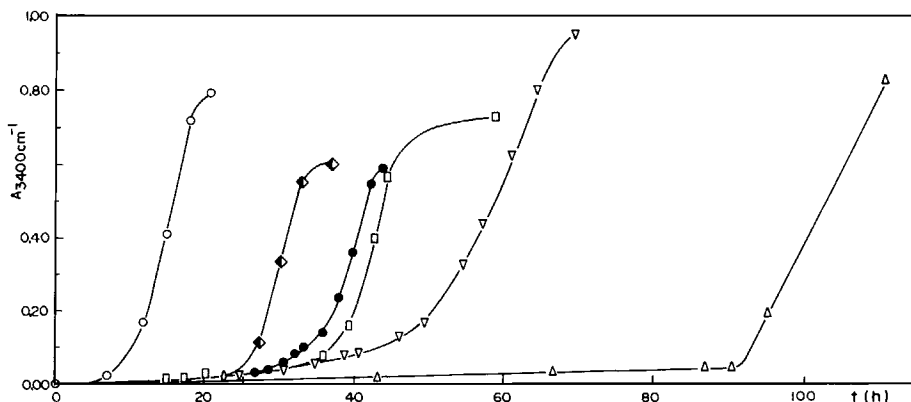


Fig. 2. Formation of hydroperoxides as a function of irradiation time for unstabilized (○) and stabilized butadiene rubber films: (◐) I/NPD; (●) TNPP/VII; (□) VII; (▽) VIII and IX; (△) VI.

TABLE I
Induction Period and Maximum Rate of Formation of Hydroperoxides for BR Containing
the Different Additives Studied in This Work

Stabilizer	IP \pm 0.5 (h)	$\Delta A/\Delta t \pm 0.5 \times 10^2$ (h ⁻¹)
None	9.2	7.3
I/NPD 0.6% A	24.2	8.0
I/NPD 0.6% B	26.4	8.0
VII 1.0%	36.3	6.7
VI 1.0%	88.3	4.4
TNPP/VII 0.9%	32.6	5.2
VIII 1.0%	45.9	4.1
IX 1.0%	45.2	3.8

Since compound VI was the stabilizer which showed the best results in our tests, we studied the variation of its photostabilizing activity as a function of concentration. In Figure 3 we compare films of BR containing different concentrations of this additive with a sample of BR containing the mixture I/NPD (sample B). We observed that there is an increase in the IP as the concentration increases and that at a concentration of 0.2% the IP is longer than for sample B. The increase in IP is not linear with concentration of the stabilizer. If we calculate the coefficient of inhibition¹⁵ for the formation of hydroperoxides, we observe that passing from 0.2% to 0.5% there is no change, but in going to 1.0% of additive there is a decrease from 5×10^2 to 2×10^2 (compare with the value of 50 for sample B). This indicates that a large increase in the concentration of the additive will not produce a corresponding increase in the material lifetime. According to our results, the second best nonstaining additive is compound VII. In Figure 4 we compare films of BR containing different concentrations of compound VII with sample B. In this case the IP for the sample containing 0.2% is lower than for sample B and the IP for the samples containing 0.4%, 0.6%, and 1.0% are the same, within experimental error. Consequently, the coefficient of inhibition decreases as the concentration of additive increases. This indicates that a compromise between IP and degradation rate must be established when using this stabilizer with BR.

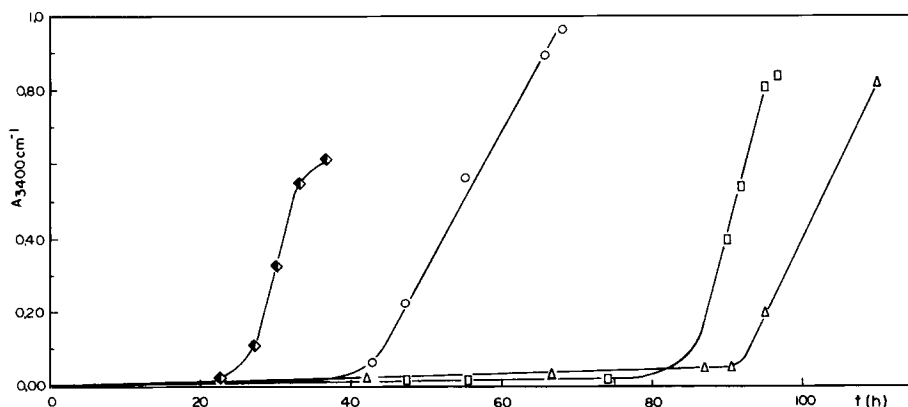


Fig. 3. Formation of hydroperoxides as a function of irradiation time for butadiene rubber films stabilized with I/NPD (◆) and 0.2% (○), 0.5% (□), and 1.0% (△) of compound VI.

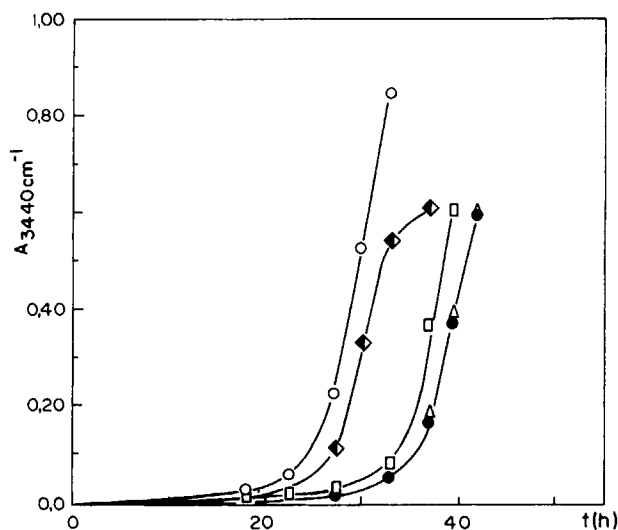


Fig. 4. Formation of hydroperoxides as a function of irradiation time for butadiene rubber films stabilized with I/NPD (◆) and 0.2% (○), 0.4% (□), 0.6% (●), and 1.0% (△) of compound VII.

In conclusion our work shows that commercially available antioxidants may be used as photostabilizers for BR and that the hindered phenol additive VI shows the best performance in comparison with the other additives studied.

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