

The Thermal Stabilization of Polyethylene Sulfide

T. C. P. LEE and R. T. WRAGG, *Dunlop Research Centre,
The Dunlop Company Limited, Birmingham, 24, England*

Synopsis

It has been shown that the resistance of certain polyethylene sulfides to thermal degradation can be markedly improved by the addition of small amounts of metal dithiocarbamates, thioureas, or diphenyl acetylene together with a suitable carbodiimide. The extent of degradation, as indicated by the concurrent changes in polymer melt viscosity in the temperature range 220°–250°C, was dramatically reduced, in particular, by a stabilizer comprised of 4% hexamethylenebis(*tert*-butyl)carbodiimide and 2% diphenylacetylene. At 250°C polyethylene sulfide (Dabco initiated) was stable in the melt viscometer for a period of 8–10 min and the resulting extrudate showed little sign of discoloration. The detailed mechanism of stabilizer action cannot be put forward at this stage because of uncertainty regarding the mode of polymer degradation which could occur by radical or ionic processes.

INTRODUCTION

The initiation of ethylene sulfide polymerization by triethylamine, metal alkyls, or metal mercaptides yields polymers which degrade rapidly at the melting point (200°–207°C).¹ On the other hand, polymers prepared by initiation with 1,4-diazabicyclo(2,2,2)octane (from here on referred to as Dabco) or zinc diethyl water² show improved thermal stability for short periods of time in the region of 210°–220°C. It has been shown that the latter polymer can be effectively stabilized for periods of 10–15 min at 250°C by the addition of small amounts of zinc oxide and a high boiling polyamine.³ This stabilizer system, however, is limited in its applicability since it is ineffective with polymers prepared by the use of other initiators. In addition, the presence of the amine causes severe oxidative discoloration when the materials are heated in air.

The present work describes three systems which are effective in stabilizing Dabco polyethylene sulfide for extended periods in the range 230°–250°C.

EXPERIMENTAL

Preparation of Polyethylene Sulfide

Toluene, previously dried by refluxing over sodium and stored over molecular sieves, was degassed on a vacuum line and distilled into a cooled (liquid N₂) reaction vessel. Ethylene sulfide (> 99.95% pure) was purified by fractionation through a 3-ft vacuum-jacketed column packed with glass

helices and finally stored over molecular sieves (size 4A). The monomer was degassed and distilled under vacuum into the reaction vessel in the usual way. The reactor, containing the frozen monomer-solvent mixture (1:4 ratio), was flushed with dry nitrogen and a stirrer and a Dry Ice condenser were fitted. The stirrer was started and the catalyst solution (sublimed Dabco in benzene) was added. When the temperature reached ca. -5°C , the polymer began to separate and after 18 hr, during which time the temperature was not allowed to exceed 20°C , an extremely thick cake had formed. The polymer was filtered off and dried in vacuo. The yields varied between 70%–90% and the theoretical molecular weights were based solely on the catalyst/monomer ratio assuming monofunctionality of the Dabco.

Melt Stability Measurements

These were carried out on a Davenport Melt Indexer. A 1.2-kg piston weight (42 psi) and a die with a bore of 0.1181-cm diameter were used in all experiments. A 5-min melt time was allowed and the extrudate obtained in the first minute was rejected.

Preparation of Carbodiimides

The general method used was as follows: A 1-liter flask was charged with aqueous sodium hypochlorite (12% w/w, 4 moles), aqueous sodium hydroxide (25%, 4 moles), and ether (200 ml). The solution was cooled to about 5°C and the appropriate thiourea (1.0 mole) was added slowly over 2 hr, with vigorous stirring. As the insoluble thiourea was converted to carbodiimide, the solution became clear. After stirring for 4 hr the ether layer was separated, washed with water, and dried (MgSO_4). After removing the solvent, the residue was either distilled under reduced pressure or crystallized from a suitable solvent.

In this manner the following carbodiimides were prepared: hexamethylenebis(*tert*-butylcarbodiimide) (80%), bp 110° – $112^{\circ}\text{C}/0.08$ mm (found: N, 19.6%; calc. for $\text{C}_{16}\text{H}_{30}\text{N}_4$: N, 20.1%); *tert*-butyl(benzyl)carbodiimide (30%), bp 71° – $73^{\circ}/0.25$ mm (found: N, 14.8%; calc. for $\text{C}_{12}\text{H}_{16}\text{N}_2$: N, 14.8%); *tert*-butyl(*p*-tolyl)carbodiimide, (35%), bp 90° – $94^{\circ}/0.5$ mm (found: N, 21.6%; calc. for $\text{C}_{12}\text{H}_{16}\text{N}_2$: N, 21.9%); di-*tert*-butylcarbodiimide (41%), bp 47° – $49^{\circ}/10$ mm (found: N, 18.0%; calc. for $\text{C}_9\text{H}_{18}\text{N}_2$: N, 18.2%); di-*p*-tolylcarbodiimide (25%), mp 54° – 55°C (found: N, 12.3%; calc. for $\text{C}_{15}\text{H}_{14}\text{N}_2$: N, 12.6%); *p*-phenylenebis(phenylcarbodiimide) (27%), a deep red crystalline solid mp 69° – 70° (found: N, 17.8%; calc. for $\text{C}_{20}\text{H}_{14}\text{N}_4$: N, 18.1%).

Carbodiimides Prepared from Isocyanates and 1-Ethyl-3-methyl-3-phospholene-1-oxide

Di-2-naphthylcarbodiimide. 2-Naphthyl isocyanate (12.5 g) was refluxed for 4 hr with 1-ethyl-3-phospholene-1-oxide (0.05 g) in xylene (125 ml). After evaporating the solution to dryness the residue was dissolved

in benzene and treated with charcoal. The solvent was then removed in vacuo to afford the carbodiimide (90%) as a brown powder mp 84°C.

Di-*m*-tolylcarbodiimide. *m*-tolyl isocyanate (12.5 g) and the phospholene oxide (0.03 g) were allowed to react at room temperature, under vacuum, for 18 hr after which time the product was distilled under reduced pressure to afford di-*m*-tolylcarbodiimide (90%), bp 142°–144°/1 mm.

Polycarbodiimide from Triphenylmethane Triisocyanate. The isocyanate (25 ml) was placed in a dry, N₂-filled flask and the phospholene oxide catalyst (0.5 ml) was added. Carbon dioxide was evolved and the polycarbodiimide was formed as a brittle mass which was crushed before use.

Polycarbodiimide from Tolyene Diisocyanate (80% 2,4; 20% 2,5). This was prepared as described in the previous example. The polycarbodiimide, a yellow sticky mass, was incorporated into the polyethylene sulfide in the form of a benzene solution.

DISCUSSION AND RESULTS

Polyethylene sulfide undergoes severe degradation by random chain cleavage at temperatures 5°–15°C in excess of its melting point. It is also apparent that the period of stability or the temperature at which thermal breakdown becomes significant varies considerably with the origin of the polymer (i.e., the initiator used to prepare it).

Because of the insolubility and high melting point of polyethylene sulfide, it is very difficult to determine the nature of the endgroups and potential sites of instability are suggested intuitively. In the case of metal mercaptide-initiated polymers, the picture is clearer since it has been shown⁴ that the catalyst sites in such materials are inherently unstable. During the polymerization of propylene sulfide with the same catalysts, a number of weak polysulfide linkages are introduced into the polymer backbone.⁵ It seems reasonable to assume, therefore, that a similar process probably occurs to some degree during the polymerization of ethylene sulfide. No system which will effectively stabilize polymers of this type against thermal degradation has yet been reported.

The Thermal Stability of Dabco-Initiated Polyethylene Sulfide

The thermal stability of Dabco polyethylene sulfide can be improved significantly and to different degrees by the incorporation into the polymer of (1) dithiocarbamates; (2) thioureas; (3) a combination of diphenylacetylene and a carbodiimide.

Dithiocarbamates

Metal salts of N-disubstituted dithiocarbamic acids, and in particular those of zinc, stabilize Dabco polyethylene sulfide, the polymer being virtually unchanged after 10–12 min at 230°C. These values appear to represent the threshold conditions and degradation becomes significant

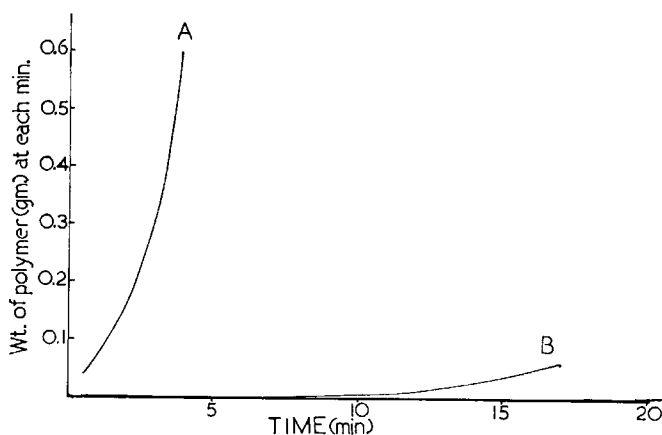


Fig. 1. The stabilizing effect of zinc dibenzyl dithiocarbamate on Dabco polyethylene sulfide temp 230°C; (A) Dabco polyethylene sulfide (DPES); (B) DPES + 2% zinc dibenzyl dithiocarbamate.

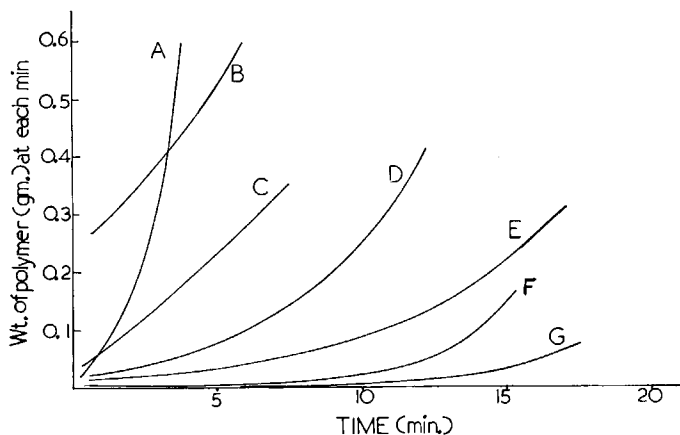


Fig. 2. The effect of zinc dibenzyl dithiocarbamate on the melt stability of polyethylene sulphide: temp 230°C; (A) DPES; (B) DPES + 0.1% zinc dibenzyl dithiocarbamate; (C) DPES + 0.3% zinc dibenzyl dithiocarbamate; (D) DPES + 0.5% zinc dibenzyl dithiocarbamate; (E) DPES + 1.0% zinc dibenzyl dithiocarbamate; (F) DPES + 2.0% zinc dibenzyl dithiocarbamate + 2% ZnO; (G) DPES + 2.0% zinc dibenzyl dithiocarbamate.

soon after this time period. Melt viscosity data as determined on a Davenport polyethylene grader¹ are shown in Figures 1 and 2. The stabilizing effect of zinc dibenzyl dithiocarbamate increases with increasing concentration up to a limiting value of about 2% as shown in Figure 2. These data could be interpreted as being indicative of more than one degradation process, the faster of which is inhibited by the dithiocarbamate and the other(s), relatively unaffected. Figure 3 shows that the stabilizing influence of zinc dibenzyl dithiocarbamate is markedly decreased with increase

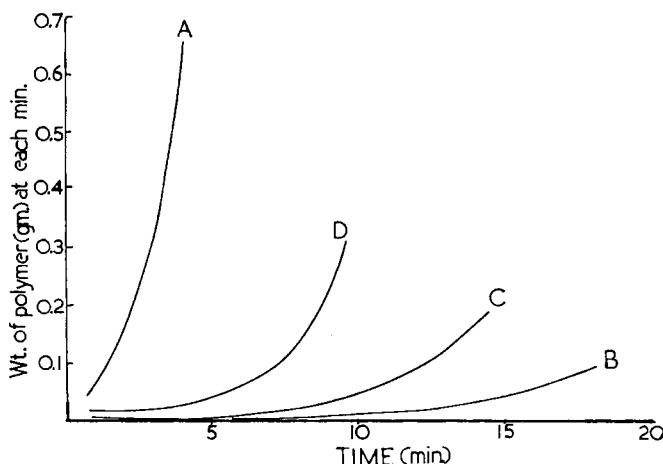


Fig. 3. The effect of temperature on the melt stability of polyethylene sulfide stabilized with zinc dibenzyl dithiocarbamate: (A) DPES, 230°C; (B) DPES + 2% zinc dibenzyl dithiocarbamate, 230°C; (C) DPES + 2% zinc dibenzyl dithiocarbamate, 235°C; (D) DPES + 2% zinc dibenzyl dithiocarbamate, 240°C.

in temperature and at 250°C the rate of degradation is comparable to that of the neat polymer at 230°C.

Thioureas

The melt flow data shown in Figure 4 clearly indicate that at 230°C Dabco polyethylene sulfide is stabilized by the addition of *N,N'*-disubstituted thioureas. What is even more significant is that the addition of zinc

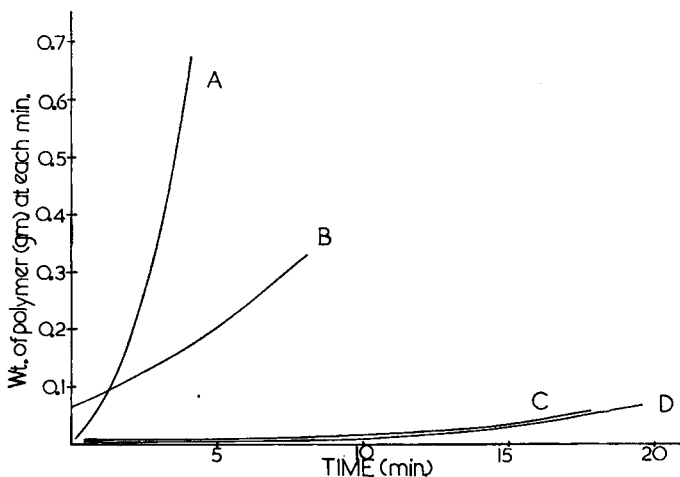
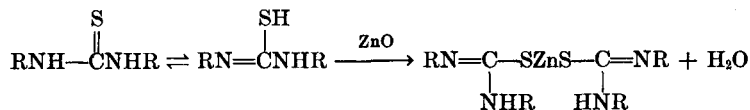


Fig. 4. The effect of thioureas on the melt stability of polyethylene sulfide: temp 230°C; (A) DPES; (B) DPES + 2% *N,N'*-diethylthiourea; (C) DPES + 2% *N,N'*-diethylthiourea + 2% ZnO; (D) DPES + 3% *N,N-p*-phenylenebis(*N',N'*-*tert*-butylthiourea) 2% ZnO.

oxide to a thiourea-polymer mix causes a further increase in stability. It is known^{6,7} that zinc oxide can react with thioureas at elevated tempera-



tures to form the thiolates which might well behave, in terms of stabilizing action, in the same manner as the dithiocarbamates.

Combinations of Diphenyl Acetylene and Carbodiimides

Carbodiimides were chosen for study because of their chemical associations with thioureas and dithiocarbamates. Thus, zinc dithiocarbamates decompose at elevated temperatures to afford thiourea which can be desulfurized under appropriate conditions to afford carbodiimides.

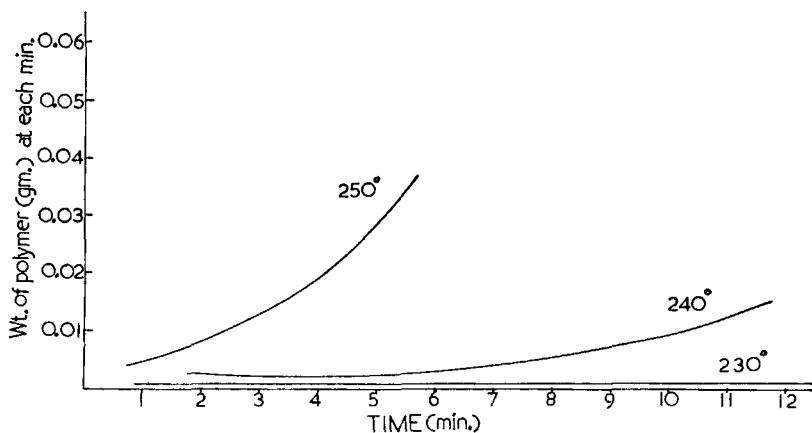


Fig. 5. The effect of temperature on the melt stabilization of polyethylene sulfide by carbodiimides. Polymer composition: DPES + 2% hexamethylenebis(*tert*-butylcarbodiimide), 2% ZnO.

A number of carbodiimides were prepared for study and it was found that the aliphatic compounds were superior to the aromatic derivatives. This would be expected from the relative stabilities of the two series. Figure 5 illustrates the melt flow data at different temperatures for Dabco polyethylene sulfide containing hexamethylenebis(*tert*-butylcarbodiimide). At 230°C complete stabilization is obtained, but at higher temperatures the material undergoes rapid degradation.

It was found that the degree of stabilization obtained by the addition of suitable carbodiimides could be enhanced by the incorporation of small amounts of diphenyl acetylene. The melt flow data described in Figure 6 illustrate the effect of the diphenyl acetylene concentration on the melt stability of Dabco polyethylene sulfide containing hexamethylenebis(*tert*-butylcarbodiimide). It can be seen that at a constant level of carbodiimide

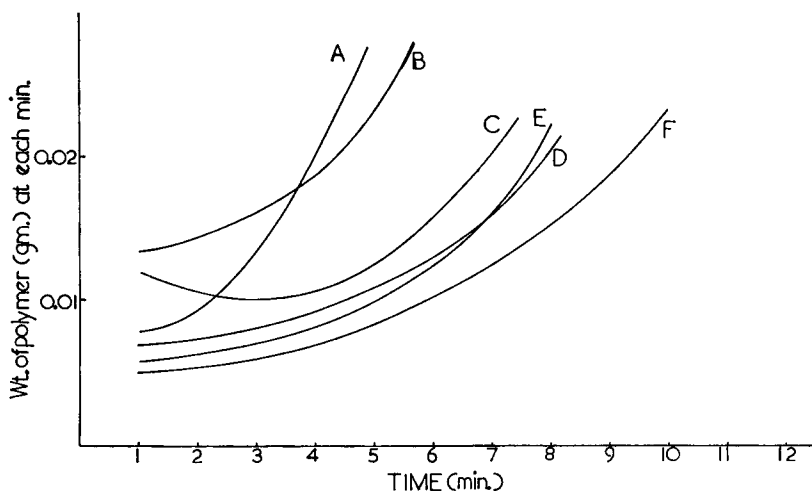


Fig. 6. The effect of diphenyl acetylene concentration on the melt stabilization of polyethylene sulfide by carbodiimides: temp 250°C; (A) DPES + 2% hexamethylenebis(*tert*-butylcarbodiimide) + 2% TiO_2 ; (B) same as (A) plus 0.5% diphenyl acetylene; (C) same as (B) plus 1% diphenyl acetylene; (D) same as (B) plus 2% diphenyl acetylene; (E) same as (B) plus 4% diphenyl acetylene; (F) same as (B) plus 6% diphenyl acetylene.

the melt stability improved with increasing diphenyl acetylene concentration. Figure 7 shows the improvement obtained by varying the stabilizer concentration at a constant ratio (2:1) of carbodiimide to diphenyl acetylene. From Figures 6 and 7 the levels of the additives were optimized and

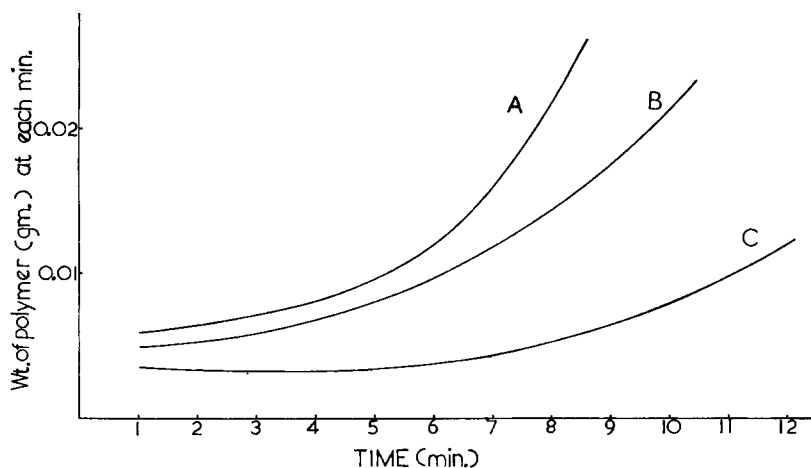


Fig. 7. The effect of carbodiimide concentration on the melt stabilization of polyethylene sulfide in the presence of diphenyl acetylene: temp 250°C; (A) 2% hexamethylenebis(*tert*-butylcarbodiimide) + 1% diphenylacetylene + 2% TiO_2 ; (C) 6% hexamethylenebis(*tert*-butylcarbodiimide) + 3% diphenylacetylene + 2% TiO_2 ; (D) 4% hexamethylenebis(*tert*-butylcarbodiimide) + 2% diphenylacetylene + 2% TiO_2 .

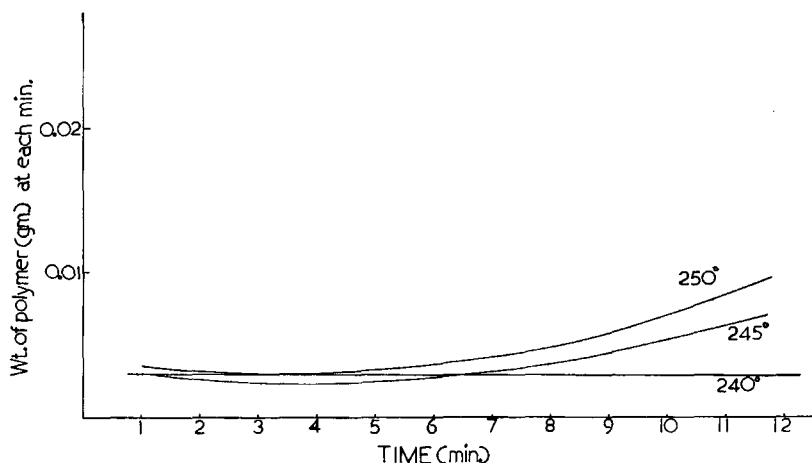


Fig. 8. Effect of temperature on the melt stabilization of polyethylene sulfide by diphenylacetylene and carbodiimides: stabilizer system 4% hexamethylenebis(*tert*-butylcarbodiimide) + 2% diphenylacetylene + 2% TiO_2 .

the melt flow time curves in Figure 8 describe the temperature stability of the system compared with the raw polymer. Figure 9 describes the melt flow data at 250°C for a series of carbodiimides in conjunction with diphenyl acetylene. The difunctional material, hexamethylenebis(*tert*-butylcarbodiimide) is superior to the other derivatives in this series and it is interesting to compare the initial viscosity with that of the systems containing dicyclohexyl and di-*n*-butylcarbodiimides. It is possible that the difunctional compound brings about chain extension by reaction with poly-

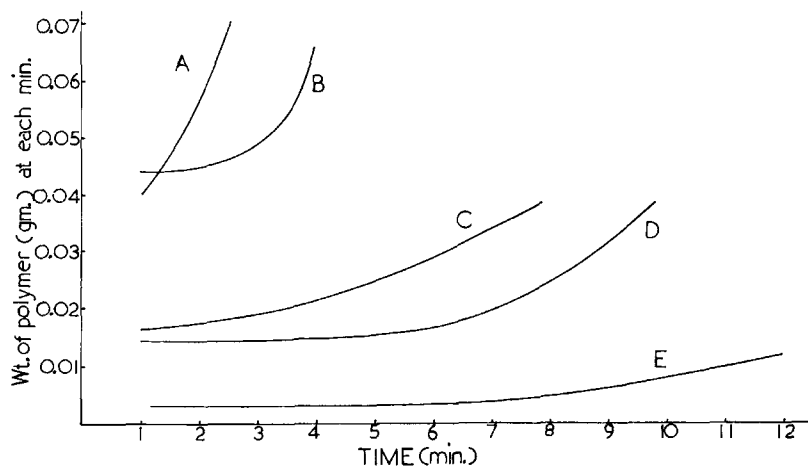


Fig. 9. Effect of carbodiimide structure on the melt stabilization of polyethylene sulfide in the presence of 2% diphenylacetylene: temp 250°C; (A) *tert*-butyl(benzyl)-carbodiimide, 4%; (B) di-*tert*-butylcarbodiimide, 4%; (C) di-*n*-butylcarbodiimide, 4%; (D) dicyclohexylcarbodiimide, 4%; (E) hexamethylenebis(*tert*-butyl)carbodiimide, 4%.

TABLE I
Efficiencies of Carbodiimides as Stabilizers

Carbodiimide	Temp studied, °C	Stabilization effect ^a
Hexamethylenebis(<i>tert</i> -butyl-	215-250	positive at all temps
Dicyclohexyl-	215-250	positive at all temps
Di- <i>n</i> -butyl-	215-250	positive at all temps
Di- <i>tert</i> -butyl-	215-250	positive at all temps but poor at 250°C
<i>tert</i> -Butyl(benzyl)-	215-250	but poor at 250°C
Di- <i>m</i> -tolyl-	215, 250	negative
Di- <i>p</i> -tolyl-	215, 250	negative
<i>p</i> -Phenylbis(phenyl-	215	positive
	250	negative
<i>p</i> -Phenylbis(<i>tert</i> -butyl-	215	no change
	250	negative
Di- α -naphthyl-	250	negative
Polymer A ^{b1}	215	positive
	250	negative
Polymer B ^{b2}	215	positive
	250	negative

^a The theoretical MW of the polyethylene sulfide varied between 3×10^5 and 4×10^5 (based on yield from a standard recipe). Except at 215°C, the composition for the melt study was 4% carbodiimide, 2% diphenylacetylene, 2% zinc oxide. At 215°C, no diphenyl acetylene was used.

^b Polymeric carbodiimide prepared from tolyl diisocyanate (b1) and triphenyl methane (b2) diisocyanate with 3-methyl-1-ethyl-3-phospholene-1-oxide as catalyst.⁸

mer endgroups. The efficacies of a number of carbodiimides as stabilizers against the thermal breakdown of Dabco polyethylene sulfide are outlined in Table I.

Polymers Prepared by Initiation with Metal Mercaptides

Zinc and cadmium mercaptides have been shown to be efficient initiators of propylene sulfide initiation⁹ and give rise to polymers containing metal-sulfur bonds. A noteworthy feature of polyethylene sulfides obtained by using these initiators is the marked drop in thermal stability and the lack of response to the stabilizing systems outlined earlier. The reason for this instability is thought to be twofold: (a) the introduction of disulfide links into the polymer backbone during polymerization⁵; (b) the ease with which metal sulfide can be eliminated by thermal breakdown as indicated by studies on the decomposition of model compounds.⁴

In contrast, polymers produced by the zinc diethyl-water initiation process³ which probably introduces metal-oxygen bonds,¹⁰ can be stabilized efficiently with a mixture of ZnO and a suitable polyamine and to a lesser degree by the addition of metal dithiocarbamates. The differences in stability of mercaptide- and Dabco-initiated polymers and the thermal stabilization of the latter are indicated in Figure 10, while the improvement

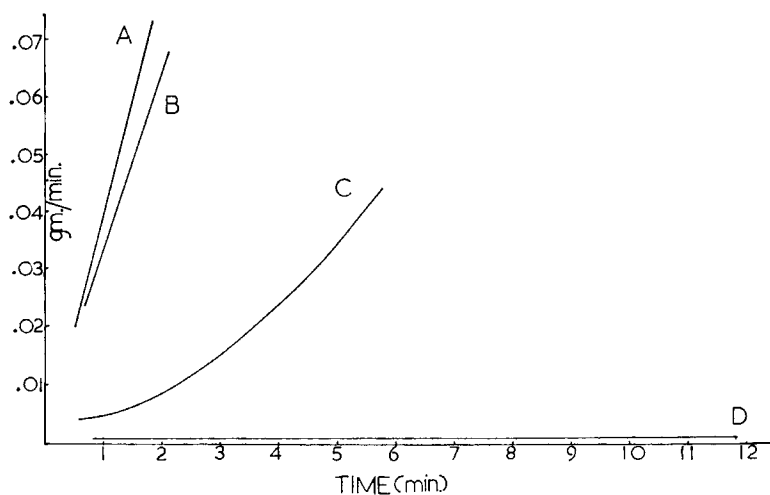


Fig. 10. Comparisons of the thermal stabilities at 230°C of metal mercaptide- and Dabco-initiated polyethylene sulfides: (A) $(\text{BuSCH}_2\text{CH}_2\text{S})_2\text{Zn}$ -initiated polymer; (B) $(\text{BuSCH}_2\text{CH}_2\text{S})_2\text{Cd}$ -initiated polymer; (C) Dabco-initiated polymer; (D) Dabco-initiated polymer stabilized with the system described for Figure 8.

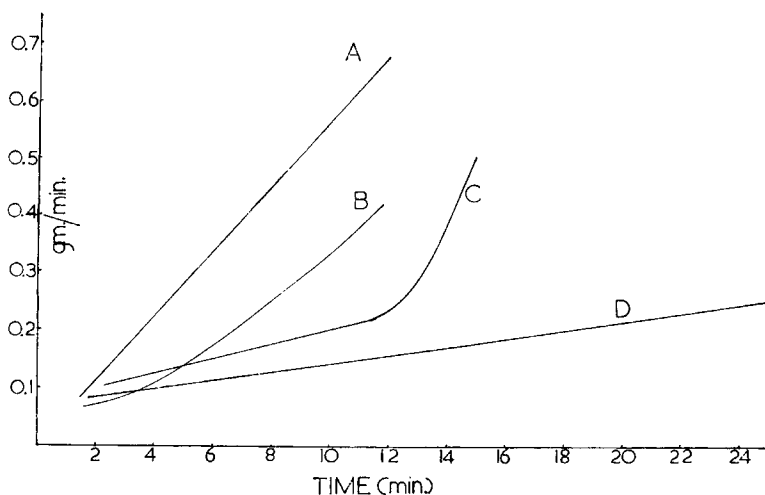


Fig. 11. The effect of polyamines on the thermal stability at 230°C of $\text{ZnEt}_2/\text{H}_2\text{O}$ -initiated polyethylene sulfide³: (A) neat polymer; (B) polymer + 2.5% polyacrylamide; (C) polymer + 2.5% *p*-aminodiphenylamine; (D) polymer + 2.5% octadecyldimethylamine.

in thermal stability of typical $\text{ZnEt}_2/\text{H}_2\text{O}$ -initiated polymers, by the addition of high-boiling amines, is shown in Figure 11.

CONCLUSIONS

Three new thermal stabilizer systems, for use with polyethylene sulfide, have been described. These compositions are most efficient when used in

conjunction with polyethylene sulfide prepared by initiation with Dabco. Metal dithiocarbamates and thioureas, which may be related in their mode of action, provide protection against thermal degradation for long periods at 230°–235°C. For stabilization at temperatures in the range 235°–250°C, the preferred stabilizer system is that comprising diphenylacetylene and hexamethylenebis(*tert*-butyl carbodiimide) or dicyclohexylcarbodiimide.

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