N-(Morpholinothio)imides as Curing Agents in Semiefficient Vulcanization Systems

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Synopsis

Semiefficient vulcanization systems (semi-EV) are often used when a stock requires good aging properties as well as good fatigue resistance. A partial replacement of sulfur in a conventional cure system with 4,4'-dithiobismorpholine or 2-mercaptabenzothiazyl 4-morpholino disulfide (BMD) is an example of semi-EV system. However, with BMD the scorch time is not always long enough for multisteps involved in the manufacturing of tires. Such new cure retarders as N-(cyclohexyl-thio)phthalimide or N, N'-bis(cyclohexylthio)oxanilide showed very little efficiency in BMD cure systems. This paper describes the usage of new curing agents, (N-morpholinothio)imides, which can overcome the disadvantage of scorchness in BMD cure system and provide excellent aging properties. This is rationalized by the formation of BMD during vulcanization. The facile formation of BMD from N-(4-morpholinothio)phthalimide (MTP) and 2-mercaptobenzothiazole (MBT) serves to illustrate the feasibility of *in situ* formation of BMD during cure and to explain long scorch time observed with N-(4-morpholinothio)imides.

INTRODUCTION

It is well known that both the thermal and oxidative aging characteristics of vulcanizates can be improved by using an efficient vulcanization (EV) system or semi-EV system.[1] These desirable aging properties are attributed to the presence of mono- and disulfidic crosslinks in the vulcanizates cured by EV or semi-EV systems. In contrast to a polysulfide crosslink, mono- and disulfide crosslinks are more thermally stable and undergo minimal crosslink modification during aging.

One way to achieve such desirable properties is to cure a stock with 2-ben-zothiazyl 4-morpholino disulfide (BMD) and low levels of sulfur. However, the BMD cure system lacks the scorch protection required for many applications. Moreover, neither N-(cyclohexylthio)phthalimide (CTP)[2] nor N,N'-bis(cyclo-hexylthio)oxanilide (BCTO)[3] shows an appreciable effect on the scorch time of BMD cure systems. This is true regardless of the level of sulfur used, as shown in Figure 1. The maximum increase in scorch time with one part CTP was only 35%, and this occurs only when three parts of BMD and no free sulfur was used. When two parts sulfur was used, scorch time was extended only 18%. Likewise, BCTO did not respond well in BMD cure systems. The poor performance of

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these retarders in BMD cure systems prompted us to design a cure system in which BMD can be formed during vulcanization.
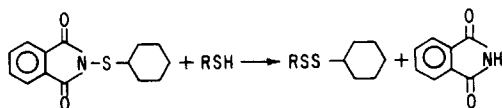
Recently, the facile formation of unsymmetrical disulfides from the reaction of N-(cyclohexylthio)phthalimide (CTP) with various mercaptans was described.[4,5] We thought that a similar reaction between N-(4-morpholinothio)-phthalimide[6] (MTP) and 2-mercaptobenzothiazole (MBT) would generate BMD:
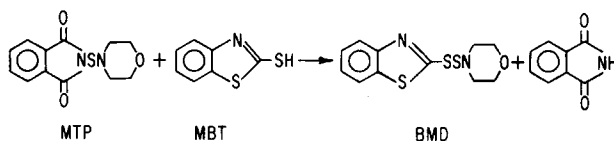
However, MTP was an unknown compound at the start of this work. In this paper, we describe the synthesis of MTP and similar compounds and determine their effectiveness as curing agents which can provide good scorch protection as well as good aging properties.
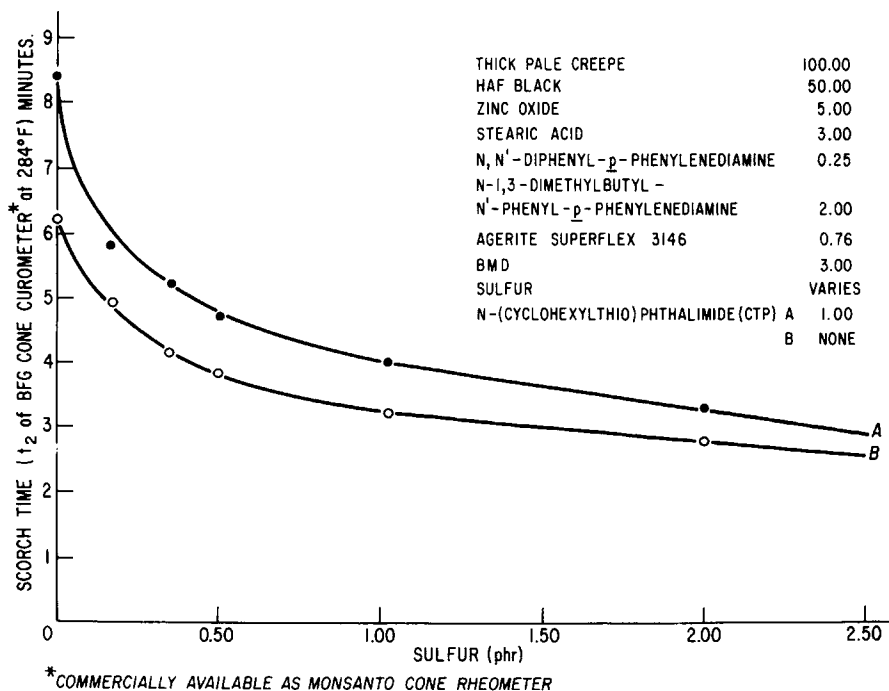

THICK PALE CREEPE	100.00
HAF BLACK	50.00
ZINC OXIDE	5.00
STEARIC ACID	3.00
N,N'-DIPHENYL-p-PHENYLENEDIAMINE	0.25
N-1,3-DIMETHYLBUTYL-	
N'-PHENYL-p-PHENYLENEDIAMINE	2.00
AGERITE SUPERFLEX 3146	0.76
BMD	3.00
SULFUR	VARIES
N-(CYCLOHEXYLTHIO)PHTHALIMIDE(CTP) A	1.00
B	NONE

*COMMERCIALLY AVAILABLE AS MONSANTO CONE RHEOMETER

Fig. 1. Effect of CTP on scorch time of a natural rubber stock with 2-benzothiazyl 4-morpholino disulfide (BMD) cure system.

EXPERIMENTAL

Instrument and Materials

Scorch time was measured by using the pressure-programmed BFG Cone Curometer (commercially available as Monsanto Cone Rheometer; see U.S. Patent 3,769,830 for the details) at 284°F. When the torque of a sample reaches 3 units above the minimum torque, 0.45 N·m (4 in.-lb) pressure was applied per minute. This is to eliminate the sample slippage during the measurement.

Carbon tetrachloride, tetrahydrofuran, and trichloroethylene were certified grade obtained from Fisher Scientific Company. N, N-Dimethylformamide was dried by molecular sieve. Dimethylacetamide (spectral grade), triethylamine, phthalimide, 2-imidazolidinone (Pract.), succinimide, hydantoin, o-benzoic sulfimide, and morpholine were purchased from Eastman Kodak Company and used without further purification. Oxanilide was either purchased from Eastman Kodak Company or prepared from oxalic acid and aniline.[7]

Synthesis of Curing Agents

N-(4-Morpholinothio)phthalimide (MTP). All glassware was flame dried before the reactants were charged. In a 1-liter, three-necked flask were placed 400 ml carbon tetrachloride and 47.2 g (0.2 mole) N, N'-dithiobismorpholine. The flask was equipped with a thermometer, a Dry Ice–acetone condensor with a drying tube, and a gas inlet adapter. The above solution was cooled to 0°C with stirring, and chlorine gas was introduced at the rate of 32.6 g/hr. A total of 14.6 g (0.205 mole) chlorine gas was introduced over a period of 27 min. During the chlorination, the pot temperature was maintained at 0 to −5°C. The resulting yellow liquid with a trace of white solid is crude 4-morpholinosulfenyl chloride. It was used for the second step of the reaction without further purification. (Caution! A violent reaction was recently reported during further work-up.[8])

In a 2-liter, three-necked flask were placed 500 ml tetrahydrofuran, 55.9 g (0.38 mole) phthalimide, and 40.5 g (0.4 mole) triethylamine. To this stirred mixture, the carbon tetrachloride solution of N-morpholinosulfenyl chloride solution was added dropwise. The addition rate was about 14 ml/min, and the temperature rose from room temperature to a maximum of 36°C during the addition. After completing the addition, the slurry was stirred for 3 hr and filtered. The solid was washed with water and dried to a constant weight. This crude product weighed 68.4 g and melted at 186–9°C. Recrystallization from ethanol–acetone gave 55.7 g of white solid, mp 212–217°C.

Additional crude product was isolated from the filtrate by adding about 200 ml ice water to the filtrate. (This step may be dangerous if there is any unreacted N-morpholinosulfenyl chloride left in the reaction mixture.) The second crop weighed 14.1 g and melted at 173–5°C.

The recrystallized sample showed the following elemental analysis:

ANAL. Calcd for $C_{12}H_{12}N_2O_3S$: C, 54.53; H, 4.58; N, 10.60; S, 12.13. Found: C, 54.76; H, 4.56; N, 10.66; S, 11.95.

Following the same procedure described above, MTP was prepared on a large scale (3.04 mole phthalimide), using DMF (3280 ml) as a solvent in the second step. After the usual work-up, both crops were washed with 1.7 liters ethanol

and dried to give 677.1 g (87.5% yield) of the desired product, mp 206–211°C. Thus, DMF is preferred solvent for the synthesis of MTP, because yields and melting points are higher than when THF is used.

Crude N,N'-Bis(4-morpholinothio)oxanilide (BMTO). Following the same procedure described above, 23.6 g (0.1 mole) N, N'-dithiobismorpholine was chlorinated in 120 ml trichloroethylene. A total of 7.3 g (0.103 mole) chlorine was added to a mixture of 22.8 g (0.095 mole) oxanilide, 20.2 g (0.2 mole) triethylamine, and 230 ml dimethylacetamide. During the addition, the pot temperature rose to 46°C. After stirring 1½ hr, the slurry was filtered and the solid was washed with water to give 36.2 g of crude product, mp 228–243°C. The IR spectrum of the crude product showed a small NH band at 3260 cm^{-1}, indicating the presence of unreacted oxanilide. Attempts were made to purify the product by recrystallization from common organic solvents without success.

ANAL. Calcd for $C_{22}H_{26}N_4O_4S_2$: C, 55.68; H, 5.52; N, 11.8. Found: C, 58.08, H, 8.63; N, 11.65.

1,3-Bis(4-morpholinothio)-2-imidazolidinone (BMTI). Following the same procedure described above, N-morpholinosulfenyl chloride was prepared from 125 ml trichloroethylene, 23.6 g (0.1 mole), N, N'-dithiobismorpholine, and 7.3 g (0.103 mole) chlorine. The resulting N-morpholinosulfenyl chloride was added dropwise to a mixture of 150 ml DMF, 8.2 g (0.095 mole) 2-imidazolidinone, and 20.2 g (0.2 mole) triethylamine. During the addition, the pot temperature rose to 51°C. After stirring an additional 1½ hr, the reaction mixture was worked up. The tan slurry was filtered. The solid was washed with trichloroethylene, then with water. After drying, the solid weighed 17.5 g, mp 200–208°C. A second crop was obtained by adding 400 ml ice water to the filtrate, followed by separation of a red layer and concentrating it to a pale-brown solid. Washing the solid with acetone gave a white solid which weighed 4.7 g. The elemental analysis of the first crop gave the following result:

ANAL. Calcd for $C_{11}H_{20}N_4O_3S_2$: C, 41.23; H, 6.29; N, 17.49. Found: C, 40.37; H, 6.29; N, 17.55.

N-(4-Morpholinothio)succinimide (MTS). As described earlier, N-morpholinosulfenyl chloride was prepared from 75 ml trichloroethylene, 11.8 g (0.05 mole) N,N'-dithiobismorpholine, and 3.65 g (0.0515 mole) chlorine. It was added dropwise to a mixture of 100 ml DMF, 9.4 g (0.095 mole) succinimide, and 10.1 g (0.1 mole) triethylamine. During the addition, an off-white slurry formed and the reaction temperature rose to 47°C. After stirring 2 hr, the slurry was filtered to remove water-soluble triethylammonium chloride. Solvents were removed from the filtrate by a flash-evaporator, then stirred into 300 ml ice water to form an off-white solid. The crude product weighed 10.8 g (52.4% yield). An analytical sample was prepared by dissolving a portion of the crude product in chloroform, then adding hexane with cooling, mp 123–130°C.

ANAL. Calcd for $C_8H_{12}N_2O_3S_1$: C, 44.43; H, 5.59; N, 12.95. Found: C, 44.25; H, 5.75; N, 12.93.

N,N'-Bis(4-morpholinothio)hydantoin (BMTH) and N-(4-Morpholinothio)hydantoin (MTH). The same amount of N-morpholinosulfenyl chloride used for the synthesis of MTS was prepared and added dropwise to a mixture of 100 ml DMF, 4.8 g (0.048 mole) hydantoin, and 10.1 g (0.1 mole) tri-

ethylamine. After completion of the addition, the reaction mixture was stirred for 2 hr. After the usual work-up, the filtrate was concentrated, using a flash-evaporator, and poured into 300 ml ice water. The resulting off-white solid was filtered and dried to give 10.0 g of crude product. It was recrystallized from hexane–chloroform, mp 127–155°C. A second recrystallization from carbon tetrachloride–benzene raised the melting point to 147–153°C. The NMR spectrum showed that the product consists of 64 mole % MTH and 36 mole % BMTH.

N-(4-Morpholinothio)-o-benzoic Sulfimide (MTBS). N-Morpholinosulfenyl chloride (0.2 mole) was prepared as usual and added dropwise to a mixture of 150 ml DMF 34.8 g (0.19 mole) of o-benzoic sulfimide, and 20.2 g (0.2 mole) triethylamine. The addition took 13 min, during which time the pot temperature rose to 46°C. After stirring an additional 1½ hr, the slurry filtered, and the isolated solid was washed with 400 ml water. After drying, it weighed 8.2 g, mp 151–157°C.

ANAL. Calcd for $C_{11}H_{12}N_2O_4S_2$: C, 43.99; H, 4.03; N, 9.33. Found: C, 43.06; H, 4.06; N, 9.07.

Synthesis of N,N'-Thiobismorpholine (TBM) from MTP and Morpholine

In a three-necked 500-ml flask were placed 11.5 g (.043 mole) MTP, 3.8 g (0.043 mole) morpholine, and 180 ml toluene. The mixture was heated with stirring to 100°C and maintained at that temperature for 5½ hr. Phthalimide (5.3 g) was removed by filtering the reaction mixture. Concentration of the filtrate left a solid, which was treated with benzene to remove benzene-insoluble phthalimide (1.4 g). A solid from the benzene filtrate recrystallized from benzene–hexane to give 3.5 g TBM, mp 113–6°C (lit.[9] mp 112°C). Both IR and mass spectra support the structure of N,N'-thiobismorpholine (TBM).

Synthesis of 2-Benzothiazyl 4-Morpholino Disulfide (BMD) from 2-Mercaptobenzothiazole (MBT) and N-(4-Morpholinothio)phthalimide (MTP)

In a three-necked 300-ml flask were placed 11.5 g (0.043 mole) MTP, 7.2 g (0.043 mole) MBT, and 180 ml toluene. The mixture was heated to 100°C with stirring and maintained at 100°C for 5 hr. The resulting slurry was filtered to remove phthalimide. The filtrate was concentrated to leave a solid, which was washed with hexane to give 12.03 g of solid (98.4% yield). Its IR spectrum is identical with that of commercial BMD (Morfax).

RESULTS AND DISCUSSION

Evaluation of MTP in Semi-EV Systems

Here, the objective is to find a cure system which gives good scorch protection with aging properties equal or better than those of a BMD cure system. This goal can be achieved by using a combination of MTP–OBTS–MBT–S, where OBTS stands for N-oxydiethylene-2-benzothiazylsulfenamide, MBT for 2-

TABLE I

Evaluation of MTP in Semi-EV System Which Consists of 2-Mercaptobenzothiazole and its Derivatives with Low Sulfur Level

Stock number	1	2	3	4	5	6[a]	7[a]
Masterbatch A	161.00	161.00	161.00	161.00	161.00	—	—
Masterbatch B	—	—	—	—	—	161.00	161.00
BMD	3.00	2.00	—	—	—	3.25	—
DTBM	—	1.10	—	—	—	—	—
OBTS	—	—	3.00	3.00	3.00	—	2.00
MBT	—	—	0.10	—	0.25	—	—
MTP	—	—	2.80	2.80	2.80	—	2.00
TMTM	—	—	—	—	—	—	0.25
Sulfur	0.50	0.50	0.50	0.50	0.50	0.50	0.65
BFG Cone Curometer at 284° F							
t_2, min	5.2	9.9	10.5	10.8	7.4	4.9	9.0
t_c, min	14.0	23.8	27.3	26.2	22.4	—	—
% Increase in scorch delay	—	90.4	101.9	107.7	42.3	—	73.1
Bloom on Cured ACS Sheet	none	slight	medium to heavy	medium to heavy	medium to heavy	none	none
Physical Properties							
Original							
300% Modulus, MPa	15.79	15.86	16.48	15.93	15.24	16.68	17.69
Tensile, MPa	27.44	28.34	26.34	25.44	28.13	28.35	27.66
Elongation, %	460	460	440	430	500	453	427
Aged 6 Days in 212° F Oven							
300% Modulus, MPa	17.86	15.17	18.41	—	17.17	19.63	17.98
Tensile, MPa	19.51	17.24	19.31	17.24	19.31	20.57	19.53
Elongation, %	330	340	320	310	340	312	315

[a] Aged 7 days in 212° F oven.

TABLE II
Recipes for Masterbatch A and B

Masterbatch A	
Pale crepe	100.00 phr
HAF carbon black	50.00
Zinc oxide	5.00
Stearic acid	3.00
N-1,3-Dimethylbutyl-N'- phenyl- p-phenylenediamine	2.00
Agerite, Superflex 3146	0.75
N,N'-Diphenyl-p-phenylenediamine	0.25
Total	161.00
Masterbatch B	
Natural rubber	70.00 phr
cis-Polyisoprene	30.00
HAF carbon black	50.00
Zinc oxide	5.00
Stearic acid	3.00
Antozite 67[a]	2.00
Agerite, Superflex 3146[b]	1.00
Total	161.00

[a] N-1,3-Dimethylbutyl-N'-phenyl-p-phenylenediamine.
[b] Diphenylamine–acetone reaction product.

mercaptobenzothiazole, and S for sulfur. A slight molar excess of both MTP and OBTS was used in stock 3 compared to the 3 phr BMD used for the control. The formulation shown as masterbatch A (Table II) was used for the evaluation, and all the stocks were cured at 286°F for 75 min. The results are shown in Table I.

Based on the data from stocks 3 and 5, it is clear that the MTP–OBTS–MBT–S cure system provides as good or better aging properties than the BMD–S (stock 1) or DTBM (4,4'-dithiobismorpholine)–OBTS–S (stock 2) system with improved scorch protection. It is also noteworthy that in the absence of MBT (see stock 4), the aging properties were inferior to those stocks (see 3 and 5) which contain varying levels of MBT. This suggests that the immediate formation of BMD from MBT and MTP at the onset of cure is essential to obtain excellent aging properties. As expected, as the level of MBT increased, the scorch time decreased. Consequently, the level of MBT can be varied according to the desired scorch time.

Unfortunately, stocks containing a high level of MTP tend to bloom after cure. We believe the bloom is due to phthalimide, which is a by-product of the reaction between MTP and MBT. Thus, we attempted to eradicate the bloom problem by reducing the level of MTP. In order to maintain equivalent aging properties, we found that MBT has to be replaced by tetramethylthiuram monosulfide (TMTM) when the MTP concentration is reduced substantially below 2.8 phr. Stocks 6 and 7 in Table I illustrate how far one has to reduce the amount of MTP before one can eliminate the bloom problem. Although no attempts were made to optimize the formulation, it appears that both MTP and TMTM are responsible for the bloom and that even a small increase in the level of either MTP or TMTM affects the bloom formation on the cured stock. For the evaluation,

TABLE III
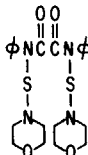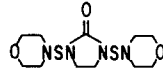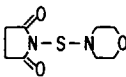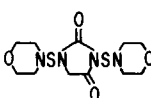Structures and Abbreviations of the MTP Analogues
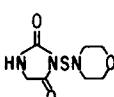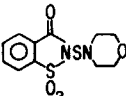
Abbreviation	Nomenclature	Structure	Remarks
BMTO	N,N'-Bis(4-morpholino-thio)oxanilide		
BMTI	1,3-Bis(4-morpholino-thio)-2-imidazolidinone		
MTS	N-(4-morpholino-thio)succinimide		
BMTH	N,N'-Bis(4-morpholino-thio)hydantoin		The reaction product consists of 36 mole per cent BMTH and 64 mole per cent MTH (by n.m.r.)
and	and	&	
MTH	N-(4-morpholino-thio)hydantoin		
MTBS	N-(4-morpholinothio)-o-benzoic sulfimide		Contaminated with o-benzoic sulfimide

TABLE IV
Comparisons of MTP and BMTO with BMD in Semi-EV System

	Stock number 8	9	10
Masterbatch B	161.00	161.00	161.00
BMD	3.00	—	—
MTP	—	2.80	—
BMTO	—	—	2.80
OBTS	—	3.00	3.00
MBT	—	0.25	0.25
Sulfur	0.50	0.50	0.50
BFG Cone Curometer at 284° F			
t_2, min	5.9	11.0	10.8
% Increase in scorch delay	—	86.4	83.1
Bloom on Cured ACS Sheet	none	medium	none
Physical Properties			
Original			
300% Modulus, MPa	15.54	15.70	16.66
Tensile, MPa	27.50	23.08	24.45
Elongation, %	461	397	404
Aged 7 Days in 212° F Oven			
300% Modulus, MPa	10.41[a]	17.98	17.81
Tensile, MPa	17.69	18.44	18.53
Elongation, %	293	307	310

[a] 200% Modulus.

TABLE V
Comparisons of MTP Analogues with BMD in Semi-EV System

Stock number	11 (control)	12	13	14	15	16
Masterbatch B	161.00	161.00	161.00	161.00	161.00	161.00
BMD	3.25	—	—	—	—	—
MTP	—	1.50	—	—	—	—
BMTI	—	—	1.50	—	—	—
MTS	—	—	—	1.50	1.50	—
BMTH and MTH	—	—	—	—	1.50	1.50
MTBS	—	—	—	—	—	1.50
OBTS	—	2.25	1.50	1.50	1.50	1.50
TMTM	—	0.25	0.30	0.30	0.30	0.30
Sulfur	0.50	0.80	0.80	0.80	0.80	0.80
BFG Cone Curometer at 284° F						
t_2, min	5.8	9.8	8.2	4.7	6.0	3.4
% Increase in scorch delay	—	68.9	41.4	−18.9	3.4	−41.4
Bloom on Cured ACS Sheet	none	none	none	slight	very slight	none
Physical Properties						
Original						
300% Modulus, MPa	16.97	18.54	20.28	18.53	18.16	16.35
Tensile, MPa	26.91	23.68	26.48	22.80	26.42	27.34
Elongation, %	420	363	375	351	405	440
Aged 7 Days in 212° F Oven						
300% Modulus, MPa	19.66	11.73[a]	12.32[a]	10.78[a]	10.83[a]	16.32
Tensile, MPa	20.18	15.38	14.36	13.73	16.98	19.44
Elongation, %	308	242	221	212	279	348

[a] 200% Modulus.

masterbatch B (Table II) was used and all the samples were cured at 284°F for 75 min.

Evaluation of Analogues of MTP in Semi-EV System

In order to eliminate the bloom problem associated with MTP, we synthesized and evaluated analogues of MTP. They are listed in Table III, and the results of their evaluation are summarized in Tables IV and V. All the samples were cured at 284°F for 75 min.

Of these compounds, N, N'-bis(4-morpholinothio)oxanilide (BMTO) gave the best results in terms of bloom and aging properties (see stock 10 in Table IV). This was followed by 1,3-bis(4-morpholinothio)-2-imidazolidinone (BMTI), which gave comparable aging properties to BMTO. The rest showed much less scorch protection than BMTO. Especially, N-(4-morpholinothio)-o-benzoic sulfimide (MTBS) gave only 3-min scorch time.

Evaluation of MTP in a Conventional Cure System

Similar to N,N'-dithiobismorpholine (DTBM), MTP by itself is a slow curing accelerator with a long scorch time (see stock 17). Although no explanation has been offered why dialkylamino sulfides should act as accelerators, it is reasonable to postulate that dialkylamino sulfides can form a thiyl radical, $R_2NS\cdot$, which is activated by the α-effect of the unshared electrons on the nitrogen atom. The thiyl radical would then attack rubber and form a new sulfenamide, rubber–SNR_2, which can form a crosslink.

In a conventional cure system (high sulfur–accelerator ratio), MTP provides longer scorch time and higher state of cure, as shown in Table VI. For example, when MTP was used in conjunction with OBTS, a 53.3% increase in scorch time was realized as demonstrated by stock 19. A mechanism by which MTP may cause scorch delay is discussed in the following section. Similar results were observed recently by J. Lawrence.[10]

Formation of 2-Benzothiazyl 4-Morpholino Disulfide (BMD) from 2-Mercaptobenzothiazole (MBT) and N-(4-Morpholinothio)phthalimide (MTP)

2-Benzothiazyl 4-morpholino disulfide (BMD) can be made in high yield by reacting MBT with an equimolar amount of MTP in a suitable solvent. In toluene at 100°C, the yield was as high as 98%. As shown in Figure 2, the progress of this reaction can be followed by UV spectrophotometry. At 100°C, the rate of reaction between MBT and MTP is slightly slower than the reaction between MBT and N-(cyclohexylthio)phthalimide (CTP), i.e., 10.0 min versus 7.7 min for $t_{30\%}$ (time required to react 30% of MBT).[11] Unlike the latter reaction, the reaction between MBT and CTP showed no clear-cut second-order kinetics. Nevertheless, we believe the mechanism by which BMD is formed would be very similar to the way cyclohexyl 2-benzothiazyl disulfide (CBD) is formed from MBT and CTP.

The facile formation of BMD from MBT and MTP lends supporting evidence to our suggestion that BMD can be formed *in situ* during vulcanization from
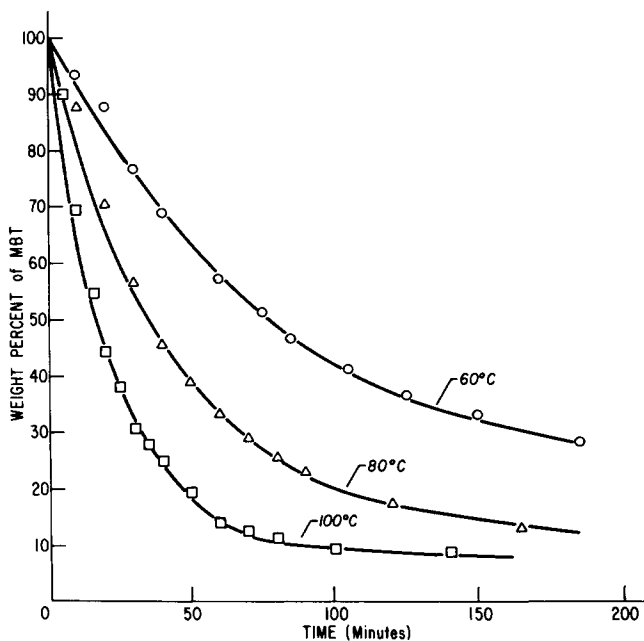
Fig. 2. Plots of weight percent of MBT as a function of time for the reaction of N-(4-morpholinothio)phthalimide (MTP) with an equimolar amount of MBT in toluene at various temperatures.

MTP (or its analogues) and MBT. If one uses a sulfenamide such as OBTS along with MTP, we expect the formation of BMD would be slower than with MBT. In addition, morpholine from OBTS would react with MTP to give N,N'-thiobismorpholine (TBM), which in turn would be involved as a curing agent in the vulcanization process:
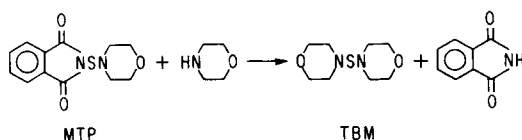

TABLE VI
Evaluation of MTP in Conventional Cure System

	Stock number 17	18	19
Masterbatch B	161.00	—	—
Masterbatch C[a]	—	158.00	158.00
MTP	3.00	—	1.00
OBTS	—	1.00	1.00
Sulfur	0.50	2.50	2.50
BFG Cone Curometer at 284° F			
ΔTorque, $N \cdot m$	5.99	10.03	12.47
t_2, min	12.9	6.0	9.2
t_c, min	33.8	20.1	29.4
% Increase in scorch delay	—	—	53.3

[a] Masterbatch C is same as masterbatch A, except C does not contain any antioxidants.

To what extent TBM contributes toward the overall good aging properties we obtain by using N-(morpholinothio) imides and OBTS, however, remains to be clarified. Formation of TBM from MTP and morpholine is not a clean reaction as described in the experimental section.

In summary, excellent aging properties can be obtained by using MTP or its analogues as curing agents in the presence of one or more conventional accelerator(s). The scorch protection of this new cure system is sufficient for most applications. Of six morpholinothioimides evaluated, both N-(4-morpholinothio)phthalimide (MTP) and N,N'-bis(4-morpholinothio)oxanilide (BMTO) appear to provide excellent scorch time and physical properties of both aged and unaged stocks.

NOMENCLATURE

BCTO	N,N'-bis(cyclohexylthio)oxanilide
BMD	2-benzothiazyl 4-morpholino disulfide
BMTI	1,3-bis(4-morpholinothio)-2-imidazolidinone
BMTO	N, N'-bis(4-morpholinothio)oxanilide
CTP	N-(cyclohexylthio)phthalimide
DTBM	4,4'-dithiobismorpholine
MBT	2-mercaptobenzothiazole
MTBS	N-(4-morpholinothio)-o-benzoic sulfimide
MTP	N-(4-morpholinothio)phthalimide
OBTS	N-oxydiethylene-2-benzothiazylsulfenamide
TMTM	tetramethylthiuram monosulfide
t_c	cure time, time (in minutes) to 90% of maximum torque
t_s	scorch time, time (in minutes) to 0.23 N·m (2 in.-lb) rise in torque

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