N,N′-Pentamethylenethiuram Disulfide- and *N,N′*-Pentamethylenethiuram Hexasulfide-Accelerated Sulfur Vulcanization. II. Relative Stability of *N,N′*-Pentamethylenethiuram Disulfide and Tetramethylthiuram Disulfide with Respect to Amine Formation

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ABSTRACT: The thermal stability of *N,N′*-dipentamethylenethiuram disulfide (CPTD) and tetramethylthiuram disulfide (TMTD) with respect to thiourea formation was compared. CPTD is stable at 120°C but decomposes to *N,N′*-dipentamethylenethiourea (CPTU) at vulcanization temperatures (140°C), while TMTD is stable to 190°C. These differences do not reside in residual impurities in the compounds. Amines, which catalyze thiourea formation, originate on decomposition of alkyldithiocarbamic acids, and these form more readily in CPTD than in TMTD since the abstraction by thiuram sulfenyl radicals of hydrogen from methylene in CPTD is easier than from methyl in TMTD. ZnO and the zinc-accelerator complex, zinc bis(pentamethylenedithiocarbamate), inhibit degradation by trapping the alkyldithiocarbamic acid before it can decompose to piperidene, that is, stabilization is achieved when the precursor to the amine, rather than the amine itself, is removed from the system. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2732–2739, 2000

Key words: thiourea, amine; tetramethylthiuram disulfide; *N,N′*-dipentamethylenethiuram disulfide; thermal stability

INTRODUCTION

The literature differs regarding the thermal stability of various alkylthiuram disulfide accelerators. Coleman et al.[1] and Dogadkin and Shershnev[2] reported that tetramethylthiuram disulfide (TMTD) degrades to tetramethylthiourea (TMTU) at vulcanization temperatures, while McGill and coworkers[3–6] reported no such degradation with either tetramethylthiuram monosulfide (TMTM) or TMTD, TMTU forming only at 190°C. It has been suggested that these discrepancies may relate to the presence of an amine impurity that can give rise to a catalytic reaction resulting in the complete decomposition of TMTD to TMTU, the impurity being trapped in closed systems, but escaping from where the system is not completely sealed.[7] In the presence of ZnO, thiourea does not form, even at 200°C,[3–5] although on heating TMTD/ZnO for 16 h at 140°C, TMTU was reported.[8] In a previous article in this series,[9] it was shown that *N,N′*-dipentamethylenethiuram disulfide (CPTD) and *N,N′*- dipentamethylenethiuram hexasulfide (CPTP6) are much less stable than is TMTD and that complete decomposition to *N,N′*-dipentamethylenethiourea (CPTU) and CS_2 occurs at vulcanization temperatures (140°C). ZnO prevents degradation.[9]

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Table I Acronyms Used

Acronym	Name
CPTD	*N*,*N'*-Dipentamethylenethiuram disulfide
CPTM	*N*,*N'*-Dipentamethylenethiuram monosulfide
CPTP	*N*,*N'*-Dipentamethylenethiuram polysulfide
CPTP6	*N*,*N'*-Dipentamethylenethiuram hexasulfide
CPTU	*N*,*N'*-Dipentamethylenethiourea
dma.dmtc	Dimethylammonium dimethyldithiocarbamate
Hdmtc	Dimethyldithiocarbamic acid
Hpmtc	Pentamethylenedithiocarbamic acid
MBT	2-Mercaptobenzothiazole
pip.pmtc	Pentamethyleneammonium pentamethylenedithiocarbamate
TMTD	Tetramethylthiuram disulfide
TMTM	Tetramethylthiuram monosulfide
TMTP	Tetramethylthiuram polysulfide
TMTU	Tetramethylthiourea
ZDMC	Zinc bis(dimethyldithiocarbamate)
ZPD	Zinc bis(pentamethylenedithiocarbamate)
ZPD(pip)	Piperidene-zinc-di-*N*-pentamethylenedithiocarbamate

On vulcanization, thioureas are commonly found in the extractable by-products of the reaction. This has been interpreted[10] as resulting from the attack by dimethylamine, formed on the decomposition of dimethyldithiocarbamic acid (Hdmtc) on TMTD, although it has also been suggested that TMTU may result from the vulcanization process itself.[11] Thioureas do not form in compounds containing ZnO that can trap Hdmtc.[1,10–13]

The decomposition of accelerators in compounds at vulcanization temperatures will decrease the amount of the accelerator available for vulcanization. This article compares the relative stability of TMTD and CPTD, identifies the agent responsible for degradation, and examines the effect of zinc compounds in preventing degradation.

EXPERIMENTAL

The materials used and compounds synthesized for the qualitative and quantitative analyses by HPLC of the reaction intermediates and products were detailed earlier[9] and the HPLC, DSC, and TG procedures were described.[9,14] Piperidene-zinc-di-*N*-pentamethylenedithiocarbamate [ZPD(pip)] was synthesized as described in the literature.[15]

ANAL. Calcd: C, 43.35%; H, 6.63%; N, 8.92%. Found: C, 44.33%; H, 6.63 %; N, 8.82%.

In the figures and tables, the concentrations of the reactants, intermediates, and products are expressed in terms of the initial concentration of the reactant. Acronyms are listed in Table I.

RESULTS AND DISCUSSION

Effect of Zinc Compounds on Thiourea Formation

HPLC analysis of TMTD, held at 140°C in sealed glass ampules for 120 min, showed no TMTU and only TMTM (29 mol %), TMTD (36 mol %), and tetramethylthiuram polysulfides (TMTP) (40 mol %). Kruger and McGill[4] and also Geyser and McGill[5] reported only TMTM, TMTD, and TMTP in isothermal studies at 150°C. By contrast, it was shown in the first article in this series[9] that CPTU is one of the major decomposition products of *N,N'*-dipentamethylenethiuram monosulfide (CPTM), CPTD, and CPTP6 at 140°C, the accelerators being stable only below 120°C. DSC studies[9] showed the accelerated formation of CPTU above 150°C, indicating the lower stability of CPTD compared to TMTD. The presence of ZnO in CPTD and CPTP6 mixtures suppressed the formation of CPTU, and DSC studies showed no CPTU even at 195°C and no degradation of *N,N'*-dipentamethylenethiuram polysulfides (CPTP), leading to CPTU, was found in isothermal studies at 140°C over a 25-min period.[9]

A comparison of TMTU formation in the absence and presence of ZnO was made by heating

Table II Mass Loss and HPLC Analysis of Reaction Products Found on Heating CPTD/ZPD (1.0:0.1 Mol Ratio) at 140°C

Time (min)	Mass Loss (%)	CPTU (mol %)	CPTM (mol %)	CPTD (mol %)	ZPD (mol %)
0	0	0	1	78	19
5	0.12	0	31	38	23
10	0.35	0	32	38	23
15	0.64	0	30	33	26
20	0.58	0	27	31	23

samples of TMTD and TMTD/ZnO in a DSC at 5°C/min. In the absence of ZnO, the decomposition of TMTD to TMTU occurred at 190°C, where 60 mol % TMTU, 5 mol % sulfur, and 11.9% mass loss was observed. TMTD/ZnO (1.0:1.0 mol ratio) heated to 190°C revealed a mass loss of 5.9% and no TMTU formation, only TMTM, TMTD, and zinc bis(dimethyldithiocarbamate) (ZDMC). The last readily forms at these temperatures although not at vulcanization temperatures as discussed earlier.[3,4,12] The presence of ZnO, therefore, inhibited the formation of TMTU. However, on heating for extended periods (16 h) at 140°C, TMTU formation, in addition to ZDMC in TMTD/ZnO (1.0:2.0 mol ratio), was reported.[8] TMTD was also found to decompose quantitatively into TMTU under the same conditions.

Zinc bis(pentamethylenedithiocarbamate) (ZPD) may be added to compounds as an accelerator or it may form *in situ* during vulcanization, where it results from the interaction of pentamethylenedithiocarbamic acid (Hpmtc) with ZnO, as will be discussed in a later article in this series. ZDMC formation in TMTD vulcanizates by the interaction of Hdmtc with ZnO was demonstrated.[10,11,16]

ZPD is stable and was found not to decompose at vulcanization temperatures. On heating CPTD/ZPD (1.0:1.0 mol ratio) in the DSC at 5°C/min, CPTU formation was delayed to higher temperatures, 11 mol % CPTU being detected at 170°C, and 43 mol %, at 180°C. When ZPD was not present, 10 mol % CPTU was found at 155°C.[9] CPTP6/ZnO (1.0:1.0 mol ratio) mixtures also showed the formation of only 1–6 mol % CPTU between 150 and 180°C, with more rapid decomposition of CPTP above 180°C (27 mol % CPTU). Even when the ZPD loading in the mix was decreased to a CPTD/ZPD mol ratio of 1.0:0.1, essentially no mass loss (0.6% after 20 min at 140°C) and no CPTU formation occurred (Table II).

Amines in the Formation of Thiourea

Amine complexes of ZPD are known and the possibility of ZPD preventing CPTU formation by its trapping of the amine was investigated. ZPD(pip) was synthesized as described and TG revealed that compared to ZPD, which was thermally stable (Fig. 1), ZPD(pip) underwent a mass loss, commencing at 75°C with complete decomposition to ZPD by 125°C. The 17.2% mass loss corresponds well with the 18.1 mass % piperidine in ZPD(pip). Heating CPTD/ZPD(pip) (1.0:0.1 mol ratio) resulted in the rapid decomposition of CPTD to CPTU (Table III), supporting the contention that amines, such as dimethylamine[7] and piperidine, can lead to thiourea formation, while at the same time showing the inability of ZPD to trap amines at vulcanization temperatures.

Thus, while the presence of ZnO[9] and/or ZPD delays the onset of the decomposition of CPTD to CPTU to higher temperatures and inhibits it at vulcanization temperatures (Table II), ZPD cannot prevent decomposition when piperidine is present (Table III). It is argued below that, since ZPD cannot trap piperidine at vulcanization tem-

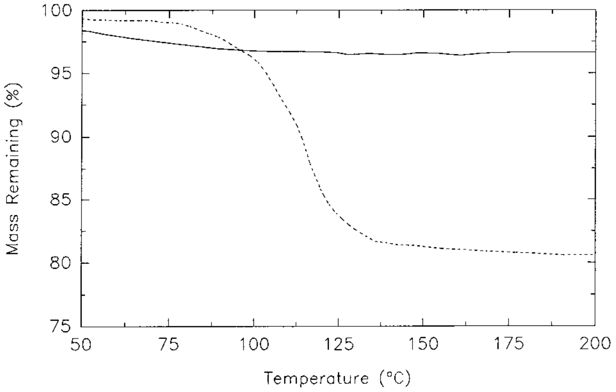


Figure 1 TG scan of ZPD and ZPD(pip) at 5°C/min: (—) ZPD; (– –) ZPD(pip).

Table III Mass Loss and CPTU Formation on Heating CPTD/ZPD(pip) (1.0:0.1 Mol Ratio) at 140°C

Time (min)	Mass Loss (%)	CPTU (mol %)	CPTM (mol %)	CPTD (mol %)	ZPD (mol %)
5	0.4	39	15	19	21
10	8.2	78	9	7	18
15	10	88	0	0	11
20	9.6	98	0	0	8

peratures [the ZPD–piperidine complex decomposes above 75°C (Fig. 1)], and since ZPD and ZnO inhibit CPTU formation, they do so by removing a precursor of piperidine, rather than piperidine itself. Furthermore, amines derived from alkylthiuram disulfide accelerators (TMTD and CPTD) are relatively volatile and would readily escape from the accelerator during storage after manufacture. Thus, it is more likely that amines are generated in the accelerator on heating and that ZnO and ZPD inhibit thiourea formation by removing the precursor from the system.

Alkyldithiocarbamic Acids in the Formation of Thiourea

It has been suggested previously that in vulcanizates dimethylamine, from the decomposition of Hdmtc, formed during the vulcanization of IR/TMTD/sulfur, was responsible for the formation of TMTU.[10] In a study of the interaction between TMTD and 2-mercaptobenzothiazole (MBT),[17] the presence of TMTU in TMTD/MBT (1.0:1.0 mol ratio) mixtures was reported at 160°C compared to 190°C for TMTU formation in TMTD alone. From a series of TG and open- and closed-pan DSC experiments, it was concluded that Hdmtc, formed from an interaction between TMTD and MBT and at higher temperatures, decomposed to dimethylamine and CS_2. TMTU was reported to form from an interaction of dimethylamine with CS_2 liberated on Hdmtc decomposition, as well as from an interaction between dimethylamine and TMTD. Tuang et al.[18] investigated the influence of temperature, the accelerator ratio, as well as the presence of other vulcanization ingredients on dimethylamine evolution from mixtures of TMTD and MBT. They found that more dimethylamine evolved when MBT was present in larger amounts.

TMTD/MBT (1.0:0.1 mol ratio) was heated at 10°C/min in a TG. The rapid mass loss, commencing at 90°C, indicated the escape of volatiles identified with Hdmtc (Fig. 2). TMTD and MBT were dried under a vacuum for 48 h and, on heating separately, did not show any mass loss at 100°C. Rapid evaporation of the sample occurred above 150°C. DSC and TG studies by Giuliani and McGill[17] on TMTD/MBT (1.0:1.0 mol ratio) also showed that a rapid mass loss commenced at 95°C in open systems, with the formation of TMTU and elemental sulfur in closed systems.

TMTD/MBT (1.0:0.1 mol ratio) was heated in open and closed DSC pans at 10°C/min. In samples heated in closed pans, large amounts of TMTU formed (Table IV), but no TMTU or sulfur was detected at any stage where the evaporation of volatiles was not restricted (Table V). The amounts of thiuram sulfides present at similar temperatures clearly differed, indicating that a different reaction had taken place.

TMTU formation was detected at 160°C in closed DSC pans, coinciding with the second mass loss (Fig. 2), whereas no TMTU was detected in open DSC pans at 160°C. TMTU is relatively volatile and was separated from other curatives *in vacuo* at 60°C by Moore and Watson,[19] and one

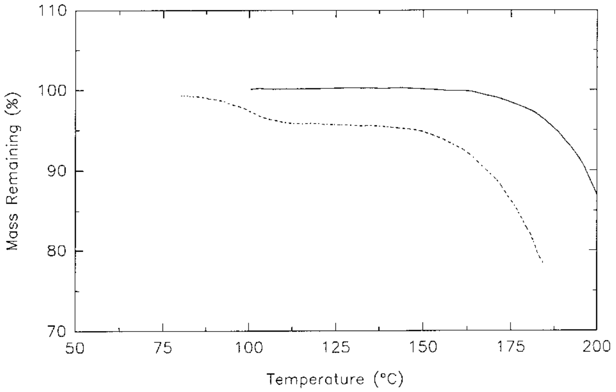


Figure 2 TG scan of TMTD/MBT (1.0:0.1 mol ratio) at 10°C/min: (—) TMTD; (– –) TMTD/MBT.

Table IV HPLC Analysis of Reaction Products Formed on Heating TMTD/MBT (1.0:0.1 Mol Ratio) Encapsulated in Closed DSC Pans at 10°C/Min

Temperature (°C)	TMTU (mol %)	TMTM (mol %)	TMTD (mol %)	TMTP (mol %)	Sulfur (mol %)
140	0	23	33	9	0
160	32	11	17	19	3
170	81	0	2	0	15

may argue that evaporation would explain the absence of TMTU. However, the simultaneous liberation of sulfur, which is less volatile, would accompany TMTU formation and should have been detected. During open-pan heating of TMTD/MBT, Hdmtc, formed in the exchange reaction between TMTD and MBT,[17] may evaporate or may decompose to dimethylamine and CS_2 and these would then evaporate, prior to interaction with TMTD; therefore, no TMTU or sulfur was detected. The less ready escape of volatiles from closed DSC pans will allow their interaction with TMTD to form TMTU.

Heating CPTD with MBT should liberate Hpmtc, which, if it decomposed, would give piperidine. The latter is less volatile than is dimethylamine. TG analysis on CPTD/MBT (1.0:0.1 mol ratio) revealed a mass loss commencing at 100°C (Fig. 3) with small amounts (3–5 mol %) of CPTU detected at 120 and 130°C (Table VI). At 150°C, 23 mol % CPTU was found, compared to only 10 mol % CPTU found in CPTD heated to 155°C on its own.[9] Decomposition of Hpmtc to piperidine and CS_2 would account for CPTU formation detected on HPLC analysis and the mass loss observed during TG analysis.

The above experiments show that alkyl dithiocarbamic acids are unstable at vulcanization temperatures, their decomposition leading to amines that can catalyze thiourea formation as depicted below[7]:

$$\mathrm{C_5H_{10}NC(S)SH \rightarrow C_5H_{10}NH + CS_2}$$

$$C_5H_{10}NC(S)SSC(S)NC_5H_{10} + C_5H_{10}NH \rightarrow C_5H_{10}NC(S)NC_5H_{10} + C_5H_{10}NC(S)SH + S \quad (1)$$

Alkylammonium Dithiocarbamates in the Formation of Thiourea

Alkylammonium dithiocarbamates were reported[11,20] in the products extracted from model compound vulcanizates. When a mixture of CPTD/pip.pmtc (1.0:0.2) was encapsulated in a DSC pan and held at 140°C for short periods, CPTU readily formed in large quantities (Table VII). Within 10 min, 94 mol % CPTU and 10 mol % sulfur formed with a concomitant mass loss of 14.9%. During thermal decomposition of CPTD, less than 20 mol % CPTU formed during the first 10 min of heating.[9] The presence of pip.pmtc accelerates the decomposition of CPTD to CPTU, and this can be attributed to the catalytic decomposition of CPTD by piperidine.

Mechanism of Thiourea Formation

The catalytic decomposition of TMTM and TMTD by amine, present as an impurity, has been put forward as the most probable route to TMTU for-

Table V HPLC Analysis of Reaction Products Formed on Heating TMTD/MBT (1.0:0.1 Mol Ratio) in Open DSC Pans at 10°C/Min

Temperature (°C)	TMTU (mol %)	TMTM (mol %)	TMTD (mol %)	TMTP (mol %)	Sulfur (mol %)
120	0	0	74	2	0
140	0	5	73	5	0
160	0	25	36	22	0
170	0	22	27	22	0
180	0	18	22	21	0

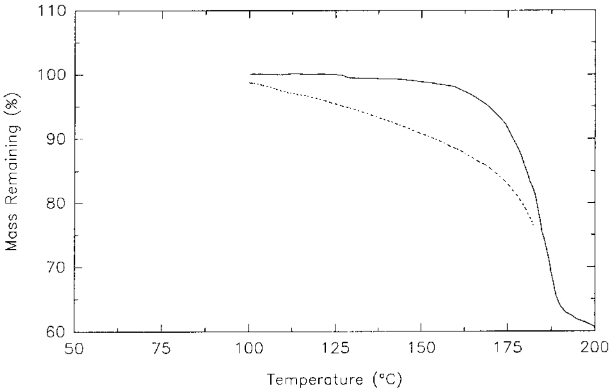


Figure 3 TG scan of CPTD/MBT (1.0:0.1 mol ratio) at 10°C/min: (—) CPTD; (– –) CPTD/MBT.

mation .[7] The data presented above support the contention for amine-catalyzed decomposition of TMTD and CPTD to the corresponding thioureas, but it is argued that the amine is formed prior to decomposition, rather than it being present as an impurity. It is evident from isothermal studies[9] of CPTM, CPTD, CPTD/sulfur, and CPTP6 that a short induction period (3–4 min) applies before CPTU formation. This indicates the formation of an agent that initiates decomposition; if an impurity were present, a delay should not be experienced. Decomposition of CPTD and TMTD can be delayed (prevented) by the presence of ZnO and ZPD, and it is suggested that ZnO and ZPD remove the amine precursor rather than amine itself.

Heating a TMTD/CPTD (1.0:0.1 mol ratio) mixture revealed that the mass loss, attributed to the escape of CS_2 during thiourea formation, commenced earlier when compared with heating TMTD alone (Fig. 4). The rapid mass loss was initiated by 150°C, the temperature region of TMTU formation, as was demonstrated for TMTD/MBT (1.0:0.1 mol ratio).

The earlier onset of thiourea formation from TMTD/CPTD provides a clue to the more ready decomposition of CPTD compared to TMTD. It is suggested that the amine precursor is dithiocarbamic acid and that the acid forms more rapidly from CPTD than from TMTD. Thiuram sulfenyl and persulfenyl radicals have been shown to exist at vulcanization temperatures,[1] and it is suggested that dithiocarbamic acid can slowly form from a dehydrogenation reaction between a sulfenyl radical and hydrogen of methylene/methyl groups of undissociated disulfide [reaction (2)]:

Table VI HPLC Analysis of Reaction Products Formed on Heating CPTD/MBT (1.0:0.1 Mol Ratio) in Open DSC Pans at 10°C/Min

Temperature (°C)	CPTU (mol %)	CPTM (mol %)	CPTD (mol %)	CPTP (mol %)	Sulfur (mol %)
120	3	6	77	15	0
130	5	18	51	19	0
140	14	26	39	22	1
150	23	22	33	22	1
160	47	11	23	15	2
170	30	19	28	17	2
180	78	9	10	0	9

Table VII Mass Loss and HPLC Analysis of Reaction Products Found on Heating CPTD/pip.pmtc (1.0:0.2), Encapsulated in DSC Pans, at 140°C

Time (min)	Mass Loss (%)	CPTU (mol %)	CPTM (mol %)	CPTD (mol %)	CPTS (mol %)	pip.pmtc (mol %)	Sulfur (mol %)
0	0	0	0	93	0	20	0
2.5	3.53	48	12	23	14	17	2
5	3.23	63	8	15	11	10	5
8	0.37	80	2	8	9	7	7
10	14.89	94	0	2	5	2	10
17	16.76	94	0	0	0	2	9

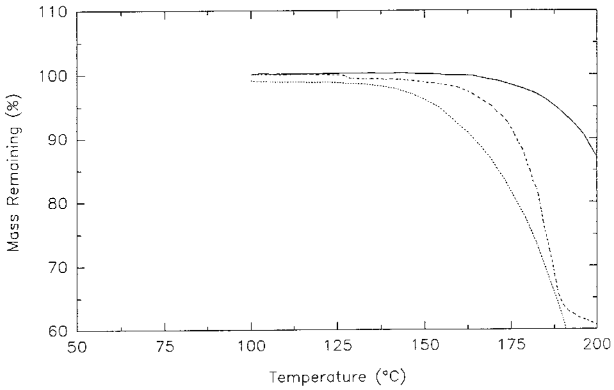
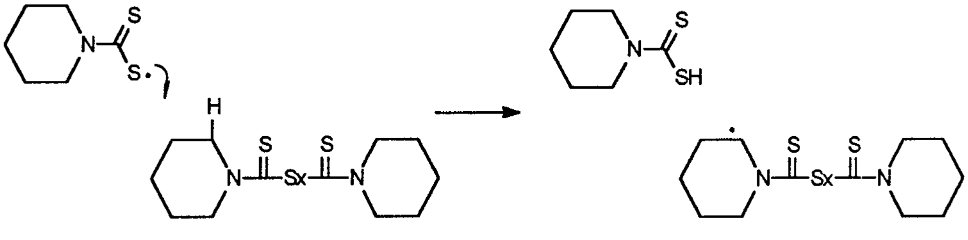


Figure 4 TG scans of TMTD, CPTD, and TMTD/CPTD (1.0:0.1 mol ratio) at 10°C/min: (—) TMTD; (·······) CPTD; (– –) TMTD/CPTD (1.0:0.1 mol ratio).



(2)

The formation of a methylene radical from CPTD is expected to be favored compared to the methyl radical, formed from dehydrogenation of TMTD, that is, Hpmtc would form at lower temperatures than would Hdmtc. The favorable formation of Hpmtc from CPTD, compared to Hdmtc formation from TMTD, would explain the more rapid decomposition of CPTD. Hpmtc decomposition to piperidine would initiate decomposition of CPTD to CPTU, but in the presence of ZnO or ZPD, interaction between Hpmtc and ZnO or ZPD would result in its removal. Reaction between ZnO and dithiocarbamic acid would result in zinc(II) dithiocarbamates, thereby preventing the formation of thiourea. In ZDMC, the coordination around the zinc ions in the crystal structure was reported to be a distorted tetrahedral,[21] and dimeric units in which the zinc is coordinated to five sulfur atoms were also reported, such as the crystal structure of zinc bis(diethyldithiocarbamate).[22] This would indicate that ZPD may trap Hpmtc by forming dimeric units in which the zinc is five-coordinate. ZPD is not as efficient as is ZnO in trapping Hpmtc and preventing CPTU formation. DSC studies show the slow formation of CPTU above 150°C in CPTP6/ZPD9 with rapid decomposition at 180°C. With ZnO, no CPTU forms by 195°C.[9] Amines cannot be trapped by ZnO or ZPD at vulcanization temperatures, and small amounts of amines that may form from trace amounts of acid that escape entrapment by ZnO or ZPD will, over extended periods, catalyze CPTU or TMTU formation as reported.[8]

CONCLUSIONS

CPTD is thermally less stable than is TMTD and rapidly decomposes to CPTD and CS_2 at vulcanization temperatures. Although amines catalyze the decomposition of alkylthiuram disulfides, these are generally volatile and will readily escape from open systems. The agent initiating decomposition is alkyldithiocarbamic acid, which, on decomposition, produces amine. Thus, trapping of the acid by ZnO or ZPD inhibits degradation. ZPD is less effective than is ZnO as an acid trap. Dithiocarbamic acids slowly form from a dehydrogenation reaction between a sulfenyl radidal and hydrogen of methylene/methyl groups of the undissociated disulfide. The formation of a methylene radical in CPTD is favored compared to the methyl radical in TMTD, accounting for the more ready formation of alkyldithiocarbamic acids and the lower stability of CPTD compared to TMTD.

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REFERENCES

1. Coleman, M. M.; Shelton, J. R.; Koenig, J. L. Rubb Chem Technol 1973, 46, 957.
2. Dogadkin, B. A.; Shershnev, V. A. Rubb Chem Technol 1960, 33, 401.
3. Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1991, 42, 2661.
4. Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1991, 42, 2669.
5. Geyser, M.; McGill, W. J. J Appl Polym Sci 1995, 55, 215.
6. McGill, W. J.; Shelver, S. R. J Appl Polym Sci 1999, 72, 999.
7. Nieuwenhuizen, P. J.; Van Duin, M.; McGill, W. J.; Reedijk, J. Rubb Chem Technol Rubb Rev 1997; 70, 368.
8. Nieuwenhuizen, P. J.; Van Duin, M.; Haasnoot, J. G.; Reedijk, J.; McGill, W. J. J Appl Polym Sci 1999, 73, 1247.
9. Reyneke-Barnard, C. P.; Gradwell, M. H. S.; McGill, W .J. J Appl Polym Sci (article 1 in this series).
10. Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 45, 749.
11. Geyser, M.; McGill, W. J. J Appl Polym Sci 1996, 60, 439.
12. Geyser, M.; McGill, W. J. J Appl Polym Sci 1996, 60, 425.
13. Craig, D.; Davidson, W. L.; Juve, A. E. J Polym Sci 1951, 6, 177.
14. Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 44, 581.
15. Higgins, G. M. C.; Saville, B. J Chem Soc 1963, 2812.
16. Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 45, 1545.
17. Giuliani, B. V. M. K.; McGill, W. J. J Appl Polym Sci 1995, 57, 1391.
18. Tuang, D.; Staudner, E.; Alexy, P.; Kysela, G.; Beniska, J. J Polym Mater 1991, 8, 185.
19. Moore, C. G.; Watson, A. A. J Appl Polym Sci 1964, 8, 561.
20. Versloot, P.; Haasnoot, J. G.; Reedijk, J.; van Duin, M.; Duynstee, E. J.; Put, J. Rubb Chem Technol 1994, 67, 252
21. Klug, H. P. Acta Crystallogr 1966, 21, 536.
22. Bonamico, M.; Mazzone, G.; Vaciago, A.; Zambonelli, L. Acta Crystallogr 1965, 19, 898.