Placrosym, VI, 1984.

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STUDIES ON PROTECTIVE SYSTEMS FOR NATURAL RUBBER VULCANISATES AGAINST OZONE ATTACK

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ABSTRACT

Comparative evaluation of three commonly used antiozonants in protecting NR against ozone cracking was made. The efficiency of the antiozonants was in the order DBPPD IPPD DPPD. It was observed that ozone resistance can be enhanced by blending with CR in appropriate ratios in which the polymers are compatible.

INTRODUCTION

Ozone attack on natural rubber vulcanisates held under strain and the resulting deterioration of the products are widely studied (Fogg, 1962; Thornley, 1964; Lake and Lindeey, 1965; Andries et al., 1979). Ozone resistance of rubber vulcanisates is influenced by several factors like the nature of the polymer, nature of cross linking system, type and quantity of the protective agent added and service conditions of the finished material. The extent of chemical unsaturation of the polymer primarily determines whether *or not it is prone to ozone attack. The stereoregularity of* the polymer has little to do with its ozone resistance. Natural rubber (NR) in both raw and vulcanised forms, is attacked by ozone and the severity of attack increases when the material is under strained condition. Braden and Gent (1963) developed the concept of critical stress on ozone cracking. Above a critical stress, cracking becomes very sensitive to strain and in this region the rate of crack growth increases exponentially. Above a certain critical strain, the increase in crack growth rate ceases.

Braden and Gent (1962) suggested that ozone degradation of polymers in general can be minimised either by reducing the rate of crack growth or by increasing the critical condition. The reduced rate of crack growth can be achieved by several methods of which one is the addition of chemicals known as antiozonants. Other than chemical methods of protection from ozone, physical methods, like coating the rubber surface with an unreactive protection layer by addition of wax or by blending with, an ozone resistant polymer, are also available. Andrews (1966) studied the ozone resistance of NR when blended with the ozone resistant rubber EPR. The inclusion of an ozone inert phase in an elastomer blend imparts some protection to the material by raising the critical energy necessary to initiate macroscopic cracking. The inert phase hinders the development of macroscopic cracks from microscopic ones by providing physical barriers to crack propagation.

The present study is taken up with the following objectives:

1) Evaluation of the effect of different curing systems on ozone cracking of NR.

2) Comparison of the performance of three indigenously available disubstituted-p-phenelene diamine antiozonants namely, N,N' diphenyl-p-phenelene diamine (DPPD), N-isopropyl, N'-phenyl-p-phenelene diamine (IPPD) and N-(1,3 dimethyl butyl) N'-phenyl-p-phenelene diamine (DBPPD).

3) Evaluation of the synergestic action of these antiozonants.

4) Study of the ozone resistance of Natural rubber-chloroprene rubber blends.

EXPERIMENTAL

Compounds containing various cure systems were prepared by mixing NR with other compounding ingredients in an open laboratory mill (Formulation given in Table 2). The optimum cure time of the compounds at 150°C was determined using Monsanto Rheometer R–100. Ozone resistance of the vulcanisates was determined according to ASTM D 1171 (1968) using a Mast Ozone Test Chamber at 50 pphm ozone concentration at 38±2°C. The intensity of the cracks developed on the test pieces, were evaluated after 24, 48 and 72 h of ozone exposure and the percentage retention of property was calculated. A butyl rubber compound (Table 1) which developed no cracks even after 72 h of ozone exposure was used as a reference standard.

Table 1. Formulation of butyl compound

Butyl rubber	100
Stearic acid	3.0
ZnO	5.0
HAF black	50
Benzothiazyl sulphide	0.5
TMTD	1.0
S	2.0

The evaluation of antiozonants was carried out by incorporating them at different levels in NR compounds. The test pieces were exposed to ozone and percentage retention of property was estimated (Tables 3, 4 and 5). For the evaluation of the synergetic action of antiozonants, combination of two antiozonants at different concentration (Table 6) were incorporated to NR compounds (cure system 1 of Table 2) and ozone resistance determined.

To study the ozone resistance of NR-CR blends both the rubbers were blended in the mill in different proportions (Table 7). The three antiozonants were added to the blends at a level of 1 phr and ozone resistance was evaluated (Table 7).

RESULTS AND DISCUSSION

Evaluation of the cure systems

Braden and Gent (1960) observed that crack growth rate decreases with an increasing degree of crosslinking in the vulcanisates. During the evaluation of the different cure systems, surface blooming was observed to a high level in system 4 and to a lesser extent in systems 2 and 3. Hence in addition to the inherent ozone resistance of these cure systems, the surface bloom also

Table 2. Composition of NR Mixers

	Cure System					
	1	2*	3*	4**	5	6
Natural rubber	100	100	100	100	100	100
Stearic acid	2.5	2.5	2.5	2.5	2.5	—
ZnO	3.5	3.5	3.5	3.5	3.5	—
SRF black (N-55)	50	50	50	50	50	50
Aromatic oil	4	4	4	4	4	4
CBS	0.5	3.0	2.2	—	0.8	—
TMTD	—	2.0	1.0	—	—	—
MBTS	—	—	—	1.5	—	—
DPG	—	—	—	—	0.6	—
Sulphur	2.5	0.33	0.25	—	1.2	—
Sulfasan R	—	—	—	2.0	—	—
Dicumyl peroxide	—	—	—	—	—	2.0
Percentage retention of property	25	10	10	35	10	0

*Surface bloom was observed
**Intensity of bloom was higher.

Table 3. Evaluation of N,N' Diphenyl-p-Phenelene Diamine—percentage retention of property

Cure System	Concentration of Antiozonant (phr)				
	0	0.5	1.0	1.5	2.0
1	25	25	60	75	75
2	90	100	100	100	100
3	95	100	100	100	100
4	100	100	100	100	100
5	25	60	60	75	80
6	0	5	20	20	20

Table 4. Evaluation of N (Isopropyl) N' Phenyl-p-Phenelene Diamine—percentage retention of property

Cure System	Concentration of Antiozonant (phr)				
	0	0.5	1.0	1.5	2.0
1	20	20	25	60	60
2	80	80	80	95	95
3	40	40	80	80	80
4	100	100	100	100	100
5	25	25	60	35	35
6	0	0	5	5	5

Table 5. Evaluation of N (1, 3 Dimethyl Butyl) N' Phenyl-p-Phenelene Diamine—percentage retention of property

Cure System	Concentration of Antiozonant (phr)				
	0	0.5	1.0	1.5	2.0
1	25	30	75	90	90
2	80	80	95	100	100
3	40	40	90	95	95
4	100	100	100	100	100
5	25	60	65	90	90
6	0	5	5	5	5

might have contributed to the ozone resistance. Observing the intensity of cracks developed on the test specimens the following rating for ozone resistance can be made. (Crack intensity increases towards right) 4>1>2=3=5>6. If the systems with the surface blooms are excluded the gradation will be 1>5>6.

Braden and Gent (1960) have reported that crack growth rate in a dicumyl peroxide vulcanisate is less compared to that in a sulfanamide accelerated sulfur cured one. The results obtained in this study are not in agreement with this report. But this abnormal behaviour may be due to the varying stiffness of the vulcanisate, since the critical condition of a vulcanisate is related to its stiffness (Braden and Gent, 1961) From the Monsanto Rheometer cure curve it was observed that the torque value for

Table 6. Evaluation of antiozonant combinations

Concentration of Antiozonants (phr)			Percentage retention of property
IPPD	DPPD	DMPPD	
0.0	2.0	—	75
0.5	1.5	—	70
1.0	1.0	—	70
1.5	0.5	—	70
2.0	0	—	60
0	—	2.0	90
0.5	—	1.5	70
1.0	—	1.0	70
1.5	—	0.5	70
2.0	—	0	60
—	0	2.0	90
—	0.5	1.5	70
—	5.0	1.0	70
—	1.5	0.5	70
—	2.0	0	75

Table 7. Formulation of NR-CR blends

	NR-CR Ratio					
	50/50	60/40	70/30	80/20	90/10	100/0
Natural rubber	50	60	70	80	90	100
Polychloroprene	50	40	30	20	10	0
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	5.0	5.0	5.0	5.0	5.0	5.0
Naphthenic oil	6	6	6	6	6	6
CBS	0.30	0.35	0.40	0.45	0.50	0.55
TMT	0.20	0.16	0.12	0.08	0.04	0.04
MgO	2.0	1.6	1.2	0.8	0.4	0.0
DOTT	0.5	0.4	0.3	0.2	0.1	0.0
S	1.5	1.7	1.9	2.1	2.3	2.5
Antiozonant	1.0	1.0	1.0	1.0	1.0	1.0

the peroxide vulcanisate was less compared to sulphur cured systems. Since the chemical contribution to network chain density can be directly assessed from Rheometer torque values, it is inferred that the network density in the peroxide vulcanisate was less and this might have contributed to its poor ozone resistance.

Evaluation of substituted para phenelene diamine antiozonants

In a rubber vulcanisate under strain, for the initiation of crack due to ozone attack, the energy of the system must be above a critical level. Once a crack is generated, the severity of cracking can be controlled if the crack growth rate can be kept low. The function of the antiozonants is to either increase the critical condition or reduce the crack growth rate. N, N'-dialkyl para phenelene diamines act in the first way (Braden and Gent, 1962, 1963) while the dialkyl or aryl alkyl para phenelene diamines act in the latter way. In all the cure systems studied the antiozonant activity, on unit weight basis is DBPPD > DPPD > IPPD. In all the sulfur/sulfur donor cure systems blooming was observed when IPPD was added at a level of 2 phr. Also it was observed that the activity of the antiozonants above a level of 1.5 phr is not very significant. The performance of the peroxide cured vulcanisate is not markedly improved even after the addition of the antiozonants. This is apparently due to the reaction between dicumyl peroxide and the amines.

Synergism of antiozonant combination

Synergism of antiozonant combinations was studied in the sulfur cure system (No. I). The performance of the different antiozonants in combination was almost similar. During the evaluation of individual antiozonants it was observed that IPPD when added to this cure system at a level of 2 phr, a bloom appeared on the surface while in the combination of two antiozonants (total concentration 2 phr) no such blooming was observed. Also the performance of antiozonant combinations was only comparable to that of individual antiozonants when added in equivalent quantities.

Evaluation of NR-CR blends

Among the various blend ratios studied, 50/50 NR-CR blends containing 1 phr of IPPD or DBPPD were found to be free from cracks even after 72 h of exposure to ozone, while slight cracking was observed in the 50/50 blend containing DPPD,

(Table 8). The performance of 60/40 NR-CR blend was poor compared to the 50/50 blend. The performance of 70/30 blend was even poorer than 90/10 blend. This abnormal behaviour may be due to the incompatibility of the two polymers in the 70/30 ratio (Marsh et al., 1968) Walters and Keyte (1965) have reported the presence of zones in NR-CR blends by phase contrast and electron microscopy. Cracking was observed in all other blends, the crack intensity increasing with a decrease in polychloroprene content. From the NR-CR blends, if the regions of incompatibility are excluded, it can be seen that the ozone resistance of the blend increases in polychloroprene content. Similar results were reported by Andrews (1966) on NR-EPR blends.

Table 8. Evaluation of natural rubber—polychloroprene blends

NR/CR ratio	Percentage of property		
	DPPD	IPPD	DBPPD
100/0	5	10	10
90/10	25	60	25
80/20	75	70	60
70/30	15	15	15
60/40	60	90	90
50/50	90	100	100

CONCLUSIONS

1) Among the cure systems evaluated, the conventional sulfur system was found to be better than Semi E.V., E.V. or peroxide systems. (Systems which showed blooming tendency were not taken into consideration.)

2) The efficiency of antiozonants was in the order DBPPD > IPPD > DPPD. The activity of antiozonants above a level of 1.5 phr was not found to be significant.

3) Ozone resistance of NR can be enhanced by blending with CR in appropriate ratios in which the polymers are compatible.

ACKNOWLEDGEMENT

The authors express their deep gratitude to the Director, Rubber Research Institute of India for the interest he had shown in this work. The valuable suggestions and assistance rendered by our colleagues in the Chemistry/Rubber Technology Division are sincerely acknowledged.

ABBREVIATIONS

TMTD	— Tetramethyl thiuram disulphide
CBS	— N-Cyclohexyl-2 benzothiazyl sulphenamide
MBTS	— Dibenzothiazyl disulphide
DPG	— Diphenyl Guanidine
DOTT	— Di O-Tolyl thiourea
HAF Black	— High Abrasion Furnace Black
SRF Black	— Semi Reinforcing Furnace Black
FEF Black	— Fast Extension Furnace Black

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