

# Retarding and Antioxidant Activity of 1-Cyclohexylthio-2-Mercaptobenzimidazole in the Vulcanization of NR Accelerated by Thiocarbamyl Sulfenamide

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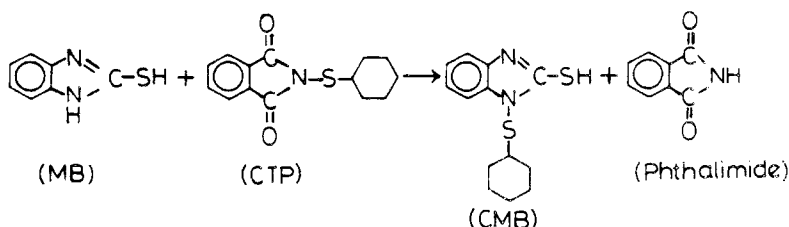
## Synopsis

The effect of 1-cyclohexylthio-2-mercaptobenzimidazole (CMB) on the vulcanization of NR accelerated by *N*-oxydiethylene thiocarbamyl-*N'*-oxydiethylene sulfenamide (OTOS) has been studied. It is found that CMB delays the onset of cure and generates 2-mercaptobenzimidazole during vulcanization. The results indicate the retarding as well as antioxidant activity of CMB.

## INTRODUCTION

In the vulcanization of rubber, accelerator, retarder, and antioxidant play a vital role. In the past the scorchy behavior of 2-mercaptobenzothiazole (MBT) could be moderated through chemical modification of the compound when benzothiazole sulfenamides appeared in the rubber industry. By prolonging the onset of cure these sulfenamides functioned both as accelerators and retarders. Later, *N*-cyclohexylthiophthalimide (CTP) emerged as an effective retarder by scavenging MBT for a certain length of time and thus could delay the process<sup>1</sup> of vulcanization of NR. Unfortunately, CTP generates phthalimide, which sometimes causes blooming on the vulcanizates. In a recent investigation it has been shown<sup>2</sup> that phthalimide might reduce the modulus and tensile strength of NR vulcanizates during aging. In the present investigation an attempt has been made to formulate a compound that would exhibit simultaneously the retarding as well as the antioxidant activity. In this way the compound can be effectively utilized as a rubber additive that would eliminate the undesirable effect of any side product generated from the parent compound. From the structure of CTP it is seen that cycloalkylthio moiety is attached to nitrogen to incorporate an S—N bond that is reactive towards accelerators,<sup>1,3,4</sup> especially MBT. It was thought that, with the introduction of an alkylthio moiety through the  $\text{>NH}$  functionality of an antioxidant, the retarding as well as antioxidant activity of the resultant compound could be observed. With this in mind, 2-mercaptobenzimidazole (MB) was selected as the representative antioxidant that has been chemically modified according to

the following reaction:



Scheme 1. Formation of CMB from MB-CTP reaction

## EXPERIMENTAL

**Materials.** *N*-oxydiethylenethiocarbamyl-*N'*-oxydiethylene sulfenamido (OTOS), *N*-cyclohexylthiophthalimide (CTP), and 2-mercaptobenzimidazole (MB) were used as obtained. Bis(oxydiethylene) thiuram disulfide (OTD),<sup>5</sup> cyclohexyl thiomorpholine (CM),<sup>6</sup> and *N*-oxydiethylene thiocarbamyl cyclohexyl disulfide (OTCD)<sup>4</sup> were prepared in the laboratory. The solvents used in the investigation were purified before use. Analytical grade zinc oxide, extra pure stearic acid, and sulfur were used as received.

### Preparation of 1-Cyclohexylthio-2-Mercaptobenzimidazole (CMB)

A mixture containing 5.22 g (0.02 mol) of CTP and 3.00 g (0.02 mol) of MB in 50 cm<sup>3</sup> of isopropyl alcohol was heated at reflux (82–83°C) for 10 h. The solution thus obtained was cooled and stirred at ambient temperature for a further period of 24 h when phthalimide precipitated out. The precipitate was removed by filtration. To the filtrate, 70 cm<sup>3</sup> of water containing 4.8 g (0.03 mol) of NaOH was added and stirring continued for 30 min. Then the reaction mixture was extracted with 60 cm<sup>3</sup> of diethyl ether. The ethereal layer was washed with water until the washings were neutral and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The ether was removed in vacuum and the solid product (mp 115–116°C) was found to be pure CMB as based on the following analyses: We found 59.20% C, 6.15% H, 10.79% N, and 23.86% S; C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub> by calculation has 59.09% C, 6.06% H, 10.60% N, and 24.25% S, NMR:  $\delta$  (CDCl<sub>3</sub>), 0.96–2.20 (m, 11 H, methylene and methine protons), 2.80–3.26 (br-S, 1 H, —SH), 7.03–7.76 (m, 4 H, Ar—H). <sup>1</sup>H NMR spectrum at 60 MHz was taken in a varian T-60 A NMR spectrometer.

**Compounding.** The rubber additives were incorporated in NR in accordance with the recipe as shown in Table I using a Berstorff Laboratory mixing mill.<sup>7</sup>

**Testing.** The stocks were cured under pressure at 140°C for optimum cure times. Tensile strength and modulus at 200% elongation were measured with an Amsler Tensile Tester following ASTM D 412-51T. The study concerning the torque developed during vulcanization was made with the Monsanto Rheometer (R-100). From the rheographs maximum torque ( $R_{\infty}$ ), scorch time ( $t_2$ ), and optimum cure time ( $t_{90}$ ) were obtained.

TABLE I  
Stock Formulations

Ingredient	Stock No.:	1	2	3
RMA 1 X (g)		100	100	100
Zinc oxide (g)		5	5	5
Stearic acid (g)		2	2	2
Sulfur (g)		0.5	0.5	0.5
OTOS (mmol)		9	9	9
MB (mmol)		—	2	—
CMB (mmol)		—	—	2

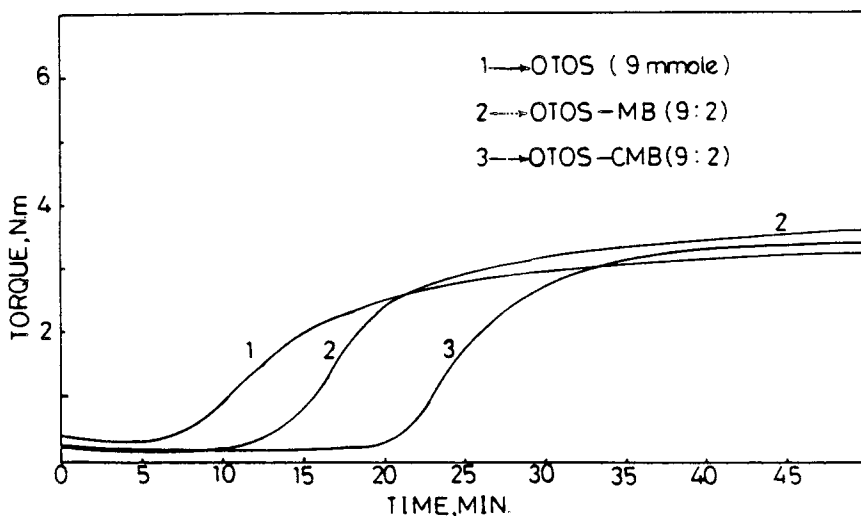


Fig. 1. Rheographs of NR gum stocks cured at 140°C: (1) OTOS (9 mmol); (2) OTOS-MB (9:2); (3) OTOS-CMB (9:2).

Aging experiment was carried out at  $100 \pm 1^\circ\text{C}$  in an oven having forced air circulation.

Various compounds formed in the reaction of OTOS-CMB heated at 140°C for 2 min both in the presence and absence of rubber were identified using hplc technique.<sup>7</sup>

## RESULTS AND DISCUSSION

OTOS has been arbitrarily selected to evaluate the effectiveness of CMB on this scorchy accelerator. Three mixes according to the recipes given in Table I were prepared, and the curing behavior of these compounds has been shown in Figure 1. It can be seen from the rheographs that MB has some retarding as well as activating effect upon OTOS. Incorporation of CMB in the mix (stock 3) enhances the scorch safety as is evinced from the  $t_2$  values provided in Table I, but the torque value in comparison with that obtained with MB is diminished to some extent. However, the  $R_\infty$  value obtained from the stock containing CMB (mix 3) is greater than that of mix 1. The results indicate that both MB and CMB react with OTOS.

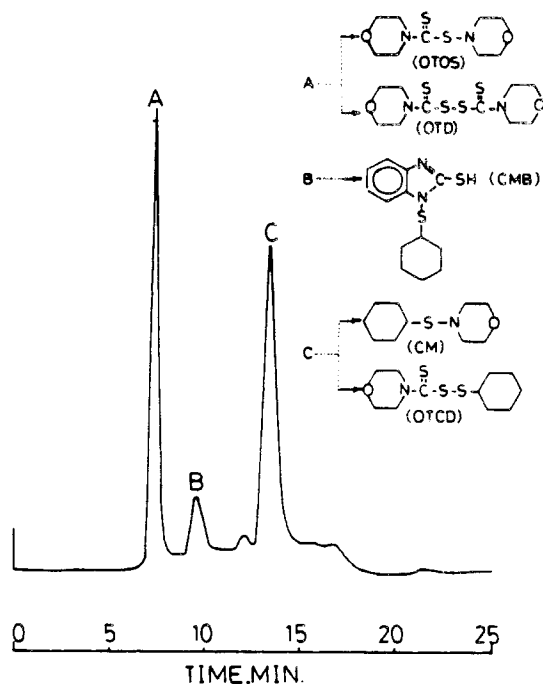


Fig. 2. High performance liquid chromatogram of OTOS (9 mmol) and CMB (2 mmol) combination when heated at 140°C for 2 min.

In order to gain insight into the reactions occurring in these systems, hplc studies were performed. OTOS was first allowed to react with CMB at 140°C in the absence of rubber. The results are depicted in Figure 2. It is evident from the chromatogram that CM, OTD, and OTCD are generated in the reaction. Carrying out the same reaction in the rubber medium large amount

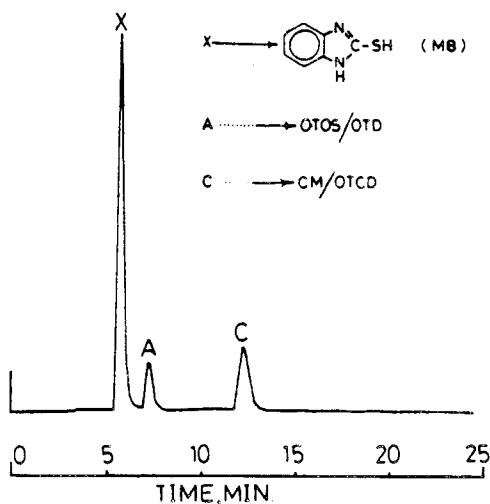
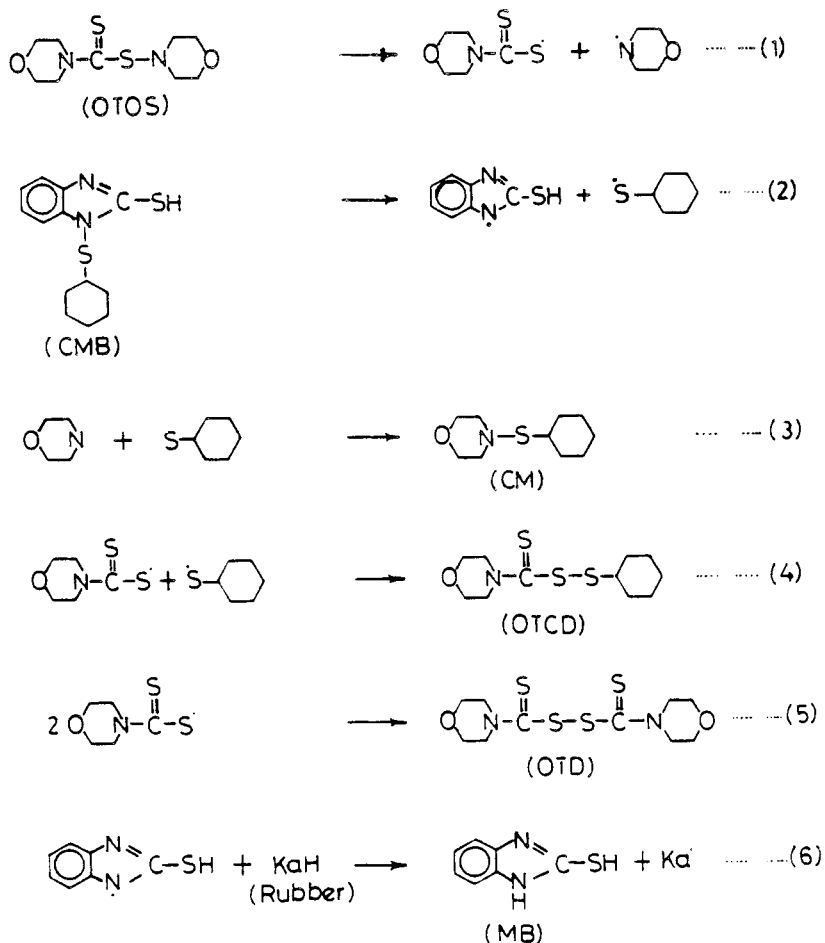


Fig. 3. High performance liquid chromatogram of undercured vulcanizate obtained at 140°C for 2 min: (A) OTOS/OTD; (B) CM/OTCD. Stock composition: NR, 100; zinc oxide, 5; stearic acid, 2; sulfur, 0.5; OTOS (9 mmol) and CMB (2 mmol).

of MB could be detected (Fig. 3). The following reaction scheme based on the free radical decomposition<sup>4,8</sup> of the reactants provides a probable route for the generation of various compounds:



Scheme 2. Formation of various products from OTOS-CMB reaction

As observed by us CM greatly influences the vulcanization reaction effected by thiocarbamylsulfenamide through the enhancement of scorch time.<sup>4</sup> Actually in both the reactions carried out in the absence or presence of rubber as mentioned earlier we have identified CM among other products. Also, from the reaction scheme it is apparent that CM is generated from the cyclohexylthio moiety present in CMB. Thus, it may be inferred that CMB behaves as a retarder.

The age resistance behavior<sup>9</sup> of CMB in terms of retention of modulus and tensile strength has been demonstrated through relevant data presented in Table II. It is seen that the modulus values of mixes 1-3 generally increase with the time of aging while the reverse is true for the tensile strength. The results indicate that the aging behavior of the vulcanizates obtained from stock 3 containing CMB is very similar to that of the vulcanizate obtained from stock 2 that contains MB. This is in good agreement with the finding of the earlier workers,<sup>10</sup> who have recently shown that MB modified chemically

TABLE II  
Physical Data of Cured Stocks Obtained at 140°C

Stock	Maximum torque $R_{\infty}$ (N m)	Scorch time $t_2$ (min)	Optimum cure time $t_{90}$ (min)	Modulus* (MPa)		Tensile strength (MPa)	
				Unaged	Aged 72 h	Unaged	Aged 96 h
1. OTOS 9	3.15	5.50	26.25	0.57	0.59	12.21	10.21
2. OTOS 9, MB 2	3.50	12.50	37.00	0.69	0.71	14.73	14.02
3. OTOS 9, CMB 2	3.30	17.50	37.00	0.66	0.69	15.50	15.01
							8.91
							13.82
							14.85

\* Modulus at 200% elongation.

at  $>NH$  and  $-SH$  functionalities retains its antioxidant property. As to the increase of modulus during aging (Table II), it is suggested that the vulcanizates were obtained at optimum cure times that record 90% of maximum torque developed during vulcanization. Evidently, the vulcanizates are not fully cured, and there remains the possibility for further vulcanization during aging. Actually, it had been shown that at  $100^{\circ}C$  the degree of chemical crosslinking in MBT-accelerated NR vulcanizates could be significantly enhanced<sup>11</sup> when vulcanization was carried out for a prolonged period. The chemical crosslinkages formed during aging are apt to increase the modulus of the vulcanizates. The increase in modulus during aging has also been observed by Haehl<sup>12</sup> in the presence of antioxygenic compounds and also by us<sup>2,9</sup> both in the presence and absence of antioxidants.

It is apparent from the results and discussion that CMB plays the dual role of a retarder as well as an antioxidant in the vulcanization of NR accelerated by OTOS.

The authors wish to record their indebtedness to Professor A. K. Chaudhuri for his valuable suggestions and thank the B. F. Goodrich Co., Monsanto Co., and Bayer (India) Ltd. for supplying Cure-rite 18, Santogard PVI, and Antioxidant MB, respectively. The authors are grateful to Mrs. Sumana Datta, Department of Organic Chemistry, for her help in various ways.

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Received October 23, 1986

Accepted February 23, 1987