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THE LONG-TERM EFFECTIVENESS OF CHEMICAL VS. POLYMERIC ANTIOZONANTS IN RUBBER

EDWARD W. BERGSTROM

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Chemical and polymeric (EPDM) antiozonants were evaluated in unsaturated elastomers. Vulcanizates inhibited with chemical antiozonants were found to have taken a pronounced set after five years or more of outdoor exposure at Rock Island, Illinois, and exhibited no ozone resistance when restressed and reexposed to ozone. Vulcanizates inhibited with polymeric antiozonants also took a pronounced set in certain cases (depending upon the type of curing system employed), but all peroxide or sulfur-accelerator- peroxide cured		

20. Abstract

vulcanizates retained their ozone resistance when restressed and reexposed to ozone. Polymeric antiozonants have proved to be more effective than the chemical type in those instances where chemical antiozonants function poorly or not at all. When certain unsaturated elastomers are blended with a fast-curing EPDM (FC-EPDM) and a sulfur-accelerator-peroxide-curing system is employed, stress-strain properties equivalent to those of the unsaturated elastomer alone can be obtained.

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OBJECTIVE:

The object of this work was to determine the effectiveness of chemical vs. polymeric antiozonants in rubber, especially after long-term outdoor exposure.

BACKGROUND:

For the purpose of this report, an antiozonant is defined as a substance which, when mixed into uncured rubber, will prevent or delay the appearance of cracking in the stressed vulcanizates when the vulcanizates are exposed to air-ozone mixtures. This definition includes waxes, substituted p-phenylene diamines, and a wide variety of miscellaneous chemicals such as derivatives of 2,2,4-trimethyl-1,2 dihydro-quinoline, dialkylthioureas, and nickel dibutyl dithiocarbamate. Also, this definition includes polymers that prevent ozone cracking such as ethylene propylene copolymer (EPM) and terpolymers (EPDM), polyvinylchloride, and halogenated butyl rubbers. The nature of these materials provides an obvious subdivision into chemical and polymeric antiozonants.

Despite the large amount of effort that has been invested in the search for improved chemical antiozonants, the substituted p-phenylene diamines originally described by Shaw et al.¹ are still the most effective. Much has been learned about the mechanism of ozone cracking and its prevention by antiozonants. Also, many modified p-phenylene diamines have been introduced, with slightly differing degrees of inhibition and specificity, so that a wide choice is available to the compounder. The manufacture and sale of chemical antiozonants is a multimillion-dollar annual business, as evidenced by the fact that in 1972 the sales of antiozonants rose to \$56 million, and worldwide sales rose to \$155 million. Domestic antiozonant sales of \$101 million and total world sales of \$279 million are forecast by 1980².

As early as 1960, Buist applied for a patent³ on the use of ethylene-propylene copolymer (EPM) for improving the ozone resistance of unsaturated elastomers such as SBR and Cis-polybutadiene. Only EPM was covered by this patent in the concentration range of 40-80 percent of the polymer blend.

1. Shaw, R.F., Ossefort, Z.T., and Touhey, W.J., Rubber World, 130, 636 August 1954.

2. Lerner, M.E., Rubber Age, 105, 57, December 1973.

3. Buist, J., British Patent 939, 359 (Application made in Canada, No. 802, 137) June 29, 1960.

Since that time, others⁴⁻¹⁰ have reported on the use of ethylene propylene elastomers to improve the ozone resistance of unsaturated elastomers. Work was performed in this Laboratory¹¹ to determine the degree of effectiveness and mechanism of protection of EPM and EPDM elastomers as antiozonants. However, data comparing long-term ozone resistance of vulcanizates containing chemical vs. polymeric antiozonants in accelerated and outdoor exposures have not been published. These data are provided in this report.

APPROACH:

Vulcanizates were prepared from the compounds whose formulations are given in Table 1. Compounding, milling, and curing were done in accordance with ASTM D15-66T.¹²

Bent loop specimens (ASTM D518-61, Method B) were used for both outdoor and accelerated (ASTM D1149-64) exposures. In some cases, 20 percent elongated specimens (ASTM D518-61, Method A) were also used. An ozone concentration of 50±5 parts per hundred million parts of air (by volume) at a temperature of 100±2°F was used for the accelerated test. Failure criterion was taken as time to first crack with the use of 20X magnification for examination of specimens in accelerated tests and 7X for specimens in outdoor tests. Other properties reported were determined according to ASTM procedures where applicable.

RESULTS AND DISCUSSION:

Prior to and since the initial discovery of chemical antiozonants by this Laboratory, as reported in 1954¹, literally hundreds of vulcanizates inhibited with chemical antiozonants have been evaluated for ozone resistance

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- 4 Sutton, M.S., Rubber World, 149, 62, 1964.
 - 5 Mitchell, J.M., Kindle, R.W., and Mazzeo, R.A., Rubber World, 98, 67, 1966 (Abstract only).
 - 6 Samuels, M.E., and Wirth, K.H., Rubber Age, 99, 73, 1967.
 - 7 Hauck, J.E., Materials Engineering, p. 50, 1968.
 - 8 Morgan, R.L. Rubber World, 158, 65, 1968.
 - 9 Andrews, E.H., Rubber Chem. Tech., 40, 636, 1967.
 - 10 Ambelang, J.C., Wilson, F.H., Jr., Porter, L.E., and Turck, D.L., Rubber Chem. Tech., 42, 1186, 1969.
 - 11 Ossefort, Z.T., and Bergstrom, E.W., Rubber Age, 101, 47, 1969.
 - 12 ASTM Standards on Rubber Products, March 1968, American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa.
 - 1 Shaw, et al., Ibid.

Table 1

Compound Formulations (Parts by Weight)

Compounding Ingredients	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SBR 1505	100														
SBR 1500	100				70	100	70	100	70						
NBR (Low Acrylonitrile-18%)			100									100	70		
EPDM or FC-EPDM A, B or C ¹ (As Ind.) ²					30		30		30		30		30		30
Stereospecific SBR A ³ or B ⁴ (As Ind.)									100	70					
NR (Pale Crepe)				100										100	70
MAF Black	50	50	50	50	50	50	50			50	50				
SAF Black							45	45				50	50	50	50
Zinc Oxide	3	3	5	3	3		3	3	3	3	3	5	5	3	3
Stearic Acid	2	2	1	2	2		2	2	2	2	2	1	1	2	2
N-cyclohexyl-2-benzothiazole-sulfenamide	1	1		1	1		0.5	0.5	1	1	1	0.5	0.5	0.5	0.5
Benzothiazyl disulfide							1.5								
Sulfur	1.75	1.75	1.5	1.75	1.75		0.2	0.2	1.75	1.75	1.75	0.2	0.2	0.2	0.2
Dicumyl Peroxide (40% active)						5	5	5				2.5	2.5	5	5
Phenyl-beta-naphthylamine	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Polymerized Trimethyl dihydroquinoline	1	1	1	1	1				1	1	1			1	1
Antiozonant															
160°F M.P. Wax															

6 inch by 6 inch by .080 inch test pads of all compounds cured 30 minutes @ 307°F

1 FC-EPDM-Fast-curing type EPDM from various manufacturers (A, B or C)

2 (As Ind.) - As Indicated in Table

3. Stereospecific SBR A-10% Styrene

4 Stereospecific SBR B-21% Styrene

Table 1 (continued)

<u>Compounding Ingredients</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u>	<u>25</u>	<u>26</u>	<u>27</u>
HYTRANS ¹ (85/15 Butadiene/Styrene) (SBR Type)	100	70	100	96.25	100	70	100	70	100	100	100	100
HYTRANS (SBR Type-37.5 parts oil extended)										100		
HYTRANS (90/10 Butadiene/Isoprene) (B/I Type)					100	70					100	
HYTRANS (B/I Type-37.5 parts oil extended)							100	70				100
FC-EPDM A ²		30		30		30		30				
SAF Black	45	45	45	45	45	45	45	45				
MAF Black									50	50	50	50
Zinc Oxide	3	3	3	3	3	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2
Phenyl-beta-naphthylamine	1	1	1	1	1	1	1	1	1	1	1	1
Polymerized trimethyl dihydroquinoline									1	1	1	1
N-cyclohexyl-2-benzothiazole-sulfenamide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	1	1	1
Sulfur	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	1.75	1.75	1.75	1.75
Dicumyl peroxide (40% active)	5	5	5	5	5	5	5	5				
N,N'-di-(3(5 methyl heptyl)-p-phenylenediamine									5	5	5	5
160°F M.P. Wax									1	1	1	1

6 inch by 6 inch by .080 inch test pads of all compounds cured 30 minutes @ 307°F

- 1 HYTRANS-Alfin catalyzed copolymers
- 2 FC-EPDM A-Fast-curing type EPDM from manufacturer A

in both accelerated and outdoor tests. These vulcanizates were based mainly on SBR, NBR, and NR elastomers although some work was also done with BR, CR, and IIR elastomers. In 1974, a list was prepared of all antiozonant-inhibited SBR, NBR, and NR vulcanizates that had remained crackfree in static outdoor tests at Rock Island, Illinois, for five years or longer. This list, given in Table 2, shows that many of the diamine-inhibited SBR vulcanizates have remained crackfree for periods as long as 22 years. Higher levels of antiozonants are required to provide good ozone resistance to nitrile and natural rubber vulcanizates during outdoor exposure.

Some of the most promising of the diamine antiozonants were incorporated into test automotive tires. Arrangements for the manufacture of these tires were made by the U.S. Army Tank-Automotive Command (TACOM), Warren, Michigan. The tires were mounted on wheel rims, inflated to the manufacturer's recommended pressures and exposed outdoors at Rock Island, Illinois, under static conditions. The tires were examined periodically for time to first crack. Results, given in Table 3, show that five of the diamine-antiozonant-inhibited tires remained crackfree outdoors for six years or longer.

Note that the results listed in Tables 2 and 3 are based on outdoor exposure at Rock Island, Illinois, where the atmospheric ozone concentration varies from 0-11 parts per hundred million by volume. This Laboratory found that diamine-antiozonant-inhibited NBR or NR vulcanizates exhibited little or no ozone resistance in accelerated tests conducted at 50 parts per hundred million ozone by volume and $100 \pm 2^{\circ}\text{F}$. (Certain waxes afforded the only significant protection to NBR and NR vulcanizates in accelerated ozone tests.) Diamine-antiozonant-inhibited NBR and NR vulcanizates may not exhibit the same degree of protection in other parts of the country where the atmospheric ozone concentration reaches significantly higher levels. At Los Angeles, California, for example, the ozone concentration has been known to reach levels of 50 to 100 parts per hundred million during periods of heavy smog. Diamine-antiozonant-inhibited SBR vulcanizates have exhibited outstanding resistance, on the other hand, in accelerated tests.

Besides the poor protection afforded NBR and NR vulcanizates in accelerated tests, other inherent limitations were found to exist regarding the performance and use of amine-based chemical antiozonants as described below:

1. They are staining and discoloring.^{13,14}

13 Bergstrom, E.W., "Antiozonants for Nitrile and Natural Rubbers," Rock Island Arsenal Laboratory Technical Report 56-1946, July 1956.

14 Bergstrom, E.W., "Ozone Resistance of SBR Vulcanizates," Rock Island Arsenal Laboratory Technical Report 60-2563, August 1960.

Table 2

Ozone Resistance of SBR, NBR, and NR Vulcanizates Inhibited
with Chemical AntiozonantsTime to First Crack for SBR VulcanizatesSBR 1505 (Compound 1)

<u>Antiozonant</u>	<u>Amt/ 100 rhc</u>	<u>Amt Wax/ 100 rhc</u>	<u>Outdoors</u>	
			<u>20% Stress</u>	<u>Bent Loop</u>
None-Control	---	---	< 1 W	< 1 W
Mixed amine flex inhibitor plus	5	5	OK 22 YR	OK 22 YR
Phenyl-alpha-naphthylamine	5			
N,N ¹ -di-sec-butyl-benzidine	5.4	1	OK 22 YR	OK 22 YR
N,N ¹ -di-sec-butyl-p-phenylenediamine	4	1	3 YR	OK 22 YR
p,p ¹ -diaminodiphenylmethane	4	1	7 YR	8 YR
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	2	1	8 YR	OK 20 YR
▲ 160°F M.P. Wax	---	15	OK 20 YR	OK 20 YR

SBR 1500 (Compound 2)

None-Control	---	---	< 1 W	< 1 W
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	3	1	3 YR	18 YR
Ortho-dianisidine	3	1	3 YR	18 YR
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	3	1	3 YR	OK 19 YR
N-phenyl-N ¹ -(1 ethyl-3 methyl pentyl)-p-phenylenediamine	3	1	15 YR	18 YR
N,N ¹ -diphenyl-p-phenylenediamine	3	3	OK 18 YR	OK 18 YR
N-phenyl-N ¹ -hexyl-p-phenylenediamine	3	3	OK 18 YR	OK 18 YR
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	3	3	9 YR	OK 17 YR
▲ p,p ¹ -diaminodiphenylmethane	4	3	16 YR	OK 17 YR
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	3	3	OK 17 YR	8 YR
N,N ¹ -dicyclohexyl-p-phenylenediamine	3	1	7 YR	13 YR
Mixed diaryl-p-phenylenediamine	3	1	6 YR	OK 16 YR
Mixed diaryl-p-phenylenediamine	3	3	OK 16 YR	OK 16 YR
N,N ¹ -di-(3 methyl cyclohexyl)-p-phenylenediamine	3	1	9 YR	10 YR
N-isopropyl-N ¹ -phenyl-p-phenylenediamine	3	1	---	OK 15 YR
N-phenyl-N ¹ -(1 methyl heptyl)-p-phenylenediamine	3	1	9 YR	OK 15 YR
N,N ¹ -diheptyl-p-phenylenediamine	3	1	7 YR	11 YR
N-octyl-N ¹ -phenyl-p-phenylenediamine	3	1	10 YR	OK 12 YR
N-sec butyl-N ¹ -phenyl-p-phenylenediamine	3	1	9 YR	OK 11 YR
▲ 160°F M.P. Wax	5	---	OK 10 YR	OK 10 YR
N-phenyl-N ¹ -(1,3 dimethyl butyl)-p-phenylenediamine	3	1	OK 9 YR	OK 9 YR
▲ 140°F M.P. Wax (free flowing powder type)	---	5	OK 6 YR	OK 6 YR

Table 2 (continued)
Time to First Crack for NBR (Low Acrylonitrile) Vulcanizates (Compound 3)

<u>Antiozonant</u>	<u>Amt/ 100 rhc</u>	<u>Amt Wax/ 100 rhc</u>	<u>Outdoors</u>	
			<u>20% Stress</u>	<u>Bent Loop</u>
None-Control	----	----	< 1 W	< 1 W
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine plus Mineral Oil	5 3	1	3 YR	OK 19 YR
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	5	1	1 YR	OK 19 YR
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	5	3	4 YR	OK 18 YR
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	5	4 YR	OK 19 YR
Benzidine	5	3	4 YR	OK 18 YR
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine plus polymerized saturated hydrocarbon	5 10	1	3 YR	OK 18 YR
N-isopropyl-N ¹ -phenyl-p-phenylenediamine	5	1	---	OK 15 YR
N-phenyl-N ¹ -(1-methyl heptyl)-p- phenylenediamine	5	1	---	OK 14 YR
N-octyl-N ¹ -phenyl-p-phenylenediamine	5	1	5 YR	OK 12 YR
N-sec butyl-N ¹ -phenyl-p-phenylenediamine A 296°F M.P. Wax	5 ----	1 5	5 YR OK 11 YR	OK 11 YR
N-phenyl-N ¹ -(1,3 dimethyl butyl)-p- phenylenediamine	5	1	OK 9 YR	OK 9 YR
A 160°F M.P. Wax	----	5	1 YR	OK 6 YR

Time to First Crack for NR (Pale Crepe) Vulcanizates (Compound 4)

N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	3	8 YR	2 M
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	5	3	11 YR	1 YR
N-phenyl-N ¹ -(1-methyl heptyl)-p- phenylenediamine	5	1	9 YR	13 YR
N,N ¹ -dicyclohexyl-p-phenylenediamine	5	1	5 YR	10 YR
N,N ¹ -diheptyl-p-phenylenediamine	5	1	5 YR	10 YR
N-phenyl-N ¹ -isopropyl-p-phenylenediamine	5	1	4 YR	11 YR
N-octyl-N ¹ -phenyl-p-phenylenediamine	5	1	8 YR	OK 12 YR
N-phenyl-N ¹ -(1,3 dimethyl butyl)-p- phenylenediamine	5	1	7 YR	OK 9 YR
140°F M.P. Wax (free flowing powder type)	----	10	OK 7 YR	OK 7 YR
None-Control	----	----	< 1 W	< 1 W

Note: W-Weeks, M-Months, YR-Years, OK-Specimens crackfree, tests continuing

Table 3

Time to First Crack for Antiozonant-Inhibited Tires

<u>Tire Description</u>	<u>Antiozonant and Wax</u>	<u>Amt. 100 rhc</u>	<u>Time to First Crack</u>
7.00 x 16, 6 PR NDCC (3-section tread)	Section 1- Control (Uninhibited)	----	4 W
	Section 2- 6 ethoxy-1,2 dihydro-2,2,4 trimethyl quinoline 140°F Paraffin Wax	4 1.5	9 M
	Section 3- 6 ethoxy-1,2-dihydro-2,2,4 trimethyl quinoline 140°F Paraffin Wax	4 3	9 M
7.00 x 16, 6 PR NDCC	N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine 115°F M.P. Wax	3 1	6 YR
7.00 x 16, 6 PR NDCC	N,N ¹ -di-2-Octyl-p-phenylenediamine	3 1	4 YR
7.00 x 16, 6 PR NDCC	N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine 115°F M.P. Wax	3 1	11 YR
7.00 x 16, 6 PR NDCC	N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine 6 ethoxy-1,2-dihydro-2,2,4-trimethyl quinoline 115°F M.P. Wax	2 2 1.5	14 YR
7.00 x 16, 6 PR NDCC	N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	3	OK 16 YR (TD)
9.00 x 20, 8 PR NDCC	6 ethoxy-1,2-dihydro-2,2,4-trimethyl quinoline 145°F Amorphous Wax	2 2.5	6 M
9.00 x 20, 8 PR NDCC	N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	6 YR

Note: PR- Ply Rating, NDCC-Nondirectional cross country
W-Week, M-Month, YR-Year, OK (TD)-Specimens still crackfree at time tests were discontinued

2. Their protective action is reduced after shelf storage of unstressed vulcanizates.^{15,16}
3. They are incompatible with peroxide cures.¹⁷
4. Reduced protection is observed during tropical exposures (possible water leaching).¹⁶
5. Protective action is lost after exposure of vulcanizates for short periods in air at 212°F (or in some cases at 158°F).^{1,13,14,18}
6. They are sensitive to compounding variables, i.e., type filler, cure, plasticizer, and nature of cure.^{13,14,17,18}
7. Protective action is reduced after periods of bin storage prior to cure.¹⁵
8. Protection in dynamic tests is limited.^{13,14}

Some of these deficiencies are differences of degree rather than kind, but in many instances little or no protection can be obtained with amine antiozonants.

In an effort to remedy some or all of these deficiencies, work was pursued in this Laboratory to determine the degree of effectiveness of polymeric antiozonants, specifically EPM and EPDM.¹¹ EPDM, especially the fast-curing type (FC-EPDM), was found to have wide usefulness as an antiozonant for diene elastomers in preliminary tests when 30 percent of the rubber hydrocarbon content of the compound is EPDM. The effectiveness of EPDM as an

15 Bergstrom, E.W., "Loss of Antiozonant Efficacy in Butadiene-Styrene (SBR) Rubber After Shelf Storage," Rock Island Arsenal Laboratory Technical Report 60-487, February 1960.

16 Bergstrom, E.W., "Ten Year Aging of Elastomeric Vulcanizates in Panama, Alaska, and Illinois," Research Directorate Technical Report R-TR-74-038, July 1974.

17 Ossefort, Z.T., Shaw, R.F., and Bergstrom, E.W., Rubber World, 135, 867, 1957.

1 Shaw, et al., Ibid.

13 Bergstrom, E.W., Ibid.

14 Bergstrom, E.W., Ibid.

18 Bergstrom, E.W., "Antiozonants in Oil Extended and Plasticized GR-S Vulcanizates," Rock Island Arsenal Laboratory Technical Report 55-4221, December 1955.

11 Ossefort, et al., Ibid.

antiozonant has since been confirmed in long-term outdoor exposure tests at Rock Island, Illinois, as shown in Table 4. Results are presented for the various types of diene compounds investigated, including the alfin catalyzed copolymers of butadiene/styrene and butadiene/isoprene (HYTRANS elastomers). These results show that, without exception, EPDM or FC-EPDM has afforded excellent ozone resistance to diene elastomers during long-term outdoor static exposure. Also, EPDM and FC-EPDM have been found¹⁶ to afford excellent ozone resistance to diene elastomers in long-term outdoor static exposure in the open sun or rain forest in Panama.

The theory was that some, or all, of the vulcanizates protected by chemical or polymeric antiozonants may have remained crackfree as long as they did because they may have taken a permanent set in the test fixtures. If this were so, there would no longer be any appreciable stress on the specimens and they would no longer be susceptible to ozone attack. Bent-loop and 20 percent elongated specimens that were still crackfree and that had been exposed outdoors at Rock Island, Illinois, for time periods ranging from 3 to 22 years were removed from test and measured for the amount of set taken. The bent-loop specimens upon removal from test were disassembled and carefully separated at the bottom of the specimen. The specimens were laid on their side on a smooth table top and allowed to spread apart at the bottom until the amount of spread was constant (generally overnight). The number of degrees that they had spread apart was then measured with a protractor, and the set taken was determined on the basis of an original specimen returning to a full 180°. The specimens that had been elongated 20 percent were marked with a two-inch bench mark while still in position in the fixture. The fixture was then disassembled, and the specimens were allowed to recover to constant length (generally overnight). The distance between the bench marks was measured, and the percent set was determined. The actual elongation remaining in the stretched specimens was also determined on the basis of original bench mark length prior to stretching of 1.66 inches. These results are given in Tables 5 and 6. The chemical-antiozonant-inhibited specimens, whether bent-loop or elongated 20 percent, took a pronounced set after just three years of outdoor exposure, as shown in Table 5. Most of the specimens exposed five years or longer took almost a complete set (80-100 percent), therefore, little or no stress remained on the specimens as shown (5 percent or less, regardless of exposure time). The base compounds had the following compression set values as determined according to ASTM D395, Method B:

Base Cpd. No.	Compression Set, %	
	<u>70 hours @212°F</u>	<u>22 hours @158°F</u>
1	48	18
2	47	18
3	46	16
4	65	30

¹⁶ Bergstrom, E.W., Ibid.

Table 4

Ozone Resistance Afforded Diene Elastomers by EPDM

<u>Base Cpd. No.</u>	<u>Elastomer Composition</u>	<u>Curing System</u>	<u>Time to First Crack Outdoors (Bent Loop)</u>
2	100 SBR 1500	Sulfur-accelerator	< 1 W
5	70/30 SBR 1500/EPDM	Sulfur-accelerator	OK 7 YR
5	70/30 SBR 1500/FC-EPDM A	Sulfur-accelerator	OK 7 YR
5	70/30 SBR 1500/FC-EPDM B	Sulfur-accelerator	OK 7 YR
5	70/30 SBR 1500/FC-EPDM C	Sulfur-accelerator	OK 7 YR
6	100 SBR 1500	Peroxide	< 1 W
7	70/30 SBR 1500/EPDM	Peroxide	OK 7 YR
7	70/30 SBR 1500/FC-EPDM A	Peroxide	OK 7 YR
7	70/30 SBR 1500/FC-EPDM B	Peroxide	OK 7 YR
7	70/30 SBR 1500/FC-EPDM C	Peroxide	OK 7 YR
8	100 SBR 1500	Sulfur-accelerator-peroxide	< 1 W
9	70/30 SBR 1500/EPDM	Sulfur-accelerator-peroxide	OK 7 YR
9	70/30 SBR 1500/FC-EPDM A	Sulfur-accelerator-peroxide	OK 7 YR
9	70/30 SBR 1500/FC-EPDM B	Sulfur-accelerator-peroxide	OK 7 YR
9	70/30 SBR 1500/FC-EPDM C	Sulfur-accelerator-peroxide	OK 7 YR
10	100 Stereospecific SBR A (10% Styrene)	Sulfur-accelerator	< 1 W
11	70/30 Stereo SBR A/FC-EPDM A	Sulfur-accelerator	OK 7 YR
10	100 Stereospecific SBR B (21% Styrene)	Sulfur-accelerator	< 1 W
11	70/30 Stereo SBR B/FC-EPDM A	Sulfur-accelerator	OK 7 YR

Table 4 (continued)

Base Cpd. No.	Elastomer Composition	Curing System	Time to First Crack	
			Bent Loop	Outdoors 20% Stress
12	100 NBR (18% Acrylonitrile)	Sulfur-accelerator-peroxide	< 1 W	< 1 W
13	70/30 NBR/EPDM	Sulfur-accelerator-peroxide	OK 7 YR	-----
13	70/30 NBR/FC-EPDM A	Sulfur-accelerator-peroxide	OK 7 YR	-----
14	100 NR (Pale Crepe)	Sulfur-accelerator-peroxide	< 1 W	< 1 W
15	70/30 NR/FC-EPDM A	Sulfur-accelerator-peroxide	OK 7 YR	-----
16	100 HYTRANS (SBR Type)	Sulfur-accelerator-peroxide	< 1 W	< 1 W
17	70/30 HYTRANS (SBR)/FC-EPDM A	Sulfur-accelerator-peroxide	OK 5 YR	OK 5 YR
18	100 HYTRANS (SBR Type-37.5 parts oil extended)	Sulfur-accelerator-peroxide	< 1 W	< 1 W
19	96.25/30 HYTRANS (SBR-oil)/FC-EPDM A	Sulfur-accelerator-peroxide	OK 5 YR	OK 5 YR
20	100 HYTRANS (Butadiene/Isoprene Type)	Sulfur-accelerator-peroxide	< 1 W	< 1 W
21	70/30 HYTRANS (B/I)/FC-EPDM A	Sulfur-accelerator-peroxide	OK 5 YR	OK 5 YR
22	100 HYTRANS (Butadiene/Isoprene Type -37.5 parts oil extended)	Sulfur-accelerator-peroxide	< 1 W	< 1 W
23	96.25/30 HYTRANS (B/I-oil)/FC-EPDM A	Sulfur-accelerator-peroxide	OK 5 YR	OK 5 YR

Note: W-Weeks
YR-Years

OK-Specimens crackfree, tests continuing

Table 5

Percent Set Taken and Percent Elongation Remaining in Chemical-Antiozonant-Inhibited Vulcanizates after Exposure Outdoors

<u>Antiozonant</u>		<u>Bent-Loop Specimens</u>		<u>Length of Time Exposed Outdoors</u>	<u>Degree Spread</u>	<u>% Set Taken</u>	<u>% Elongation Remaining (Based on original specimen elongation of 12-25%)</u>
<u>Amt/100 rhc</u>	<u>Amt Wax/100 rhc</u>	<u>Amt/100 rhc</u>	<u>Wax/100 rhc</u>				
<u>SBR 1505 (Compound 1)</u>							
<u>Antiozonant</u>							
N,N ¹ -di-sec butyl p phenylenediamine	4	1	1	23 YR	10	94	0.7-1.5
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	2	1	1	21 YR	10	94	0.7-1.5
<u>SBR 1500 (Compound 2)</u>							
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	3	1	1	20 YR	10	94	0.7-1.5
N-phenyl-N ¹ -(1,3 dimethyl butyl)-p-phenylenediamine	3	1	1	9 YR	24	87	1.5-3.3
140°F M.P. Wax (free flowing powder Type)	-	5	5	7 YR	30	83	2.0-4.3
140°F M.P. Wax (free flowing powder Type)	-	10	10	7 YR	24	87	1.5-3.3
<u>NBR (Low acrylonitrile) (Compound 3)</u>							
N-phenyl-N ¹ -(1 methyl heptyl)-p-phenylenediamine	5	1	1	15 YR	10	94	0.7-1.5
N-octyl-N ¹ -phenyl-p-phenylenediamine	5	1	1	13 YR	20	89	1.3-2.8
N-phenyl-N ¹ -(1,3 dimethyl butyl)-p-phenylenediamine	5	1	1	10 YR	30	83	2.0-4.3
<u>NR (Pale Crepe) (Compound 4)</u>							
140°F M.P. Wax (free flowing powder Type)	-	10	10	7 YR	6	97	0.3-0.8
<u>HYTRANS (SBR Type) (Compound 24)</u>							
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	1	1	5 YR	30	83	2.0-4.3
<u>HYTRANS (SBR Type-37.5 parts oil extended) (Compound 25)</u>							
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	1	1	5 YR	30	83	2.0-4.3
<u>HYTRANS (Butadiene/Isoprene Type) (Compound 26)</u>							
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	1	1	5 YR	50	72	3.4-7.0
<u>HYTRANS (B/I Type-37.5 parts oil extended) (Compound 27)</u>							
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	1	1	5 YR	30	83	2.0-4.3

Table 5 (continued)

Specimens Elongated 20%

<u>Antiozonant</u>	<u>Amt/</u> <u>100 rhc</u>	<u>Amt</u> <u>Wax/</u> <u>100 rhc</u>	<u>Length of Time</u> <u>Exposed Outdoors</u>	<u>Bench</u> <u>Mark</u> <u>Length</u>	<u>% Set</u> <u>Taken</u>	<u>%</u> <u>Elongation</u> <u>Remaining</u>
<u>SBR 1505 (Compound 1)</u>						
Mixed amine flex inhibitor plus	5	5	23 YR	1.95	87.5	2.5
Phenyl-alpha-naphthylamine	5					
N,N-di-sec butyl-benzidine	5.4	1	23 YR	2.00	100	0
160°F M.P. Wax	---	15	21 YR	2.00	100	0
<u>SBR 1500 (Compound 2)</u>						
N,N-diphenyl-p-phenylenediamine	3	3	19 YR	1.95	87.5	2.5
N-phenyl-N-hexyl-p-phenylenediamine	3	3	19 YR	2.00	100	0
Mixed diaryl-p-phenylenediamine	3	3	17 YR	2.00	100	0
160°F M.P. Wax	---	5	11 YR	1.95	87.5	2.5
N-phenyl-N-(1,3 dimethyl butyl)-p-phenylenediamine	3	1	10 YR	2.00	100	0
140°F M.P. Wax (free flowing powder type)	---	5	7 YR	1.95	87.5	2.5
1:1 Hindered diaryl-p-phenylenediamine: phenyl-beta-naphthylamine	4	1	3 YR	1.90	72.5	5.5
<u>NBR (Low acrylonitrile) (Compound 3)</u>						
296°F M.P. Wax	---	5	12 YR	1.95	87.5	2.5
N-phenyl-N-(1,3 dimethyl butyl)-p-phenylenediamine	5	1	10 YR	1.95	87.5	2.5
<u>HYTRANS (SBR Type) (Compound 24)</u>						
N,N-di-3(5 methyl heptyl)-p-phenylenediamine	5	1	5 YR	1.95	87.5	2.5
<u>HYTRANS (SBR Type)-37.5 parts oil extended (Compound 25)</u>						
N,N-di-3(5 methyl heptyl)-p-phenylenediamine	5	1	5 YR	1.95	87.5	2.5
<u>HYTRANS (Butadiene/Isoprene Type -37.5 parts oil extended) (Compound 27)</u>						
N,N-di-3(5 methyl heptyl)-p-phenylenediamine	5	1	5 YR	1.95	87.5	2.5

Note: YR-years

Table 6

Percent Set Taken and Percent Elongation Remaining in Polymeric-Antiozonant-Inhibited
Vulcanizates after Exposure Outdoors

Base Cpd. No.	Elastomer Composition	Curing System	Length of Time Exposed Outdoors	Degree Spread	% Set Taken	% Elongation Remaining (Based on original specimen elongation of 12-25%)
5	70/30 SBR 1500/FC-EPDM A	Sulfur-accelerator	7 YR	70	61	4.7-9.8
5	70/30 SBR 1500/FC-EPDM B	Sulfur-accelerator	7 YR	70	61	4.7-9.8
5	70/30 SBR 1500/FC-EPDM C	Sulfur-accelerator	7 YR	80	56	5.3-11.0
7	70/30 SBR 1500/FC-EPDM A	Peroxide	7 YR	90	50	6.0-12.5
7	70/30 SBR 1500/FC-EPDM B	Peroxide	7 YR	90	50	6.0-12.5
7	70/30 SBR 1500/FC-EPDM C	Peroxide	7 YR	100	44	6.7-14.0
9	70/30 SBR 1500/EPDM	Sulfur-accelerator-peroxide	7 YR	30	83	2.0-4.3
9	70/30 SBR 1500/FC-EPDM A	Sulfur-accelerator-peroxide	7 YR	40	78	2.6-5.5
9	70/30 SBR 1500/FC-EPDM B	Sulfur-accelerator-peroxide	7 YR	34	81	2.3-4.7
9	70/30 SBR 1500/FC-EPDM C	Sulfur-accelerator-peroxide	7 YR	40	78	2.6-5.5
11	70/30 Stereospecific SBR A (10% Styrene)/FC-EPDM A	Sulfur-accelerator	7 YR	80	56	5.3-11.0
11	70/30 Stereospecific SBR B (21% Styrene)/FC-EPDM A	Sulfur-accelerator	7 YR	44	76	2.9-6.0
13	70/30 NBR/FC-EPDM A	Sulfur-accelerator-peroxide	7 YR	30	83	2.0-4.3
17	70/30 HYTRANS (SBR Type)/ FC-EPDM A	Sulfur-accelerator-peroxide	5 YR	10	94	0.7-1.5
19	96.25/30 HYTRANS (SBR Type-37.5 parts oil extended)/FC-EPDM A	Sulfur-accelerator-peroxide	5 YR	10	94	0.7-1.5
21	70/30 HYTRANS (Butadiene/ Isoprene Type)/FC-EPDM A	Sulfur-accelerator-peroxide	5 YR	15	92	1.0-2.0
23	96.25/30 HYTRANS (Butadiene /Isoprene Type-37.5 parts oil extended)/FC-EPDM A	Sulfur-accelerator-peroxide	5 YR	0	100	0

Table 6 (continued)

Specimens Elongated 20%

<u>Base Cpd No</u>	<u>Elastomer Composition</u>	<u>Curing System</u>	<u>Length of Time Exposed Outdoors</u>	<u>Bench Mark Length</u>	<u>% Set Taken</u>	<u>% Elongation Remaining</u>
17	70/30 HYTRANS (SBR Type)/ FC-EPDM A	Sulfur-accelerator-peroxide	5 YR	2.00	100	0
19	96.25/30 HYTRANS (SBR Type- 37.5 parts oil extended)/ FC-EPDM A	Sulfur-accelerator-peroxide	5 YR	2.00	100	0
21	70/30 HYTRANS (Butadiene/ Isoprene Type)/FC-EPDM A	Sulfur-accelerator-peroxide	5 YR	2.00	100	0
23	96.25/30 HYTRANS (Butadiene/ Isoprene Type-37.5 parts oil extended)/FC-EPDM A	Sulfur-accelerator-peroxide	5 YR	2.00	100	0

Note: YR-years

The compression set values are typical for those found for general-purpose, sulfur-accelerator-cured SBR, NBR, and NR vulcanizates in which chemical antiozonants are generally used. The set taken by the vulcanizates exposed outdoors may partially be explained by a study¹⁹ conducted by this Laboratory in 1960 which showed that temperatures as high as 140°F were reached on the surface of rubber specimens exposed outdoors in direct sunlight during the hot summer months.

The results, in Table 6, show that the use of antiozonants (EPDM or FC-EPDM) also leads to high permanent set after just seven years of outdoor exposure, depending upon the basic elastomer type and curing system employed. The HYTRANS and NBR vulcanizates, for example, showed a very pronounced set, whereas, the set of the sulfur-accelerator-cured SBR 1500 vulcanizates was lower than that found for chemical-inhibited SBR 1500 vulcanizates. The set taken by the peroxide-cured SBR 1500 vulcanizates is the lowest of all, which is to be expected. The generally higher set of the sulfur-accelerator-peroxide-cured SBR 1500 when compared with the sulfur-accelerator-cured SBR 1500 is somewhat unexpected.

To determine if any of the vulcanizates that had taken a pronounced set were still resistant to ozone attack, bent-loop specimens were prepared from the specimens originally elongated 20 percent, and the original bent-loop specimens were elongated 20 percent. The specimens were allowed to set overnight wrapped in polyethylene and were then exposed to 50±5 pphm ozone at 100±2°F in an ASTM D1149 ozone test cabinet. The results of these ozone tests are given in Table 7 and 8. The results, in Table 7, show that none of the vulcanizates containing chemical antiozonants exhibited any ozone resistance when restressed and reexposed to ozone. This result is similar to the lack of ozone resistance found in unstressed vulcanizates of this type after short periods of indoor or outdoor shelf storage.¹⁵ Note that some of the specimens exhibited cracking when restressed prior to ozone exposure; this can be attributed to mechanical stress-cracking due to surface embrittlement of these specimens during outdoor exposure.

The results, in Table 8, show that the retention of ozone resistance is dependent on the type of curing system employed. All peroxide or sulfur-accelerator-peroxide-cured vulcanizates containing polymeric antiozonants retained their ozone resistance when restressed and reexposed to ozone, whereas the sulfur-accelerator-cured vulcanizates did not. The fact that the peroxide or sulfur-accelerator-peroxide-cured blends retained their ozone resistance makes a very strong case for the use of polymeric antiozonants in place of chemical antiozonants, especially when coupled with the other advantages of using polymeric antiozonants, as shown in Table 9.

¹⁹ Bergstrom, E.W., "Internal and Surface Temperatures of Rubber Exposed to Direct Sunlight," Rock Island Arsenal Laboratory Technical Report 60-2561, August 1960.

¹⁵ Bergstrom, E.W., Ibid.

Table 7

Ozone Resistance of Vulcanizates Inhibited with Chemical Antiozonants When Restressed after Varying Periods of Outdoor Exposure and Reexposed to Ozone

<u>Bent-Loop Specimens (Originally Elongated 20%)</u>					
<u>SBR 1505 (Compound 1)</u>	<u>Antiozonant</u>	<u>Amt/100rhc</u>	<u>Amt Wax/100rhc</u>	<u>Length of Time Remained Crack Free Outdoors</u>	<u>Time to First Crack 50±5pphm O₃ @100±2°F (Restressed and Reexposed)</u>
Mixed amine flex inhibitor plus		5	5	23 YR	Cracked when flexed
Phenyl-alpha-naphthylamine		5			
N,N'-di-sec butyl benzidine		5.4	1	23 YR	< 2 HR
A 160°F M.P. Wax		---	15		Cracked when flexed
<u>SBR 1500 (Compound 2)</u>					
N,N'-diphenyl-p-phenylenediamine		3	3	19 YR	< 2 HR
N-phenyl-N'-hexyl-p-phenylenediamine		3	3	19 YR	< 2 HR
Mixed diaryl-p-phenylenediamine		3	3	17 YR	< 2 HR
A 160°F M.P. Wax		----	5	11 YR	Cracked when flexed
N-phenyl-N'-(1,3 dimethyl butyl)-p-phenylenediamine		3	1	10 YR	< 2 HR
140 F M.P. Wax (free flowing powder		----	5	7 YR	< 2 HR
1:1 Hindered diaryl-p-phenylenediamine:		4	1	3 YR	< 2 HR
phenyl-beta-naphthylamine					
<u>NBR (Low acrylonitrile)(Compound 3)</u>					
A 296°F M.P. Wax		----	5	12 YR	Cracked when flexed
N-phenyl-N'-(1,3 dimethyl butyl)-p-phenylenediamine		5	1	10 YR	< 2 HR
HYTRANS (SBR type)(compound 24)					
N,N'-di-3(5 methyl heptyl)-p-phenylenediamine		5	1	5 YR	< 2 HR
<u>HYTRANS (SBR type-37.5 parts oil extended)</u>					
1 (Compound 25)					
N,N'-3(5 methyl heptyl)-p-phenylenediamine		5	1	5 YR	< 2 HR
<u>HYTRANS (Butadine/Isoprene type -37.5 parts oil extended)(Compound 27)</u>					
N,N'-di-3(5 methyl heptyl)-p-phenylenediamine		5	1	5 YR	< 2 HR

Table 7 (Continued)

Specimens Elongated 20% (Originally Bent Loop)		Amt Wax/ 100 rhc	Amt Wax/ 100 rhc	Length of Time Remained Crack Free Outdoors	Time to First Crack 50±5 pphm O ₃ @100±2°F (Restressed and Reexposed)
<u>SBR 1505 (Compound 1)</u>					
<u>Antiozonant</u>					
N,N ¹ -di-sec butyl-p-phenylenediamine	4	1	23 YR	< 2 HR	
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	2	1	21 YR	< 2 HR	
<u>SBR 1500 (Compound 2)</u>					
N-phenyl-N ¹ -cyclohexyl-p-phenylenediamine	3	1	20 YR	< 2 HR	
N-phenyl-N ¹ -(1,3 dimethyl butyl)-p-phenylenediamine	3	1	9 YR	< 2 HR	
A 140°F M.P. Wax (free flowing powder type)	--	5	7 YR	< 2 HR	
A 140°F M.P. Wax (free flowing powder type)	--	10	7 YR	1 D	
<u>NBR (Low acrylonitrile)(Compound B)</u>					
N-phenyl-N ¹ -(1 methyl heptyl)-p-phenylenediamine	5	1	15 YR	< 2 HR	
N-octyl-N ¹ -phenyl-p-phenylenediamine	5	1	13 YR	< 2 HR	
N-phenyl-N ¹ -(1,3 dimethyl butyl)-p-phenylenediamine	5	1	10 YR	< 2 HR	
<u>NR (Pale Crepe)(Compound 4)</u>					
140°F M.P. Wax (free flowing powder type)	--	10	7 YR	cracked when flexed	
<u>HYTRANS (SBR Type) (Compound 24)</u>					
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	1	5 YR	< 2 HR	
<u>HYTRANS (SBR Type-37.5 parts oil extended) (Compound 25)</u>					
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	1	5 YR	< 2 HR	
<u>HYTRANS (Butadiene/Isoprene Type)(Compound 26)</u>					
N,N ¹ -di-3(5 methyl heptyl)-p-phenylenediamine	5	1	5 YR	< 2 HR	

Table 7 (continued)

<u>Antiozonant</u>	<u>Specimens Elongated 20% (Originally Bent Loop)</u>		<u>Time to First Crack 50±5 ppbm O₃ @100±2°F (Restressed and Reexposed)</u>
	<u>Amt/ 100 rhc</u>	<u>Amt Wax/ 100 rhc</u>	
<u>HYTRANS (B/I type-37.5 parts oil extended (Compound 27)</u>			
<u>N,N¹-di-3(5 methyl heptyl)-p- phenylenediamine</u>	5	1	< 2 YR
			5 YR

Note: HR - Hours
D - Day

Cracked when flexed - Cracks visible to naked eye or under 20X magnification when specimens were bent or stretched prior to ozone exposure.

Table 8

Ozone Resistance of Vulcanizates Inhibited with Polymeric Antiozonants When Restressed after Varying Periods of Outdoor Exposure and Reexposed to Ozone

Bent-Loop Specimens (Originally Elongated 20%)

<u>Base Cpd. No.</u>	<u>Elastomer Composition</u>	<u>Curing System</u>	<u>Length of Time Remained Crack Free Outdoors</u>	<u>Time to First Crack 50±5 pphm O₃ @100±2°F (Restressed and Reexposed)</u>
17	70/30 HYTRANS (SBR Type)/ FC-EPDM A	Sulfur-accelerator- peroxide	5 YR	OK 7 D
19	96.25/30 HYTRANS (SBR Type- 37.5 parts oil extended)/ FC-EPDM A	Sulfur-accelerator- peroxide	5 YR	OK 7 D
21	70/30 HYTRANS (Butadiene/ Isoprene Type)/ FC-EPDM A	Sulfur-accelerator- peroxide	5 YR	OK 7 D
23	96.25/30 HYTRANS (Butadiene/ Isoprene Type-37.5 parts oil extended/ FC-EPDM A	Sulfur-accelerator- peroxide	5 YR	OK 7 D

Specimens Elongated 20% (Originally Bent Loop)

<u>Base Cpd. No.</u>	<u>Elastomer Composition</u>	<u>Curing System</u>	<u>Length of Time Remained Crack Free Outdoors</u>	<u>Time to First Crack 50±5 pphm O₃ @100±2°F (Restressed and Reexposed)</u>
5	70/30 SBR 1500/FC-EPDM A	Sulfur-accelerator	7 YR	1 D
5	70/30 SBR 1500/FC-EPDM B	Sulfur-accelerator	7 YR	1 D
5	70/30 SBR 1500/FC-EPDM C	Sulfur-accelerator	7 YR	< 2 HR

Table 8 (continued)

Base Cpd. No.	Elastomer Composition	Curing System	Length of Time Remained Crack Free Outdoors	Time to First Crack 50±5 pphm O ₃ @ 100±2°F (Restressed and Reexposed)
7	70/30 SBR 1500/FC-EPDM A	Peroxide	7 YR	OK 7 D
7	70/30 SBR 1500/FC-EPDM B	Peroxide	7 YR	OK 7 D
7	70/30 SBR 1500/FC-EPDM C	Peroxide	7 YR	OK 7 D
9	70/30 SBR 1500/EPDM	Sulfur-accelerator-peroxide	7 YR	OK 7 D
9	70/30 SBR 1500/FC-EPDM A	Sulfur-accelerator-peroxide	7 YR	OK 7 D
9	70/30 SBR 1500/FC-EPDM B	Sulfur-accelerator-peroxide	7 YR	OK 7 D
9	70/30 SBR 1500/FC-EPDM C	Sulfur-accelerator-peroxide	7 YR	OK 7 D
11	70/30 Stereospecific SBR A (10% Styrene)/FC-EPDM A	Sulfur-accelerator	7 YR	1 D
11	70/30 Stereospecific SBR B (21% Styrene)/FC-EPDM A	Sulfur-accelerator	7 YR	< 2 HR
13	70/30 NBR/FC-EPDM A	Sulfur-accelerator-peroxide	7 YR	OK 7 D
17	70/30 HYTRANS (SBR type)/FC-EPDM A	Sulfur-accelerator-peroxide	7 YR	OK 7 D
19	96.25/30 HYTRAN (SBR type-37.5 parts oil extended)/FC-EPDM A	Sulfur-accelerator-peroxide	7 YR	OK 7 D
21	70/30 HYTRANS (Butadiene/Isoprene Type)/FC-EPDM A	Sulfur-accelerator-peroxide	7 YR	OK 7 D
23	96.25/30 HYTRANS (Butadiene/Isoprene Type-37.5 parts oil extended)/FC-EPDM A	Sulfur-accelerator-peroxide	7 YR	OK 7 D

Note: HR- Hours
D- Days
OK- Specimens remained crackfree for time period indicated

Table 9

Advantages of Polymeric Antiozonants Over Chemical Antiozonants

Chemical Antiozonants

1. They are staining and discoloring.
2. Protective action reduced after shelf storage of unstressed vulcanizates.
3. They are incompatible with peroxide cures.
4. Reduced protection observed during tropical exposure.
5. Protective action lost after exposure of vulcanizates for short periods in air at 212°F.
6. They are sensitive to compounding variables, i.e., filler type, cure, plasticizer and nature of cure.
7. Protective action reduced after periods of bin storage prior to use.
8. Protection in dynamic tests is limited.

Polymeric Antiozonants

1. Nonstaining or discoloring.
2. Protective action remains intact after shelf storage of unstressed vulcanizates.
3. Unaffected by peroxide cures.
4. Protection in tropical exposure not diminished.
5. Protective action remains intact after exposure of vulcanizates for short periods in air at 212°F.
6. Sensitive to cure type only-very effective with peroxide or sulfur-accelerator-peroxide cures. Hydrocarbon plasticizers were found to exhibit a beneficial effect on ozone resistance.
7. Protective action remains intact after periods of bin storage prior to use.
8. Give improved protection over chemical antiozonants in dynamic tests.

Before the advent of the fast-curing EPDM elastomers (FC-EPDM), the use of unsaturated elastomer/EPDM blends was criticized because of the poorer stress-strain properties of the blends. When unsaturated elastomers are blended with FC-EPDM, however, and the sulfur-accelerator-peroxide-curing system is employed, equivalent stress-strain can be obtained, as shown in Table 10.

CONCLUSIONS:

Vulcanizates containing chemical antiozonants exhibited from 80 to 100 percent set after five years or more of outdoor exposure at Rock Island, Illinois. No ozone resistance was evident when these specimens were restressed and reexposed to ozone.

Vulcanizates inhibited with polymeric antiozonants (EPDM or FC-EPDM) also took a pronounced set in certain cases, depending upon the type of curing system employed, but all peroxide or sulfur-accelerator-peroxide-cured vulcanizates retained their ozone resistance when restressed and re-exposed to ozone.

Polymeric antiozonants have proved to be more effective than chemical antiozonants in those instances in which chemical antiozonants function poorly or not at all.

When unsaturated elastomers are blended with a fast-curing EPDM (FC-EPDM) and a sulfur-accelerator-peroxide curing system is employed, stress-strain properties equivalent to those of the unsaturated elastomer alone can be obtained.

RECOMMENDATIONS:

Polymeric antiozonants should be used in place of chemical antiozonants, where feasible, and particularly in those cases in which chemical antiozonants function poorly or not at all.

A five-year time limit should be placed on the outdoor exposure of antiozonant-inhibited vulcanizates because of the pronounced set that such vulcanizates take after this time period. The high set is evidenced whether the antiozonant is chemical or polymeric in nature.

Table 10

Physical Properties of Polymeric-Antiozonant-Inhibited Vulcanizates

<u>Physical Property</u>	<u>SBR 1500</u>		<u>NBR (Low Acrylonitrile)</u>		<u>NR (Pale Crepe)</u>	
	<u>100</u>	<u>70/30</u> <u>SBR 1500/</u> <u>FC-EPDM A</u>	<u>100</u> <u>NBR</u>	<u>70/30</u> <u>NBR/</u> <u>FC-EPDM A</u>	<u>100</u> <u>NR</u>	<u>70/30</u> <u>NR/</u> <u>FC-EPDM A</u>
Tensile, psi	3520	3350	2300	2040	3060	3040
Modulus, 300% Elongation, psi	2090	1770	1820	1630	1890	1690
Ultimate Elongation, %	450	510	350	360	410	430
Hardness, Shore A	68	68	69	70	62	63
Compression Set, ASTM D395, Method B 70 hours @212°F	38	37	36	36	45	44

Note: All compounds were vulcanized with a sulfur-accelerator-peroxide curing system.

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