

Prevulcanization Inhibitor of Sulfur-Free Thiuram Vulcanization

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Synopsis

On the basis of Mooney scorch measurements at 120°C and of continuous measurements of vulcanization in a Vuremo curemeter at 145°C, sulfenamides which function as inhibitors of the sulfur-free thiuram vulcanization have been investigated. It was found that the actual prevulcanization inhibitor is 2-mercaptobenzothiazole. Its formation from sulfenamides is activated by zinc dimethyldithiocarbamate since the vulcanization of rubber by thiuram disulfides in the presence of zinc oxide is always accompanied by the formation of zinc dithiocarbamate. It seems probable that the inhibition effect of 2-mercaptobenzothiazole is attributable to the formation of a complex with zinc dimethyldithiocarbamate which decreases the reaction rate in the initial steps of the sulfur-free thiuram vulcanization and thus causes the scorch delay.

INTRODUCTION

The acceleration/vulcanization characteristics of factory formulations in the rubber industry require control. Processing safety without undesirable changes in curing characteristics or vulcanizate properties is of prime importance in all compounded rubber stocks.

In this paper, we describe a class of compounds which function as inhibitors for the sulfur-free thiuram vulcanization. The role these compounds play in the chemistry of scorch delay will also be examined. The compounds are sulfenamides, derivatives of 2-mercaptobenzothiazole.

EXPERIMENTAL

Compounding

The mix formulation was natural rubber (pale crepe), 100.0 parts, zinc oxide, 5.0 phr, tetramethylthiuram disulfide, 3.0 phr, and 2-mercaptobenzothiazole and sulfenamides, variable. The specification¹⁻³ of the sulfenamides is given in Table I.

Mixing was by masterbatch technique on a laboratory mill with 600 × 300 mm rolls at 50°C. Mooney viscosity of natural rubber compounds was 10°ML (1 + 4) at 100°C. This, according to Wolstenholme,⁴ is equivalent to a number-average molecular weight 1.2×10^6 .

TABLE I
Specification of the Sulfenamides^a

Sulfenamide (abbreviation)	Chemical name	Melting point, °C	Trade name	Manufacturer
TBBS	N- <i>tert</i> -butyl-2-benzothiazole sulfenamide	105	Santocure NS	Monsanto Chemicals Limited
MBS	2-(4-morpholiniothio)-benzothiazole	80	Santocure MOR	
DCBS	N,N'-dicyclohexyl-2-benzothiazole sulfenamide	90	Vulkacit DZ	Farbenfabriken Bayer, AG, Leverkusen, West Germany
CBS	N-cyclohexyl-2-benzothiazole sulfenamide	94	Sulfenax CB	Chemické závody J. Dimitrova, n.p. Bratislava, Czechoslovakia
MBTS	2,2'-dithiobis(benzothiazole)	163	Pneumax DM	
MBT	2-mercaptobenzothiazole	172	Pneumax MBT	

^a From refs. 1, 2, and 3.

Measurement of Induction Periods and Rate Constants of Vulcanization

The rubber compounds were cured at 145°C on a Vuremo curemeter Type AC-01 (Metrimpex, Budapest, Hungary). The apparatus and curemeter measurements have been fully described in a previous publication.⁵

The extent of vulcanization was expressed in Vuremo units (torque) and plotted against time of cure. Thus, cure curves were obtained. The induction periods t_i and the rate constants k of the vulcanization were calculated in accordance with the method of Scheele⁶ proposing a first-order reaction from the linearized cure curves, where the logarithm of the extent of vulcanization is plotted against cure time.

Measurement of Network Chain Density

The ultimate extent of the vulcanization reaction was expressed as the network chain density γ , in moles/cm³. The time schedule for mixing, curing, swelling, and deswelling was standardized as far as possible.⁵

The swollen and deswollen weights were used to calculate the volume fraction of rubber v_r in the network swollen to equilibrium. For calculation of network chain density, the Flory-Rehner equation⁷ was used, with effective values of the natural rubber-toluene interaction parameter of 0.39 published by Meissner and Janáček.⁸

RESULTS AND DISCUSSION

The effect of increasing concentrations of the different types of sulfenamides on Mooney scorch is shown in Figure 1. 2-Mercaptobenzothiazole (MBT) has the greatest influence on the scorch delay process.

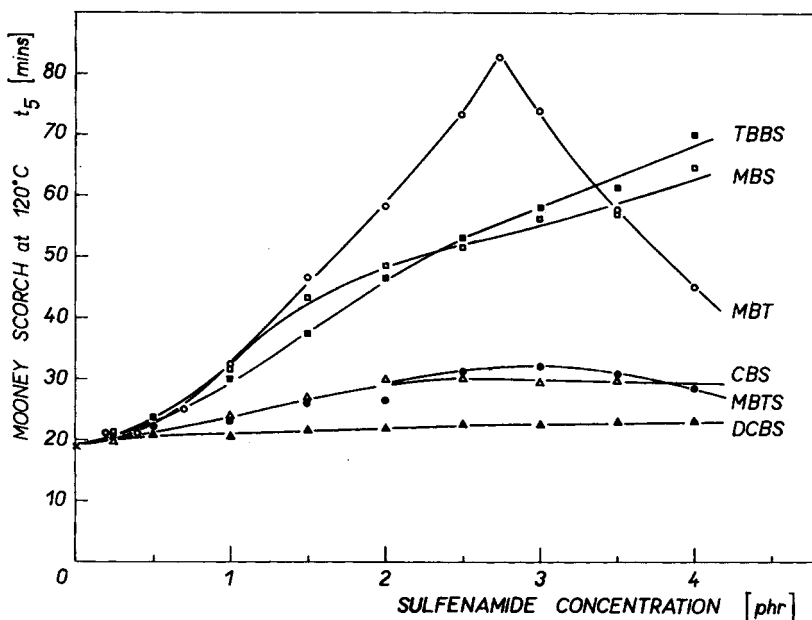


Fig. 1. Effect of sulfenamide concentration on Mooney scorch t_5 , at 120°C. Mix formulation: natural rubber (pale crepe), 100 phr; ZnO, 5 phr; TMTD, 3 phr; sulfenamide, variable.

In this case, the induction period of the vulcanization at 145°C (Fig. 2), as indicated by the cure curves, corresponds exactly to the Mooney scorch measurement (Fig. 1) determined at 120°C. It is mainly during this period of the vulcanization process that MBT is effective. Once cure starts, rates of crosslinking (Fig. 3) are essentially unchanged (slightly increased).

In the presence of sulfenamides, the rate constant of crosslinking is more significantly increased in the following order: 2,2'-dithiobis(benzothiazole) (MBTS), *N*-*tert*-butyl-2-benzothiazole sulfenamide (TBBS), 2-(4-morpholiniothio)benzothiazole (MBS), and *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS). Upon increasing the concentration of *N,N'*-dicyclohexyl-2-benzothiazole sulfenamide (DCBS), only the rate of crosslinking is slightly decreased.

The ultimate extent of crosslinking (Fig. 4) is increased in the presence of TBBS, MBTS, CBS, and MBS, unchanged in the presence of DCBS, and decreased in the presence of MBT.

These results lead us to suppose that MBT is the actual prevulcanization inhibitor of the sulfur-free thiuram vulcanization. This opinion is in accord with findings of Tarasova and co-workers⁹ that the formation of MBT from sulfenamides is activated by the presence of zinc dithiocarbamates in rubber mix, for it is generally accepted⁶ that the vulcanization of rubber by thiuram disulfides in the presence of zinc oxide is always ac-

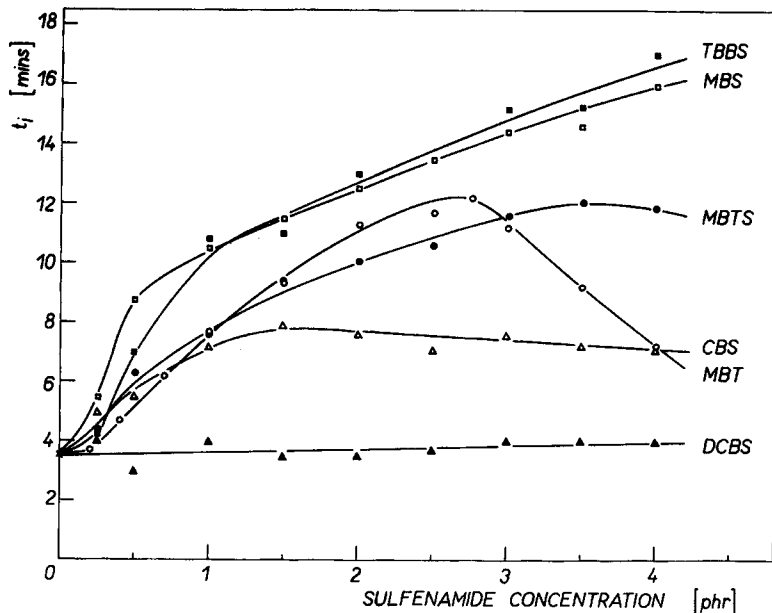


Fig. 2. Effect of sulfenamide concentration on induction period t_i of vulcanization at 145°C. Mix formulation as in Fig. 1.

accompanied by the formation of zinc dithiocarbamate. Two thirds of the thiuram disulfide which is introduced is converted during the vulcanization to zinc dithiocarbamate, regardless of the temperature, of the concentration of thiuram disulfide, of zinc oxide content, or of the chemical constitution of the 1,5-polyene under study.

The kinetics of the MBT formation depends on the structure of the substituents in the sulfenamides. Figure 1 shows that sulfenamides with

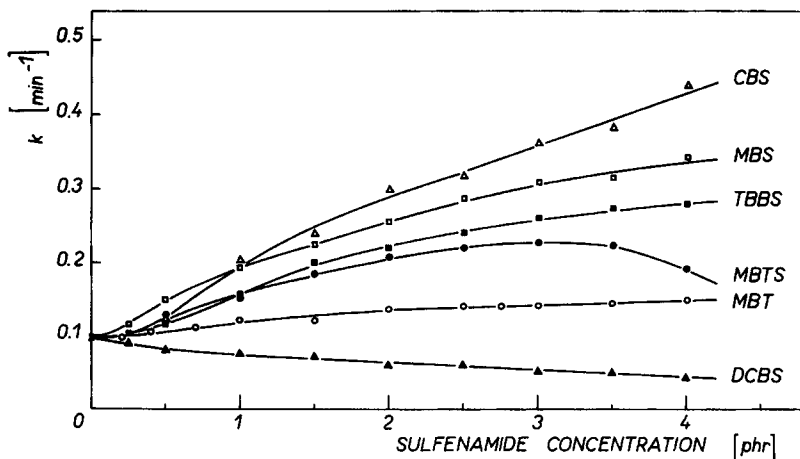


Fig. 3. Effect of sulfenamide concentration on rate constant k of vulcanization at 145°C. Mix formulation as in Fig. 1.

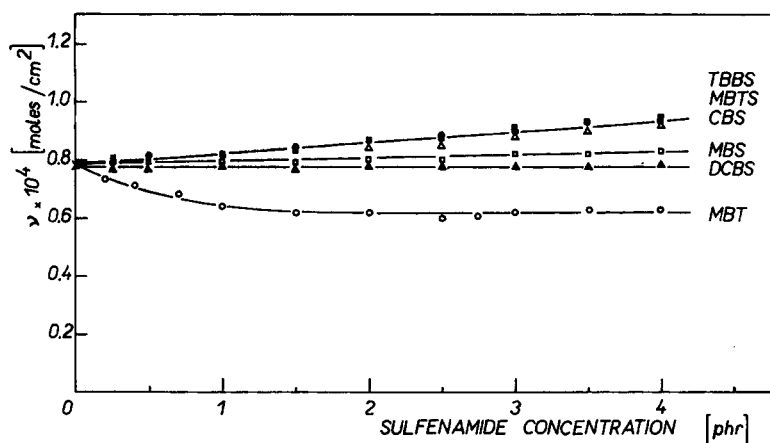


Fig. 4. Effect of sulfenamide concentration on ultimate extent ν of vulcanization, at 145°C. Mix formulation as in Fig. 1.

aliphatic substituents are the most active. The polar groups decrease the activity of the electrons of sulfur and nitrogen atoms⁹ and therefore slow down the formation of MBT.

Figure 5 shows that scorch delay over the range from 0.75 to 2.75 phr of MBT, as measured by Mooney scorch t_5 at 120°C, is directly proportional to the concentration of MBT.

Table II shows that since MBT is effective mainly during the inhibition period, it has the dramatic influence on processing safety without significant alteration of stress-strain properties of the vulcanizate. The thermal stability of vulcanizates containing MBT is even slightly improved.

The scorch delaying action of MBT can be explained on the basis of the mechanism of sulfur-free thiuram vulcanization.^{10,11} The initial step of

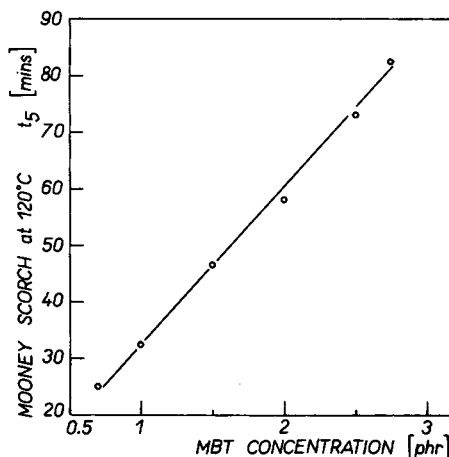


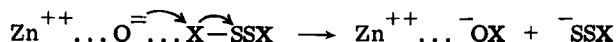
Fig. 5. Effect of MBT concentration on Mooney scorch t_5 at 120°C. Mix formulation: natural rubber, 100 phr; ZnO, 5 phr; TMTD, 3 phr; MBT, variable.

TABLE II
Influence of Concentration of MBT on Mooney Scorch and Physical Properties of Vulcanizates of Natural Rubber^a

MBT concentration	0 phr	1 phr	2 phr	3 phr
Mooney scorch t_5 at 120 °C, min	19.0	32.5	58.0	78.5
Cure time at 145 °C	50 min	45 min	50 min	55 min
Network chain density $\nu \times 10^4$, moles/cm ³	0.77	0.68	0.65	0.63
300% Modulus, kg/cm ²	14.0	13.5	13.0	12.5
Tensile strength, kg/cm ²	170	160	173	153
Ultimate elongation, %	687	758	775	760
Aged 3 Days at 100 °C				
Network chain density $\nu \times 10^4$, moles/cm ³	0.64	0.49	0.48	0.51
300% Modulus, kg/cm ²	10.0	10.0	11.0	12.0
Tensile strength, kg/cm ²	63	77	93	96
Ultimate elongation, %	633	682	717	705
Aged 8 Days at 100 °C				
Network chain density $\nu \times 10^4$, moles/cm ³	0.53	0.47	0.47	0.43
300% Modulus, kg/cm ²	5.0	10.5	10.5	10.5
Tensile strength, kg/cm ²	22.5	23.0	37.0	17.5
Ultimate elongation, %	620	440	538	410
Aged 14 Days at 100 °C				
Network chain density $\nu \times 10^4$, moles/cm ³	0.50	0.46	0.42	0.41
300% Modulus, kg/cm ²	4.5	10.0	10.0	9.5
Tensile strength, kg/cm ²	6.0	15.0	12.5	12.5
Ultimate elongation, %	455	387	353	358

^a ZnO, 5 phr; TMTD, 3 phr; MBT, variable.

the vulcanization is based on the nucleophilic attack of a basic oxyanion (from $\dots\text{Zn}^{++}\dots\text{O}^-\dots$) on the electrophilic thiocarbon atom of tetramethylthiuram disulfide (TMTD):

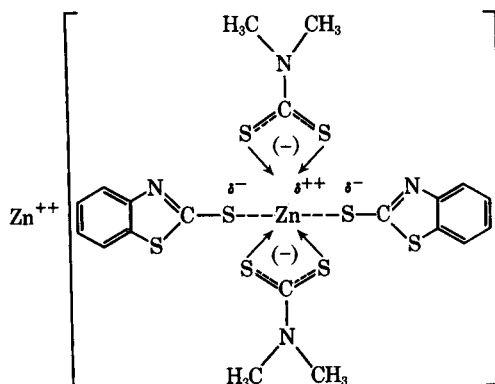


where X represents $(\text{CH}_3)_2\text{N}-\text{C}(\text{S})-$

The perthioanion SSX^- then preferentially attacks a disulfidic sulfur atom in TMTD to give tetramethylthiuram trisulfide. Further attack by the oxy anion from ZnO yields higher polysulfides. Interchange between these polysulfides and zinc dimethyldithiocarbamate (ZnDMDC) would then yield the actual sulfur-donating reagents which react with rubber macromolecules to give rubber-bound intermediate compound and finally cross links.

If MBT is added to the vulcanization system, it will engage in a Zn-DMDC interchange reaction to give complexes of MBT with ZnDMDC. The two-thirds yield of ZnDMDC⁶ from initial TMTD (3.0 phr) gives 0.83×10^{-2} moles per 100.0 g rubber. The maximum inhibition of vulcanization by MBT was found at a concentration of 2.75 phr (see Fig. 1), i.e., 1.65×10^{-2} moles MBT per 100.0 g rubber. The molar ratio MBT:ZnDMDC = 1.65:0.83 = 2:1, i.e., ZnMBT:ZnDMDC = 1:1, lead us to

suppose the following structure of the complex of MBT with ZnDMDC, which also is in accord with the views of Bateman and co-workers¹⁰:



It seems probable that the inhibiting effect of MBT on the sulfur-free thiuram vulcanization is attributable to the formation of these MBT-ZnDMDC complexes which slows down the interchange between the thiuram polysulfides and ZnDMDC and thus causes the scorch delay.

References

1. B. Meissner, in *Gumárenské suroviny*, I. Franta, Ed., SNTL/SVTL, Prague, 1963, pp. 211-247, 339-344.
2. Monsanto Chemicals Limited, *Monsanto Rubber Chemicals Handbook*, Oxley Press Limited, 1967, pp. 176-177.
3. Bayer A. G., *Die Vulkanisationsbeschleuniger der Sulfenamidklasse*, Farbenfabriken Bayer AG, Leverkusen, 1964, p. 92.
4. W. E. Wolstenholme, *Rubber Chem. Technol.*, **38**, 777 (1965).
5. V. Ducháček, *J. Appl. Polym. Sci.*, **15**, 2079 (1971).
6. W. Scheele, *Rubber Chem. Technol.*, **34**, 1306 (1961).
7. P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.*, **11**, 521 (1943).
8. B. Meissner and J. Janáček, *Coll. Czech. Chem. Commun.*, **26**, 3101 (1961).
9. Z. N. Tarasova, I. I. Eitingon, L. G. Senatorskaia, T. V. Fedorova, V. I. Chodzhaieva, and B. A. Dogadkin, *Vysokomol. Soedin*, **13**, 1962 (1971).
10. L. Bateman, C. G. Moore, M. Porter, and B. Saville, in *Chemistry and Physics of Rubber-Like Substances*, L. Bateman, Ed., Wiley, New York, 1963, pp. 449-561.
11. V. Ducháček, *Angew. Makromol. Chem.*, **23**, 21 (1972).

Received April 20, 1972

Revised June 16, 1972