

## SOME OBSERVATIONS ON THE MECHANISM OF CURE RETARDATION

P.N. Son\*

The B.F. Goodrich Company, Research and Development Center,

### 要 約

우수한 加黃지연제는 MBT와 빠른 速度로 反應하여 스크오치타임이 긴 加黃促進劑인 2-싸이클로헥실디티오벤조티아졸(CDB)을 生成한다. 이것은 CDB를 分離하여 고무에 配合한 後 加黃特性을 測定함으로써 確認된 것이다.

N-(싸이클로헥실티오)프탈이미드(CTP)와 같은 새로운 가황지연제는 加黃中 싸이클로헥실폴리설파이드(CPS)를 生成하며 이 CPS가 黃을 供給할 수 없으므로 一部の 黃이 낭비되므로 따라서 CTP를 使用할 때에는 追加의 黃을 使用하여야만 滿足할만한 여러 物性值를 갖춘 加黃體를 얻을 수가 있다. CDB의 늦은 加黃速度를 認知하므로써 CTP와 같은 가황지연제를 使用할 때에 加黃速度가 늦는 理由를 이해할 수가 있는 것이다.

### INTRODUCTION

In 1968, a new retarder called N-(cyclohexylthio) phthalimide (CTP) became commercially available<sup>1</sup>. And it was soon found that it outperformed all the previously known retarders such as N-nitrosodiphenylamine, phthalic anhydride, and benzoic acid. An equally interesting aspect of the new retarder is its chemistry of retardation. Thus, Leib and co-workers<sup>2</sup> advanced a retardation mechanism in which N-(cyclohexylthio) phthalimide traps out 2-mercaptobenzothiazole (MBT), forming 2-cyclohexyldithiobenzothiazole (CDB). By removing MBT, the autocatalytic conversion of sulfenamide to the crosslink precursor ArS<sub>2</sub>Ar (Ar denotes 2-benzothiazolyl group) is prevented. The present paper attempts to describe the fate of the disulfide CDB during cure and to amplify the chemistry of cure retardation by the new retarder CTP.

### EXPERIMENTAL

Scorch time was measured using the pressure-programmed BFG Cone Curometer<sup>3</sup> at 284°F. In order to eliminate sample slippage during measurement, a steady pressure (2 or 3 in-lb/min was used depending on the sample) was applied after a 3 unit rise from the minimum torque.

The Brabender Plasticorder was also used to measure scorch time. It was manufactured by C.W. Brabender Instruments, Inc.

The preparation 2-cyclohexyldithiobenzothiazole (CDB) was described in a previous paper<sup>4</sup>. N-(Cyclohexylthio) phthalimide (CTP) was purified by recrystallizing Santogard PVI(Monsanto Company) from heptane; m.P., 93-95°C.

N-tert-Butyl-2-benzothiazole sulfenamide(BBT S) was prepared via a conventional method using bleach as the oxidizing agent. 2-(4-Morpholiniothio) benzothiazole (OBTS) was recrystallized

\* 本學會 正會員(孫平來)

from benzene to give a water white crystal; m. p., 80-81°C.

Preparation of dicyclohexyl polysulfide. A 500 ml three-necked flask was charged with 130 ml of methylene chloride, 3.2g (0.1g-atom) of sulfur, and 0.2g of *n*-butylamine. To the above slurry was added 11.6g (0.1 mole) of cyclohexyl mercaptan in 20 ml methylene chloride at room temperature. The addition took 50 min. The mixture was refluxed for two h, during which time the reaction became a clear yellow solution. The resulting yellow liquid was fractionated to give 7.4g of a yellow liquid; b.p., 150°-154°C/0.35mm. The mass spectroscopy showed that the major component (>90 per cent) of the distilled fraction is dicyclohexyl trisulfide which is contaminated with di- and tetrasulfide.

*N*-(2-Benzothiazolythio)phthalimide (BTP).-2-Benzothiazole sulfenyl chloride was prepared by the known procedure—chlorination of 2,2'-benzothiazolyl disulfide.

To a stirred DMF (300ml) solution of phthalimide (44.1g, 0.3 mole) and triethylamine (40.4g, 0.4 mole) was added portion-wise 60.3g (0.3mole) of 2-benzothiazole sulfenyl chloride. The reaction temperature was controlled by an ice-water bath. The addition took 50 min. After stirring an additional hour, the resulting straw-colored slurry was filtered to remove the solid. The solid was washed with water, leaving 67g of pale pink solid. Recrystallization from EtOH-CHCl<sub>3</sub> followed by recrystallization from chloroform alone gave 10.2g of solid which has a m.p. of 159-172°C. The structure of the product was confirmed by its n.m.r. and infrared spectrum.

## RESULTS AND DISCUSSION

In order to find out the function of 2-cyclohexyldithiobenzothiazole (CDB) during the cure, it was prepared from 2-mercaptobenzothiazole (MBT) and 2-(cyclohexylthio) phthalimide (CTP)<sup>4</sup>. Somewhat surprisingly, the disulfide CDB was much less scorchy than 2-(4-morpholiniothio) benzothiazole (OBTS). But its cure rate was slower than OBTS, as shown in Figure 1 and Table II. The composition of the natural rubber

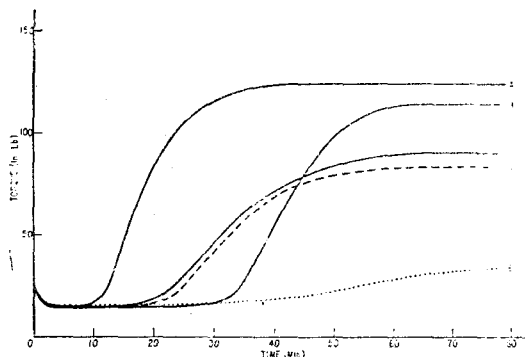


Fig. 1. Programmed BFG Cone Curometer curves (284°F) of stocks A through E.

masterbatch used for the evaluation is shown in Table I. Scorch time was obtained using the pressure-programmed BFG Cone Curometer<sup>3</sup> at 284°F. Stock D, which contains 1.1 Phr 2-cyclohexyldithio-benzothiazole (CDB), gave a scorch time of 18.2 min which is 140 per cent longer than that of Stock A which has an equimolar amount (1 phr) of OBTS.

We obtained a similar cure curve (Curve C) by substituting CDB in Stock D with 0.64 phr 2-mercaptobenzothiazole (MBT) and an equimolar amount of *N*-(cyclohexylthio) phthalimide (CTP). The scorch time of the above stock (Stock C) was 16.0 min. This suggests that the reaction between MBT and the new retarder CTP is very facile even in rubber.

The importance of the non-scorchy property of the incipient disulfide from MBT and the alkylthio moiety of the retarder becomes evident when *N*-(2-benzothiazolythio) phthalimide (BTP) is examined. Thus, it is not surprising that 1.2 phr of BTP in conjunction with 1.0 phr of OBTS resulted in a 41 per cent decrease in scorch time because the incipient disulfide resulting from MBT and BTP would be *bis* (2-benzothiazolyl) disulfide (MBTS), which is scorchier than OBTS. The foregoing observations indicate that a good retarder should not only react fast with

Table I. Masterbatch

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Natural rubber	100.0
HAF carbon black	50.0
Zinc oxide	5.0
Stearic acid	3.0
Sulfur	2.5

**Table II. Scorch Time of Various Stocks**

Stock <sup>a</sup>	A	B	C	D	E
OBTS <sup>a</sup>	1.00	1.00 <sup>c</sup>	—	—	—
CTP <sup>d</sup>	—	1.00	1.00	—	1.00
MBT	—	—	0.64 <sup>c</sup>	—	—
CDB	—	—	—	1.10 <sup>c</sup>	—
Scorch time <sup>e</sup> (284°F), min	7.6	23.0	16.0	18.2	33.0

<sup>a</sup> 160.5g of masterbatch of Table I plus ingredients shown in this Table.

<sup>b</sup> 2-(4-Morpholinthio) benzothiazole.

<sup>c</sup> Equimolar concentration.

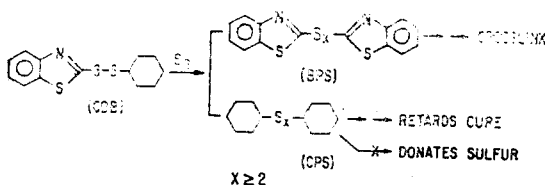
<sup>d</sup> N-(cyclohexylthio) phthalimide.

<sup>e</sup> Time required to raise torque 1 chart unit from the minimum torque.

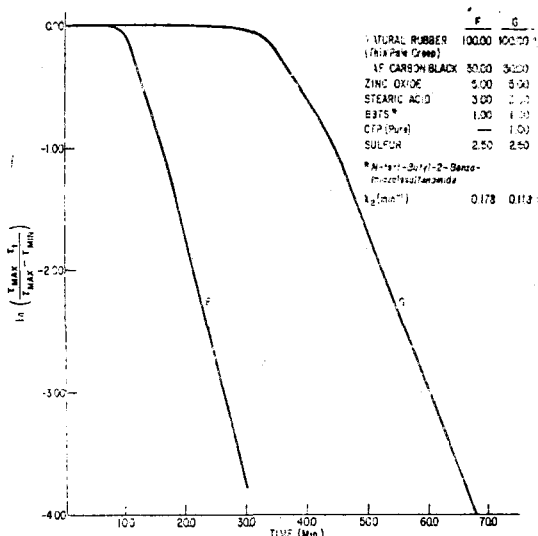
MBT but also should form a non-scorchy accelerator.

Since CDB is a fairly good accelerator, it is reasonable to assume that CDB (in the presence of sulfur) would form *bis*(2-benzothiazolyl) polysulfide (BPS) and cyclohexyl polysulfide (CPS). The assumption was indirectly supported by examining an aged sample of NS-50 which is a 50:50 mixture of *N-t*-butyl-2-benzothiazole sulfenamide and N-(cyclohexylthio) phthalimide. It contained, among other things, cyclohexyl disulfide<sup>5</sup>. BPS would react with rubber to form crosslinks as usual while CPS would influence scorch

**FUNCTION of CDB in CURE**



time. For example, in a natural rubber stock with 1 phr OBTS, 1 phr CPB extended scorch time 31 per cent (by Brabender) at 288°F. Although CPS is not as good a retarder as CTP, it is a potent retarder which should not be overlooked. Surprisingly, CPS is not a curing agent. Thus, in the absence of sulfur, a natural rubber stock containing 1 phr OBTS and 3.2 phr CPB (mainly trisulfide) showed very little sign of



**Fig. 2. First order plots of pressure-programmed BFG Cone Curometer data for stocks F and G at 284°F.**

cure (2.5 in-lb torque) after heating 125 min at 284°F. This may explain why the new retarder (CTP) causes low states of cure and requires additional sulfur in order to obtain comparable physical properties to those of the control.

This argument is further supported by evidence from the Curometer studies that the effect of retardation of cure by CTP is not confined only to the induction period, but also affects the cure rate of stocks containing the retarder. Using Coran's kinetic model<sup>6</sup> and the pressure-programmed BFG Cone Curometer<sup>3</sup>, we found that the retarder not only decreased the specific rate constant  $k_1$  but also  $k_2$  as shown in Figure 2. For example, the addition of 1.0 phr retarder CTP to the control Stock F brings about a decrease in the rate constant  $k_2$  from 0.178 min<sup>-1</sup> (Stock F) to 0.118 min<sup>-1</sup> (Stock G). Employing the known method<sup>6</sup>, other kinetic parameters were calculated and are listed in Table III. In order to show how each kinetic parameter of Stock G contributes toward the observed 16 min increase in scorch time, the scorch times of hypothetical Stocks 1-3 were calculated by changing one rate constant at a time. As shown by Stock 1 in Table III, the largest increase in scorch time (14 min) was obtained by substituting the  $k_1$  value of Stock F for the  $k_1$  value of Stock G. Only 2.1 min increase is possible by substituting the

Table III. Kinetic Parameters for Stocks F and G and Calculated Scorch Times for Hypothetical Stocks 1-6<sup>a</sup>

	$k_1, \text{min}^{-1}$	$k_2, \text{min}^{-1}$	$k_3/k_4'$	Scorch time, min	Change in scorch time, min
Stock F (control)	0.0410	0.178	22,500	8.0	—
Stock G (control+IphrCTP)	0.0017	0.118	7,790	24.0	+16.0
(% of Stock F)	(4.2)	(66.3)	(34.6)	(300.0)	
Stock 1	0.0017	0.178	22,500	22.0	+14.0
2	0.0410	0.118	22,500	10.1	+2.1
3	0.0410	0.178	7,790	5.7	-2.3
4	0.0017	0.118	22,500	30.1	+22.1
5	0.0017	0.178	7,790	17.6	+9.6
6	0.0410	0.118	7,790	7.1	-0.9

<sup>a</sup> Italicized figures are those of Stock G.

$k_2$  value of Stock F for that of Stock G. On the other hand, the decrease in  $k_4/k_3'$  (the quenching ratio) shortens the scorch time by 2.3 min (see the hypothetical Stock 3) rather than extending it. However, a quantitative interpretation of these data should be exercised with reservation. For the sum of the "change in scorch time" of

Stocks 1 through 3 is not equal to 16 min, which is the observed scorch time increase of Stock G. Stocks 4 through 6 further exemplify the non-additivity of change in scorch time. Here two rate constants are changed at a time.

Although the contribution of the quenching ratio ( $k_4/k_3'$ ) toward the extension of scorch time

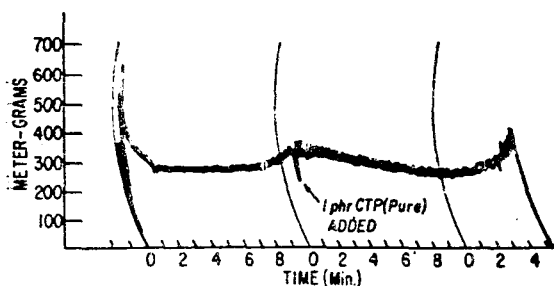


Fig. 3. A Brabender curve of stock A to which 1 phr CTP (pure) was added after a torque rise of two chart units at 150°C (stock temp.).

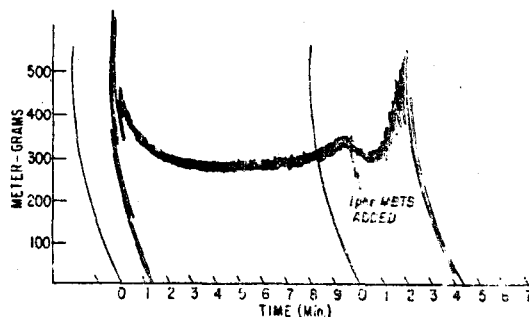


Fig. 5. A Brabender curve of stock A to which 1 phr MBTS is added after a torque rise of three chart units at 145°C (stock temp.).

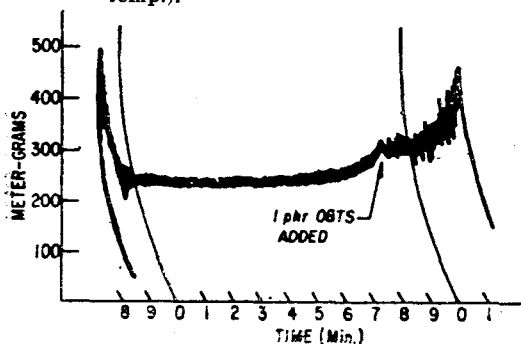


Fig. 4. A Brabender curve of stock A to which 1 phr OBTS is added after a torque rise of three chart units at 140°C (stock temp.).

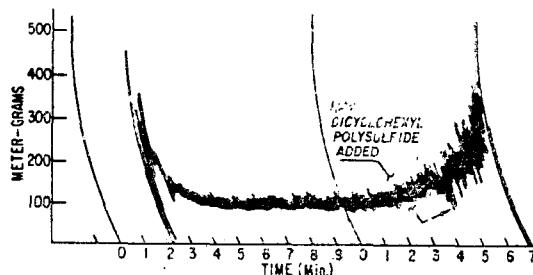


Fig. 6. A Brabender curve of stock A to which 1 phr dicyclohexyl polysulfide is added after a torque rise of three chart units at 142°C (bath temp.); scorch time, 11.0 min.

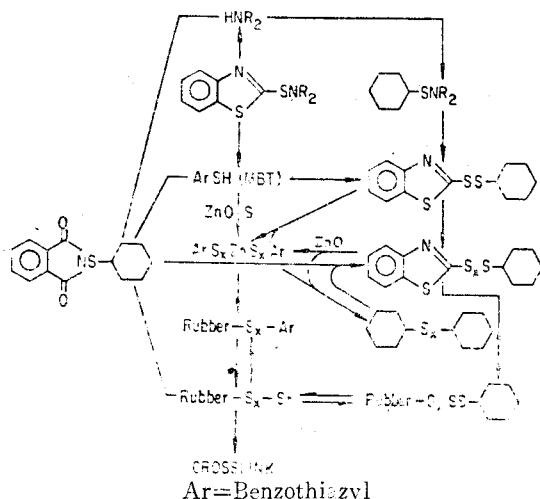
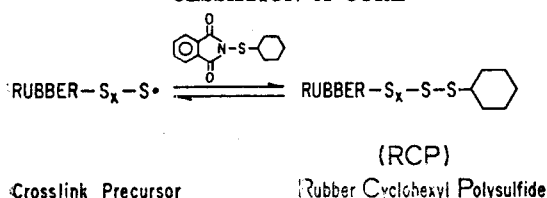


Fig. 7. Reaction scheme for cure retardation.

was found to be negative, the following study using the Brabender Plasticorder shows otherwise. Figure 3 shows how 1 phr of CTP can extend scorch time after the cure starts in. Thus, by adding 1 phr of CTP after a two unit rise on the chart at 150°C, more than 12 min extension of scorch time can be obtained. Similarly, 1 phr of MBTS stops crosslinking for one minute, while 1 phr of N-oxydiethylene-2-benzothiazole sulfenamide (OBTS) stops crosslinking for 3.2 min (see Figures 4 and 5). On the contrary, CPS failed to stop crosslinking, as shown in Figure 6. Thus, a retarder may or may not be able to stop crosslinking. However, those compounds which do stop crosslinking are not necessarily retarders in the conventional sense. Since the retarder (CTP) does not devulcanize cured stocks<sup>5</sup>, the immediate cessation of cure upon the addition of CTP seems possible only through the interception of the crosslink precursor by the retarder CTP. The resulting rubber cyclohexyl polysulfide (RCP) would regenerate crosslink precursors by simple thermal scission, and cure would resume when the retarder is depleted.

CESSATION of CURE



In addition, when benzothiazole sulfenamide was used with the new retarder CTP, a cyclohexylthioamine<sup>7,8</sup> would form and be involved in the retardation mechanism in a manner similar to that of CTP. These observations suggest that cure retardation by N-(cyclohexylthio) phthalimide (CTP) involves more than the removal of 2-mercaptobenzothiazole during the induction period.

SUMMARY

1. A good retarder reacts fast with MBT and forms a non-scorchy accelerator.
2. The decrease in cure rate ( $k_1$ ) is attributable to the slow cure rate of 2-cyclohexyldithiobenzothiazole (CDB).
3. Cyclohexyl polysulfides (CPS) and cyclohexylthioamine are believed to be also involved in the cure retardation.
4. The new retarder can stop crosslinking by intercepting the crosslink precursors.
5. Formation of cyclohexyl polysulfides and their lack of curing property may be responsible for the low state of cure when the new retarder is used.

These results are schematically summarized in Figure 7.

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