Stabilization of Unsaturated Elastomers
with Phenolic Antioxidants*

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Synopsis

An investigation of the thermo-oxidative stabilization of ethylene–propylene–diene monomer (EPDM), polybutadiene, and emulsion styrene–butadiene rubbers (SBR) with a large number of variously substituted phenolic antioxidants disclosed a limited number of specific antioxidants to be remarkably effective as processing and storage stabilizers for the unsaturated elastomers. The most effective antioxidants of this investigation promise to provide better stabilization of unvulcanized rubbers than currently achievable with present stabilizers. Stabilizer performance in EPDM was assessed by both carbonyl absorbance and gel content measurement after oven aging at 100° and 150°C. Gel measurement after oven aging was found most useful for the other two elastomers. In all instances, good correlation was found between onset of gel formation and onset of color development. The specificity of stabilizer performance is interpreted in terms of functionality, compatibility, stability, and volatility.

INTRODUCTION

Unsaturated synthetic elastomers, being highly sensitive to oxidation, require the addition of stabilizers to provide protection during processing, storage, and end use. Stabilizers in common use for elastomers include aromatic amines, phosphites, and phenolic antioxidants. The aromatic amines are effective stabilizers of elastomers; however, they are prone to discoloration and consequently are suitable for use mainly in carbon-filled products. The phosphites have the advantage of being low cost, but are susceptible to hydrolysis and, as shown in this report, are of relatively low effectiveness.

This report is a summation of investigations on the effectiveness of phenolic antioxidants in preventing manifestations of oxidative degradation in uncured EPDM, polybutadiene, and emulsion SBR. These investigations were carried out with a relatively large number of phenolic antioxidants, including the Ciba-Geigy Irganox antioxidants, other commercial antioxidants, and Ciba-Geigy developmental and research antioxidants. This study assesses the effectiveness of phenolic antioxidants as

* Presented at International Rubber Conference 1971, Division of Rubber Chemistry, Inc., American Chemical Society, Cleveland, Ohio, October 12–15, 1971.

stabilizers for preventing oxidative deterioration of uncured, unsaturated elastomers during processing, isolation, and storage and identifies the most effective stabilizers for these substrates.

EXPERIMENTAL

EPDM Rubber

Substrate

Antioxidant-free EPDM rubber was prepared by thrice-repeated solution in toluene of a commercial 5-ethylidene-2-norbornene terpolymer and coagulation in isopropanol. The resulting material was dried under vacuum at ambient temperature to constant weight. The complete removal of antioxidant by this procedure was demonstrated by the absence of antioxidant UV absorption in a chloroform solution of the rubber and by marked instability on oven aging.

Test Methods

Carbonyl Absorbance by Infrared Spectroscopy. This test method, used for screening a large number of antioxidants, is a nonautomated version of one described by Bishop.[1] Five drops of a toluene solution containing 2.5% w/w of the stabilizer-free EPDM rubber and 0.0025% w/w of stabilizer were placed on a circular 1-in.-diameter, 0.2-in.-thick sodium chloride disc which had been heated previously in an oven at 75°C. The solution was spread evenly with a glass rod, and the solvent was evaporated quickly. The rubber film thickness was monitored by the baseline method based on absorbance of the C—H band at 1460 cm^{-1}. The target thickness corresponded to a C—H absorbance of 0.25. Duplicate films were prepared with each stabilizer. Groups of rubber films on sodium chloride discs were exposed at 150°C in a forced-draft oven equipped with a rotating mechanism to provide uniform heat and air flow history. The samples were periodically removed from the oven, and the carbonyl absorbance at 1715 cm^{-1} was determined by the baseline method. Failure was arbitrarily selected as the time to reach 0.02 carbonyl absorbance (corrected to 0.25 C—H absorbance). Results were expressed as stabilization factors, which are ratios of failure times for the test stabilizer to the failure time for the control stabilizer (tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionyloxymethyl]methane) in the same oven-aging series.

Gel Content and Color Development. Stabilizers were incorporated at 0.1% into the unstabilized EPDM rubber by milling with cam blades under nitrogen in a Brabender Plasticorder at 130°C for 5 min. The milled rubber was compression molded into 25-mil sheets from which about 1-g samples were cut for oven aging in a forced-draft oven at 100° and 150°C. Samples were removed periodically from the oven and the gel content and Gardner color were determined. The gel content, defined as the per cent insoluble in toluene after 48 hr at ambient temperature with

occasional agitation, was determined by evaporating a filtered aliquot to dryness. The time to failure, defined as the time to onset of gel formation, was estimated by extrapolating relatively steep plots of gel content versus oven aging time to zero gel content. The time to failure for color development was selected as the time when an abrupt increase in discoloration began.

Polybutadiene Rubber

Substrate

At the outset, stabilizer-free polybutadiene rubber was prepared by thrice-repeated solution of a commercial, nonstaining, solution-polymerized polybutadiene rubber (40–50% cis content) in toluene and coagulation in isopropanol. The resulting material was dried under vacuum at ambient temperature to constant weight. Subsequently, after the extracted, stabilizer-free polybutadiene rubber proved unstable for Brabender Plasticorder incorporation of stabilizers, the commercial rubber was used as received for stabilizer evaluation by the gel content and color development method.

Test Method

Stabilizers, usually at 0.125%, were incorporated in the commercial solution polybutadiene rubber (as received) by milling under nitrogen with cam rollers in a Brabender Plasticorder at 110°C for 4 min. The procedure for gel content and color development in other respects was identical with that used for EPDM rubber; oven aging was at 100°C.

Emulsion SBR

Substrate

Aqueous emulsions of antioxidants in xylene solution were prepared with rosin acid salt and were thoroughly mixed with unstabilized SBR emulsion (20% rubber, type 1500 SBR). The rubber was coagulated with a salt–hydrochloric acid solution, washed well with distilled water, and dried at 40–45°C to constant weight under vacuum.

Test Method

The emulsion SBR was compression molded into 25-mil-thick plaques, and 1-g samples were aged at 100°C in a forced-draft oven with a rotating mechanism. Samples were removed periodically for gel measurements (% toluene insoluble) and for Gardner color measurements.

RESULTS AND DISCUSSION

EPDM Rubber

The performance results in EPDM rubber of effective polyolefin antioxidants disclose similarities between antioxidant effectiveness in EPDM

TABLE I

Failure Times for Select Stabilizers in EPDM Rubber and Polypropylene (150° Oven Aging, 25 mil Plaques)

Stabilizer	Hours to Failure	
	EPDM**	Polypropylene*
$ROC_{18}H_{37}$	22	125
$ROC_6H_9(CH_3)_3OR$	45	600
$ROCH_2C(CH_3)_2CH_2OR$	57	395
$(ROCH_2CH_2)_2S$	65	750
$(ROCH_2)_4C$	110	1200

*0.2% Stabilizer; failure by embrittlement

**0.1% Stabilizer; failure by gel formation
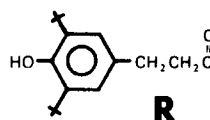
TABLE II

Evidence of Improved Stabilizer Compatibility in EPDM Rubber

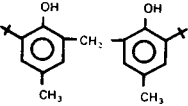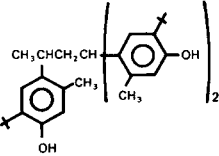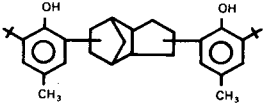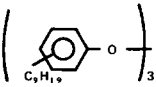| Stabilizer	Stabilization Factor* EPDM** Polypropylene***		Stabilizer	Stabilizer Factor* EPDM** Polypropylene***	
	0.77	0.17		0.20	0.02
	0.36	0.06		0.20	0.03
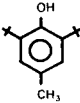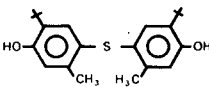
* Stabilization Factor = $\dfrac{\text{Hrs to Failure for Test Stabilizer}}{\text{Hrs to Failure for Control Stabilizer}}$

** Carbonyl Absorbance Test Method; 150°, 0.1%

*** Oven Aging, 150°; 0.2%

rubber and in polypropylene. Although uncured EPDM rubber is inherently less stable than polypropylene, as evidenced by data in Table I, there is a degree of parallelism in antioxidant performance in the two substrates. This is not entirely unexpected since EPDM rubber has a relatively high polyolefin content. Most of the same antioxidant properties which are important for polypropylene stabilization, notably volatility,

TABLE III
Stabilizer Performance in EPDM Rubber by the Carbonyl Absorbance Test Method
(150°C)

Stabilizer (0.1%)	Stabilization Factor*	Stabilizer (0.1%)	Stabilization Factor*
BHT (structure)	0.16	(structure)	0.20
(structure)	0.20	(structure)	0.36
$ROC_{18}H_{37}$	0.41	$ROC_6H_9(CH_3)_3OR$	0.54
$(ROCH_2 CH_2)_2 S$	0.70	$ROCH_2C(CH_3)_2OR$	0.72
(structure)	0.77	$(ROCH_2)_4C$	1.00
TNPP (structure)	0.10	TNPP + styrenated m-cresol	0.26

*Stabilization Factor = $\dfrac{\text{Hrs to Failure for Test Stabilizer}}{\text{Hrs to Failure for Control Stabilizer}}$
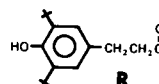
compatibility, mobility, radical trapping effectiveness, and discoloration resistance, appear to be also important for EPDM rubber stabilization. Greater antioxidant compatibility is one property in which EPDM rubber has an apparent advantage over polypropylene due to the greater amorphous content of the former. Data in Table II, which show some relatively poor polypropylene antioxidants perform relatively better in EPDM rubber, would support this observation. (The greater amorphous content, however, may be an overall disadvantage from a stabilization point of view if, as commonly believed, the ordered regions of a polymer are less susceptible to oxidation than the amorphous regions.)

The carbonyl absorbance test method was used to screen a large number of antioxidants for effectiveness in EPDM rubber. Some results are compiled in Table III. The relatively poor performance of tris(nonylphenyl) phosphite (TNPP) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) may be noted. It should be emphasized that the carbonyl absorbance method was used for screening purposes only.

TABLE IV
Stabilizer Performance in EPDM Rubber By Gel and Color Formation Test Method
(100°C Oven Aging)

Stabilizer (0.1%)	Hours to Failure	
	Gel*	Color Dev.
TNPP + Styrenated m-cresol**	~100	<500
$ROC_{18}H_{37}$	2440	3360
$ROC_6H_9(CH_3)_3OR$	2690	3360
$ROCH_2C(CH_3)_2CH_2OR$	3360	4000
$(ROCH_2CH_2)_2S$	4030	4350
$(ROCH_2)_4C$	4530	>4700

*Onset of gel (Extrapolated)

**0.5%

$$HO-\bigcirc-CH_2CH_2\overset{O}{\underset{\|}{C}}\quad \mathbf{R}$$
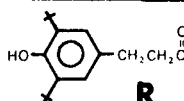
TABLE V
Stabilizer Performance in EPDM Rubber By Gel and Color Formation Test Method
(150°C Oven Aging)

Stabilizer (0.1%)	Hours to Failure	
	Gel*	Color Dev.
TNPP-Styrenated phenol**	10	10
$ROC_{18}H_{37}$	22	25
$ROC_6H_9(CH_3)_3OR$	45	55
$ROCH_2C(CH_3)_2CH_2OR$	57	60
$(ROCH_2CH_2)_2S$	65	65
$(ROCH_2)_4C$	110	120

*Onset of gel (Extrapolated)

**0.5%

$$HO-\bigcirc-CH_2CH_2\overset{O}{\underset{\|}{C}}\quad \mathbf{R}$$
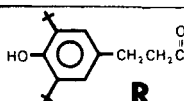
TABLE VI
Performance of Commercial EPDM Rubbers on Oven Aging at 100° and 150°C

Hours to Onset of Gel Formation		
	100°	150°
Rubber A	~100	10
Rubber B	840	—
Rubber C	2020	~10
Rubber D	5380	>125

Those compounds which looked promising in the carbonyl absorbance test were subsequently evaluated in extracted, antioxidant-free EPDM rubber by the gel and color development tests at 100° and 150°C.   Most commercial antioxidants had been eliminated on the basis of poor performance in the carbonyl absorbance screening test and were not evaluated in the gel test.   Gel content data for some of the most effective compounds, compiled in Tables IV and V, show tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxymethyl]methane to be the most effective antioxidant. All the compounds in Tables IV and V provided longer lifetimes than were achieved with samples of all but one of the representative commercial EPDM rubber, the data for which are compiled in Table VI.

The discoloration of oven-aging samples generally increased abruptly soon after gel formation was first detected, as shown in Tables V and VI. Once gel was formed, both gel content and discoloration increased rapidly, suggesting a common mechanism for both phenomena.

By the criteria of this study, tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxymethyl]methane was the most effective EPDM rubber stabilizer encountered among all the commercial and experimental compounds evaluated and is the stabilizer of choice where high performance is required.   However, other esters of 3-(3,5-di-*tert*-butylphenyl)propionic acid, notably diesters of 2,2'-thiodiethanol, neopentyl glycol, and trimethylhexanediol and the octadecyl ester, were also effective; and since these are more hexane soluble than the pentaerythritol tetraester, one of them may be preferable where hexane solubility is required.

Polybutadiene Rubber

Unvulcanized polybutadiene rubber was found to be more sensitive to oxidative degradation than most polymeric substrates, and the degree of stabilization achievable is relatively low compared with polyolefins and even EPDM rubber: In our evaluations at 100°C, the stabilizer system of the commercial polybutadiene rubber provided only 4 hr of stability to the onset of gel.   The best stabilizers at 0.125% were capable of providing about 120 hr of protection to onset of gel at 100°C (versus >4000 hr for EPDM rubber).

The most effective antioxidants for polybutadiene rubber are not the same as the most effective EPDM stabilizers.   Thus, whereas tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxymethyl]methane was the most effective EPDM stabilizer and whereas other 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid derivatives were also highly effective EPDM stabilizers they were considerably less effective in polybutadiene rubber. Conversely, the best polybutadiene stabilizers were only moderately effective in EPDM rubber.   Phosphites and commercial phosphite–phenolic antioxidant combinations, however, were of relatively low order of effectiveness in both substrates.

6-(4-Hydroxy-3,5-di-*tert*-butylanilino)-2,4-bis(*n*-octylthio)-1,3,5-triazine was found to be the most effective phenolic antioxidant for polybutadiene
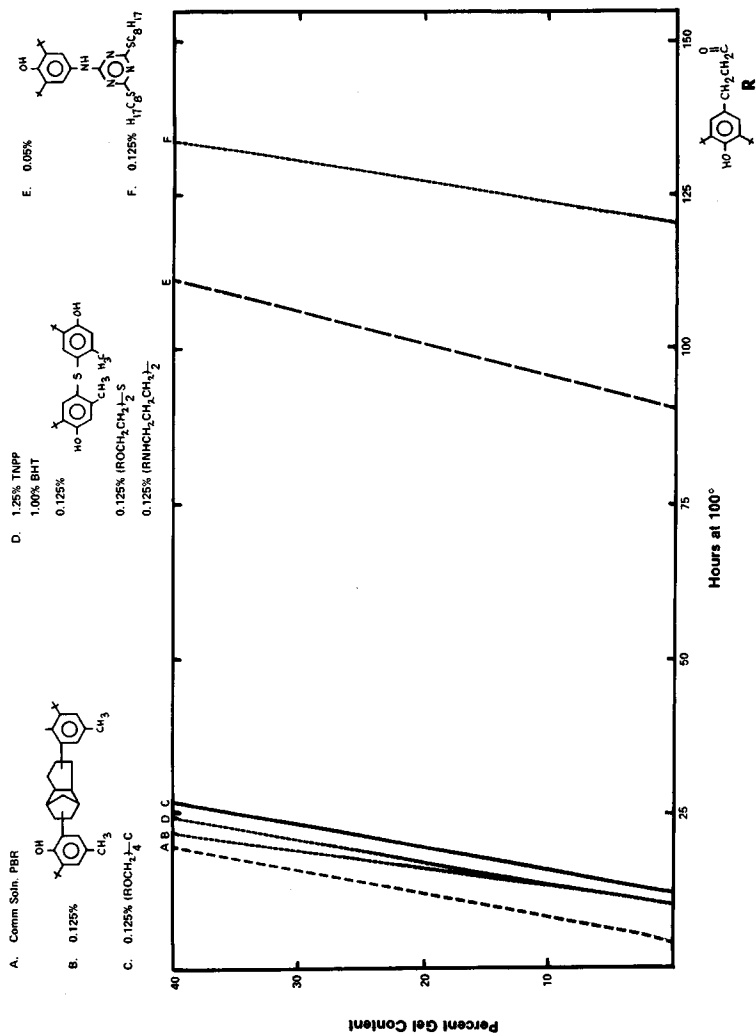
Fig. 1. Solution-polymerized polybutadiene; gel formation of 25-mil unvulcanized plaques during oven aging at 100°C.
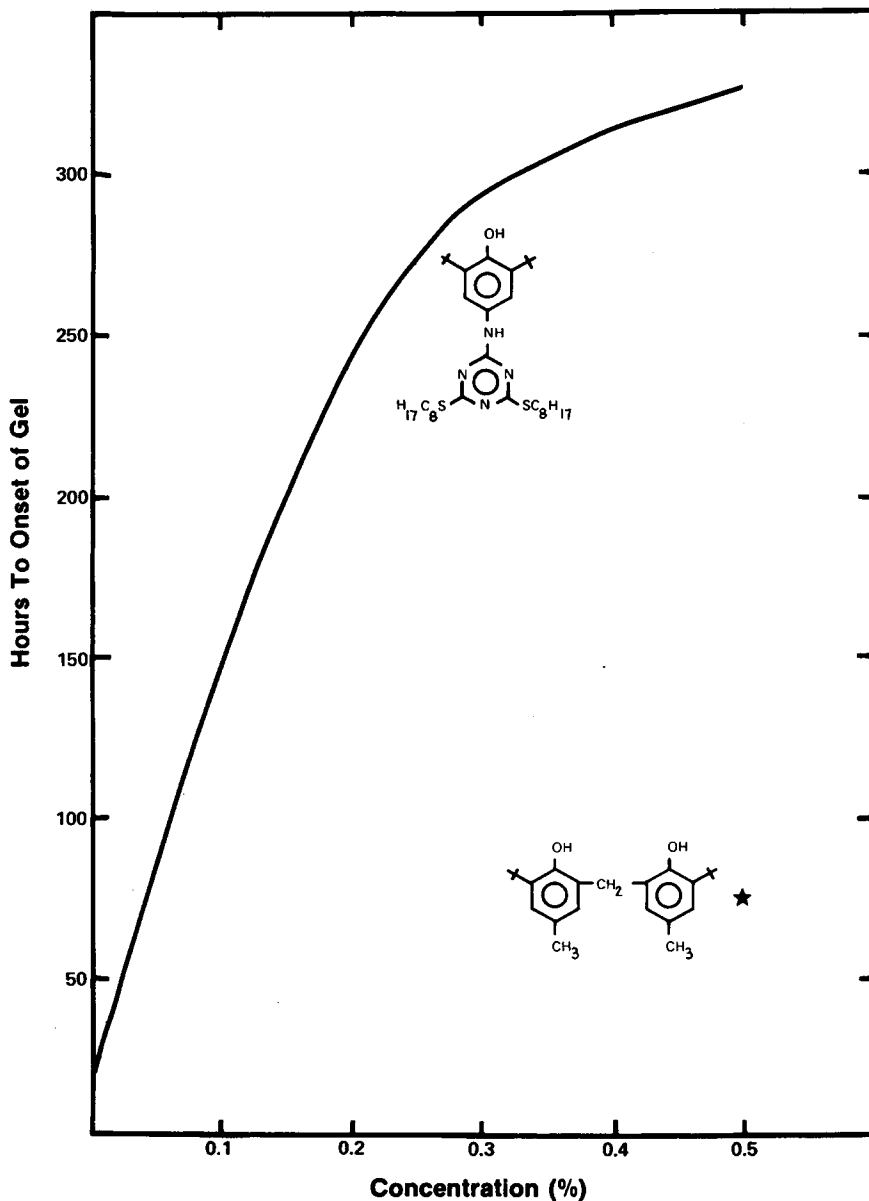
Fig. 2. Effect of stabilizer concentration on polybutadiene rubber stability.

rubber stabilization.   The gel content results for this compound and other phenolic antioxidants plotted in Figure 1 clearly demonstrate the superiority of the 4-hydroxy-3,5-di-*tert*-butylanilino-substituted triazine derivative. An especially remarkable aspect of this compound is that it maintains relatively high effectiveness at concentrations as low as 0.01%, as shown in Figure 2.   An important consequence of the low concentration effectiveness
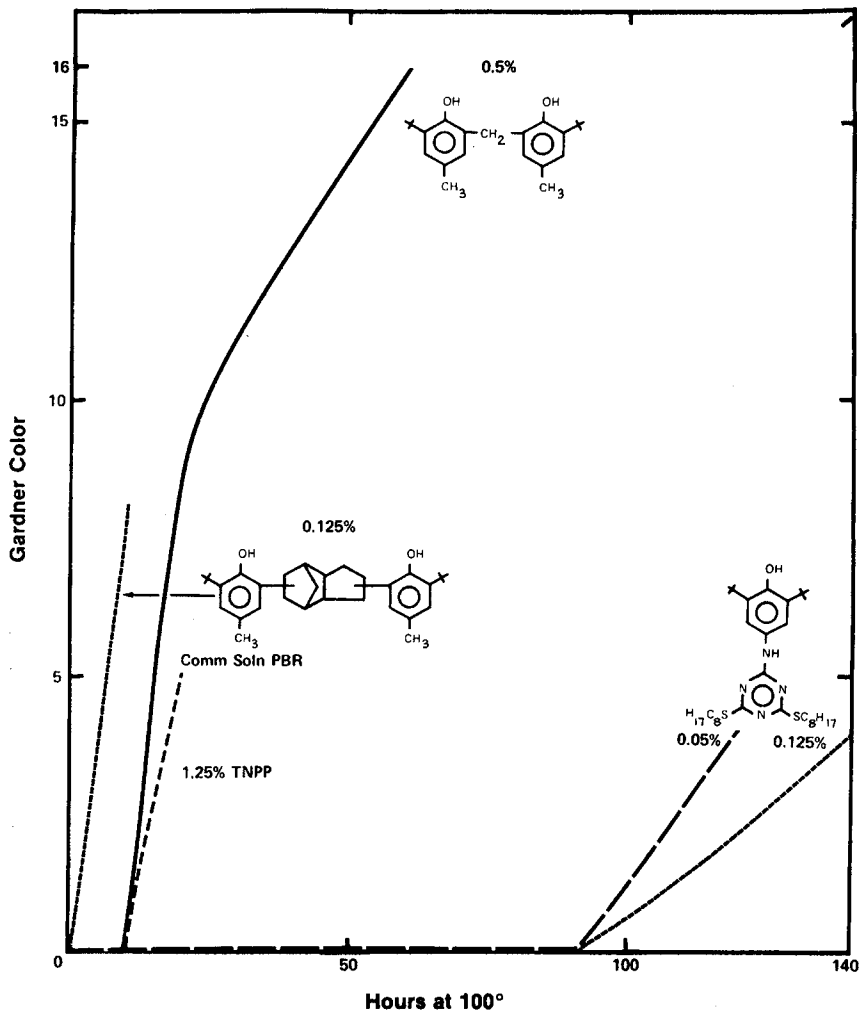
Fig. 3. Stabilizer color performance in polybutadiene.

of 6-(4-hydroxy-3,5-di-*tert*-butylanilino)-2,4-bis(*n*-octylthio)-1,3,5-triazine is a highly favorable stabilization cost in relation to presently used poly-butadiene rubber stabilizers.

6 - (4 - Hydroxy - 3,5 - di - *tert* - butylanilino) - 2,4 - bis(*n* - octylthio)-1,3,5-triazine, in addition to superior performance in preventing gel formation, also demonstrates superior performance in preventing discoloration on oven aging at 100°C. The color data in Figure 3 demonstrate its superiority in this property and also show that the relationship found for EPDM rubber between onset of gel formation and abrupt color development appears to hold true for polybutadiene rubber as well.

It is not known why 6-(4-hydroxy-3,5-di-*tert*-butylanilino)2,4-bis(*n*-octylthio)-1,3,5-triazine should be markedly superior to other phenolic

stabilizers for polybutadiene stabilization.   However, since, as one would expect, the oxidation potential of this stabilizer should be different from those of 2,2'-bis(4-methyl-6-*tert*-butylphenol) and 3,5-di-*tert*-butyl-4-hy-droxyphenylpropionic acid derivatives and, just as antioxidants and anti-ozonants, appears to be associated with specific ranges of oxidation potentials different from one another,[2] so it is conceivable that differences in oxidation potentials among antioxidants could cause differences in specificity. One manifestation of specificity difference, applicable in the present instance, can be that antioxidants with the requisite oxidation potentials are more effective in preventing crosslinking and gel formation in highly unsaturated hydrocarbons than stabilizers with less favorable oxidation potentials.

Emulsion SBR

The performance in emulsion SBR of several representative phenolic antioxidants measured by the gel method is depicted in Figure 4.   These data show stabilizer performance in this substrate to have similarity to performance in polybutadiene, but the correlation is limited.   Both substrates display comparable degrees of oxidative instability.   The relatively high
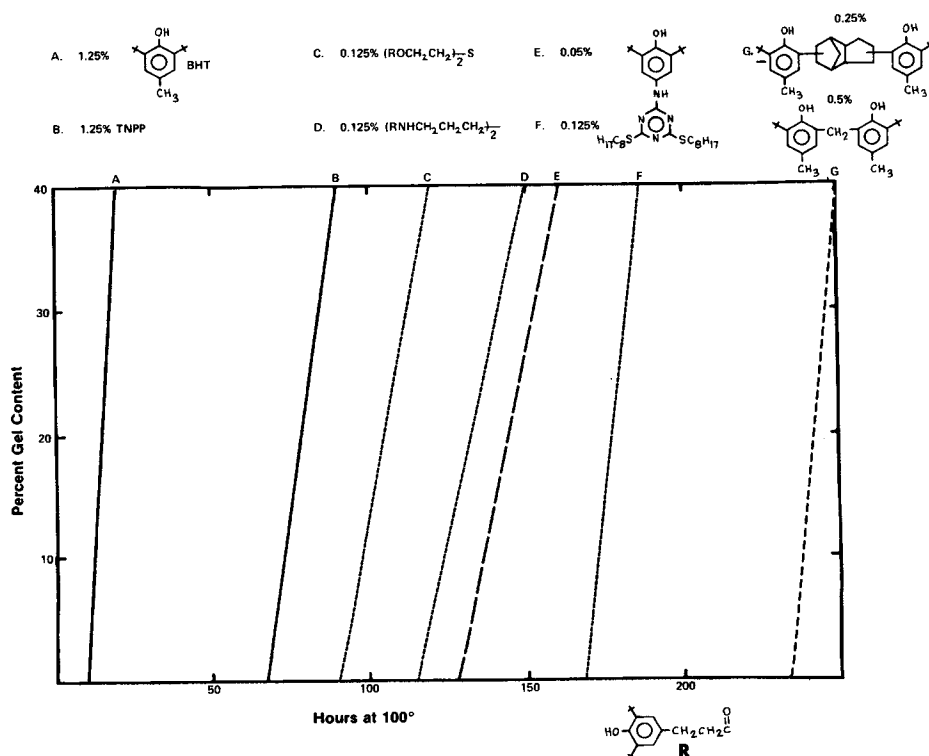

Fig. 4. Emulsion SBR; gel formation of 25-mil unvulcanized plaques during oven aging at 100°C.
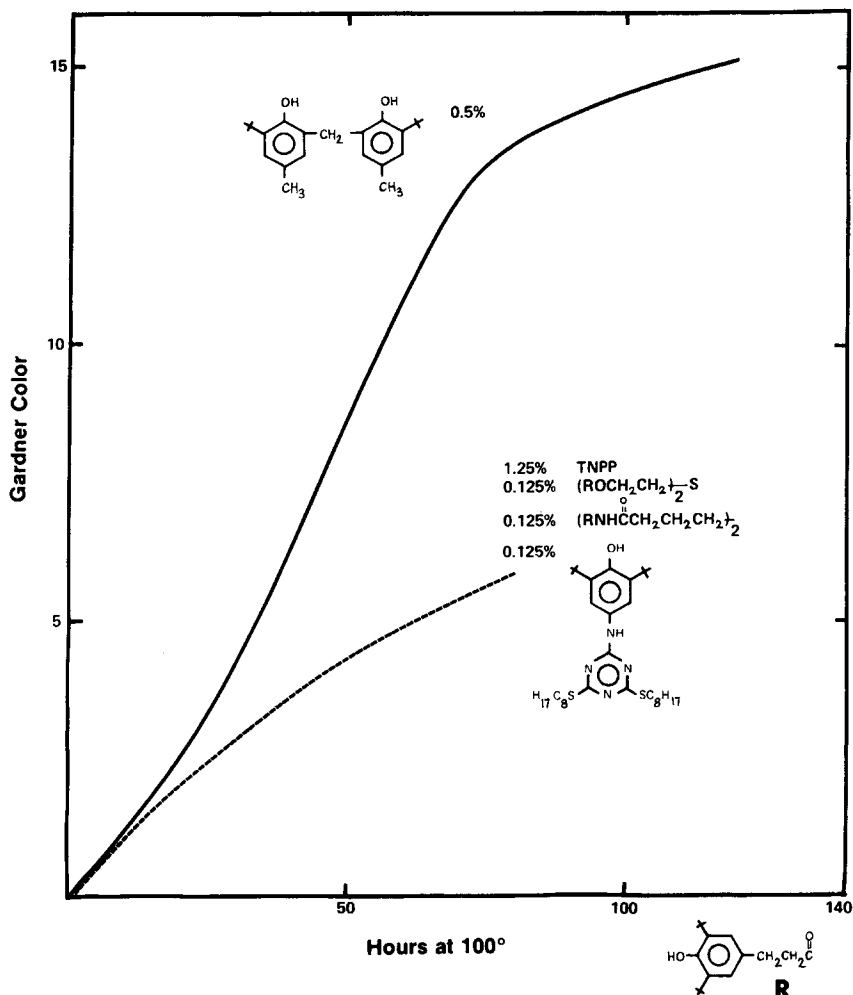
Fig. 5. Stabilizer color performance in emulsion SBR.

order of effectiveness of 6-(4-hydroxy-3,5,-di-*tert*-butylanilino)-2,4-bis(*n*-octylthio)-1,3,5-triazine and the relatively low order of effectiveness of BHT and TNPP are noteworthy. As with polybutadiene rubber, some of the phenolic stabilizers were found to exhibit effectiveness at relatively low concentration, thus making them competitive with low-cost stabilizers used for SBR stabilization.

The most effective phenolic antioxidants were found to be comparable to aromatic amines in the inhibition of gel formation at 100°C in uncured emulsion SBR. Thus, at 0.5%, N,N'diphenyl-*p*-phenylenediamine, N,N'-di-*β*-naphthyl-*p*-phenylenediamine, polymerized 1,2-dihydro-2,2,4-tri-methylquinoline, and N-isopropyl-N'phenyl-*p*-phenylenediamine were effective for 160–170 hr in preventing gel formation at 100°C. 6-(4-Hy-

droxy-3,5-di-*tert*-butylanilino)-2,4-bis(*n*-octylthio)-1,3,5-triazine, for example, at 0.5% was effective for 234 hr.

Color development did not parallel gel formation in emulsion SBR. In general, higher Gardner color values were obtained before the onset of gel formation than had been experienced with EPDM or polybutadiene rubber. 2,2'-Methylenebis(4-methyl-6-*tert*-butyl)phenol was especially prone to discoloration on heating. Some data are shown in Figure 5.

SUMMARY AND CONCLUSIONS

Certain phenolic antioxidants were found to be highly effective stabilizers for preventing gel formation and color in uncured elastomers. The most effective phenolic compounds are more effective at much lower concentrations than stabilizers commonly used for unsaturated elastomers, such as BHT, TNPP, and 2,2'-bis(4-methyl-6-*tert*-butyl)phenol.

Especially noteworthy are the effectiveness of 6-(4-hydroxy-3,5-di-*tert*-butylanilino)-2,4-bis(*n*-octylthio)-1,3,5-triazine in highly unsaturated elastomers such as solution polybutadiene and emulsion SBR, and of esters of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid in EPDM rubber. These stabilizers offer the opportunity of achieving stabilization levels unattainable with other additives.

References

1. W. A. Bishop, *Anal. Chem.*, **33,** 456 (1961).
2. J. Furukawa, S. Yamashita, and T. Kotani, *Advan. Chem. Ser.*, **No. 85,** 110 (1968.)