

Mechanisms of Antioxidant Action: Tellurium Dithiocarbamates as Antioxidants for Polypropylene

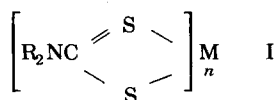
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Synopsis

The tetrakis (dialkyldithiocarbamato)tellurium(IV) complexes are highly effective thermal antioxidants and melt stabilizers for polypropylene and the evidence suggests that they are converted to the bis(dialkyldithiocarbamato)tellurium(II) complexes and the corresponding dithiocarbamoyl disulfides during processing. The Te(IV) complexes are also effective photoantioxidants and their activity increases with increasing processing time. The bischelates are in general less effective when used alone.

INTRODUCTION

Metal thiolates, of which the dithiocarbamates (I) are the best known examples, have long been recognized as effective thermal antioxidants and in some cases photoantioxidants for polyolefins.¹⁻⁵



Their antioxidant activity is known to be associated with their ability to destroy hydroperoxides in a nonradical process, thereby removing the indigenous oxidation initiators.⁶

The behavior of the metal dithiocarbamates as photoantioxidants is much more variable than under thermal oxidative conditions. Whereas the nickel(II) and cobalt(III) chelates are effective photoantioxidants,⁷ the group II chelates are relatively ineffective,⁸ and the iron(II) and (III) chelates are effective photoactivators for polyolefins.^{7,9} These differences in behavior have been shown^{8,9} to be a function of the photostability of the chelates and of the metal ion liberated by photolysis.

The tetrakis (dithiocarbamato)tellurium(IV) complexes (I, M = Te, N = 4) are well-known rubber accelerators which confer a high level of thermal oxidative stability on the vulcanizates.¹⁰ They appear to behave similarly to the group II metal dithiocarbamates in inhibiting thermal oxidation, and it was therefore of some interest to examine their effectiveness as both thermal and photoantioxidants for polypropylene.

TABLE I
Structures and Characteristics of Dithiocarbamatotellurium Chelates (I)^a

Structure (I)	Code name	M_p (°C)
R = Et, $n = 4$	Te(DEC) ₄	123–124
R = Et, $n = 2$	Te(DEC) ₂	162–163
R = iBu, $n = 4$	Te(DiBC) ₄	124
R = PhCH ₂ , $n = 4$	Te(DBzC) ₄	160 (dec)

^a Complete details of characterisation will be given in Ref. 11.

EXPERIMENTAL

Materials. The polymer was Profax HF-22 containing no additives and was supplied by ICI Ltd. Tetrakis(diethylthiocarbamato) tellurium(IV) was obtained as ethyl tellurac from the Vanderbilt Co. The tetrakis(dibenzylthiocarbamato)tellurium(IV) and tetrakis(di-isobutylthiocarbamato)tellurium(VI) were prepared as described elsewhere.¹¹ The structures, code names, and characteristics of the antioxidants are given in Table I.

Processing. PP was processed at 180°C with the antioxidants for various time (5, 10, and 20 min) in a closed Hampden-RAPRA Torque Rheometer and the polymers were compression-molded to films as described previously⁸ and the effects of thermal and photo-oxidation (sun lamp–blue lamp combination) were studied as described earlier.⁸

Thermal Stability of Te(DEC)₄ in Solution. Te(DEC)₄ (2 g) was dissolved in xylene (30 mL) and refluxed for 5 h (140°C). The color of the solution changed from canary yellow to red during the early stages of the reaction. The products of the reaction were found to be Te(DEC)₂ and tetraethyl thiuram disulfide (TETD) by preparative thin layer chromatography (silica gel plates) and column chromatography (silica), respectively, eluting with CHCl₃. The products were identified by melting point and chemical analysis.¹¹

Photochemical Reaction of Te(DEC)₄ and Te(DEC)₂ with Oxygen in Solution. Irradiation of the chelates in chloroform (5% solution) in the presence of air with a sunlamp (> 290 nm) led over a period of 14 days to the fading of the color and the formation of a white precipitate. At low concentrations (< 10⁻⁶M) the solutions were decolorized after only 10 min. The white precipitate was identified by IR to be TeO₂ [$\nu(\text{TeO}) = 650 \text{ cm}^{-1}$]. The solutions were examined by TLC and were found to contain only the corresponding tetraalkylthiuram disulfides. The solutions were stable in the presence of oxygen and in the absence of UV, also in the presence of UV, and in the absence of oxygen. More details are given elsewhere.¹¹

RESULTS

Figure 1 shows that both the bis and tetrakis(diethylthiocarbamato) tellurium complexes are effective melt stabilizers for PP for up to 20 min in a closed mixer at 180°C. Carbonyl formation is also considerably retarded relative to the control without antioxidant. Other dialkylthiocarbamates behave very similarly.

Films made from polymer processed for 10 min at 180°C were heated in a Wallace, single cell air oven at 140°C, and the formation of carbonyl was

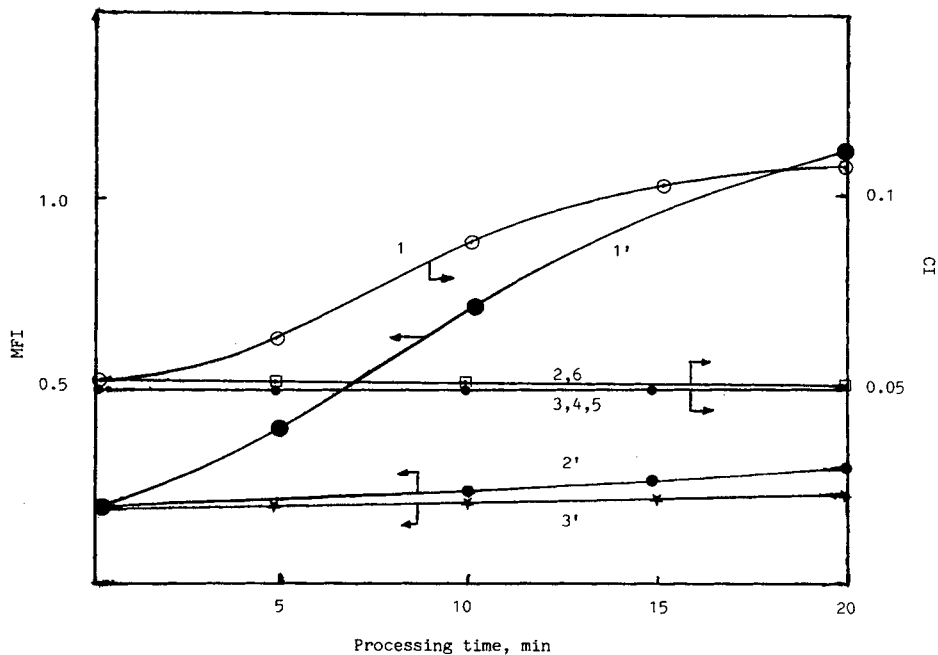


Fig. 1. Effect of tellurium dithiocarbamates on the change in melt flow index (MFI) and carbonyl index (CI) of polypropylene processed at 180°C in a closed mixer (all concentrations 2.8×10^{-4} mol/100 g): (1) 1' PP without additive; (2) 2' Te(DEC)₂; (3) 3' Te(DEC)₄; (4) Te(DBzC)₄; (5) Te(DiBC)₄; (6) Te(DEC)₂.

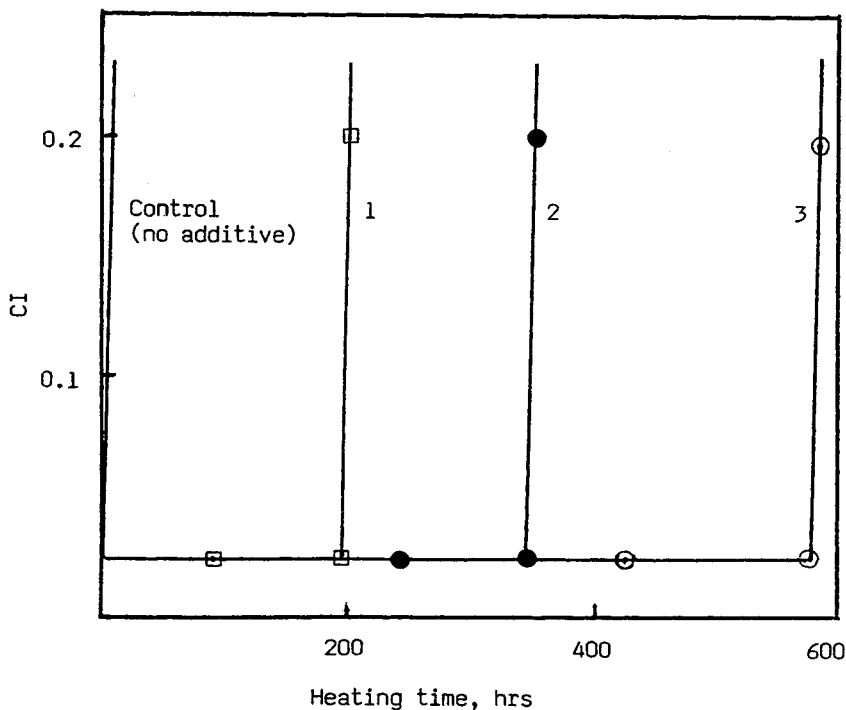


Fig. 2. Effect of *tetrakis*(dibenzylthiocarbamato)tellurium(IV), Te(DBzC)₄, at various concentrations on the thermal oxidation of polypropylene in an air oven at 140°C, processed for 5 min in a closed mixer: (1) 0.7×10^{-4} mol/100 g; (2) 1.4×10^{-4} mol/100 g; (3) 2.8×10^{-4} mol/100 g.

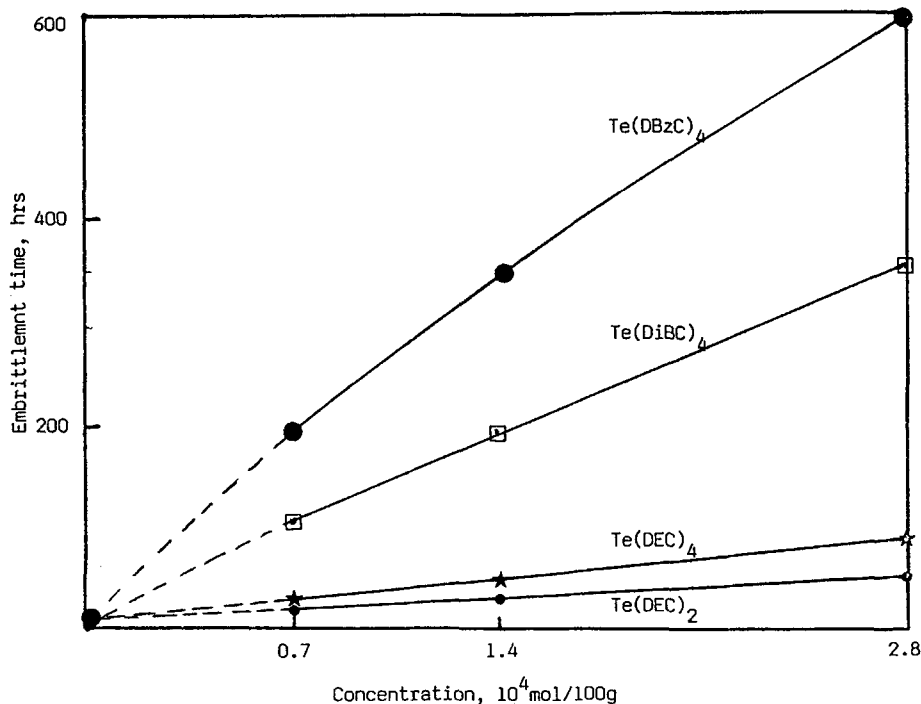


Fig. 3. Effect of the concentration of tellurium dithiocarbamates on the embrittlement time of polypropylene in an air oven at 140°C.

followed as a function of time of heating. A typical oxidation curve is shown in Figure 2. No carbonyl was formed during the induction period which, as is usual in the case of dithiocarbamates, terminated very sharply and embrittlement occurred within a few hours of the end of the induction period.

Figure 3 relates embrittlement time to antioxidant concentration for a number of Te chelates. The higher molecular weight additives, $\text{Te}(\text{DBzC})_4$ and $\text{Te}(\text{DiBC})_4$, were very much more effective than the ethyl analogue, $\text{Te}(\text{DEC})_4$, and the latter was about twice as effective as $\text{Te}(\text{DEC})_2$. The antioxidant activities of all the additives were almost linear with concentration.

The superiority of $\text{Te}(\text{DEC})_4$ over $\text{Te}(\text{DEC})_2$ was studied in more detail. $\text{Te}(\text{DEC})_4$ was found to disproportionate on heating in xylene at 140°C, giving

TABLE II
Comparison of Thermal Antioxidant Activity of
 $\text{Te}(\text{DEC})_4$ with a Synergistic Mixture of $\text{Te}(\text{DEC})_2$
and TETD (All Concentrations 1.4×10^{-4} mol/100 g)

Antioxidant	Embrittlement time (h)
Control	0.5
$\text{Te}(\text{DEC})_2$	22
TETD	7
$\text{Te}(\text{DEC})_4$	32
$\text{Te}(\text{DEC})_2$ + TETD	35

a mixture of $\text{Te}(\text{DEC})_2$ and tetraethyl thiuram disulphide (TETD) (see Experimental section). Table II compares the antioxidant activities of an equimolar mixture of $\text{Te}(\text{DEC})_2$ and TETD (both at 1.4×10^{-4} mol/100 g) with $\text{Te}(\text{DEC})_4$ at the same molar concentration. It can be seen that these are very similar and superior to the sum of the individual effects of $\text{Te}(\text{DEC})_2$ and

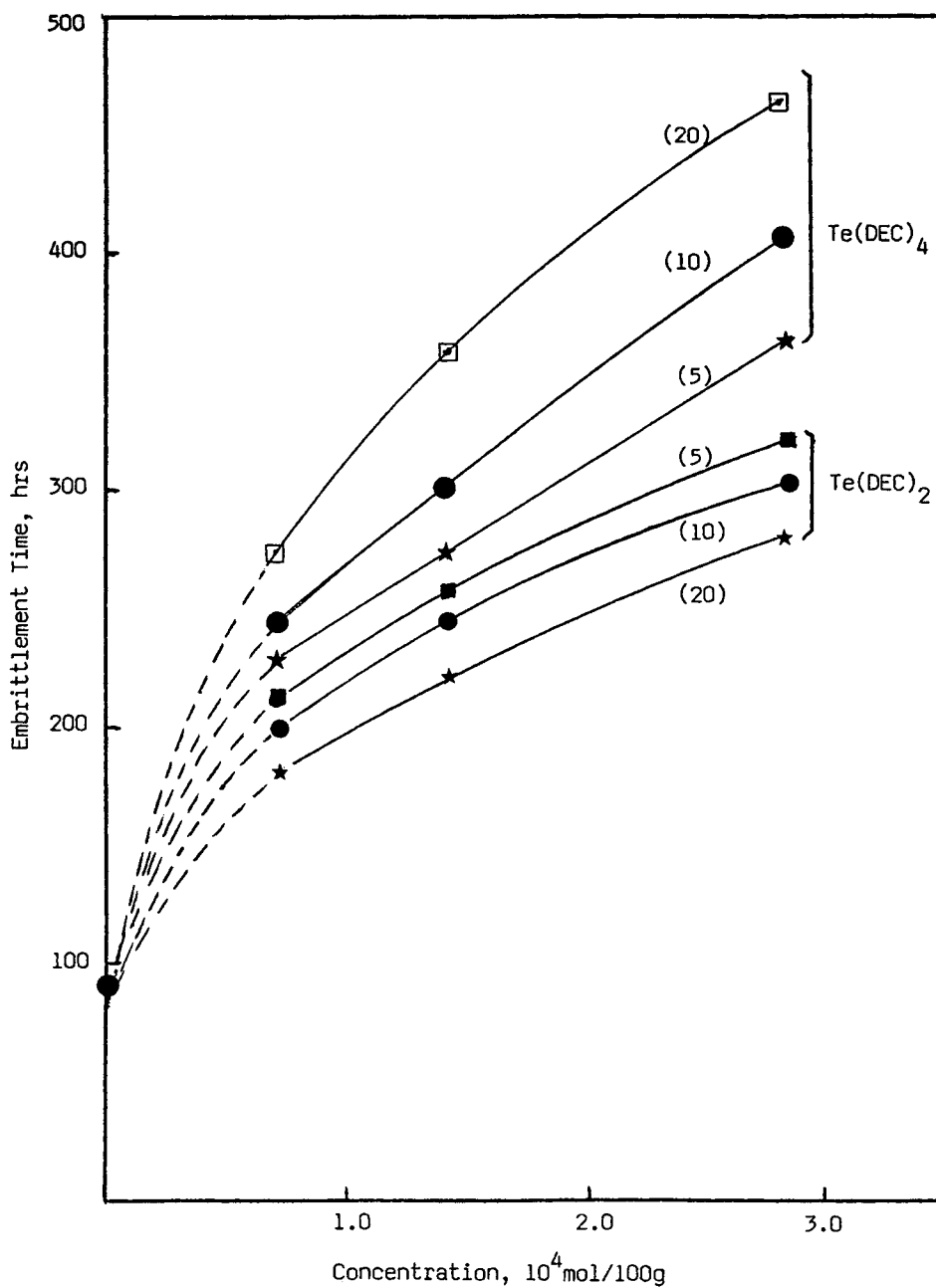


Fig. 4. Effect of the concentration of tellurium dithiocarbamates on the UV embrittlement time of polypropylene. Numbers in parenthesis are processing times at 180°C (min).

TABLE III
Effect of Thermal Processing on the Photoantioxidant Activity
of Tellurium Dithiocarbamates

	Processing time (min)	0.7 ^a	1.4 ^a	2.8 ^a
Te(DiBC) ₄	5	160	270	340
	10	190	280	387
	20	320	310	395
Te(DBzC) ₄	5	—	—	159
	10	—	—	185
	20	—	—	199

^aAntioxidant concentration, 10⁻⁴ mol/100 g.

TETD. This indicates a moderate synergistic effect of the mixture produced during processing from the parent Te(DEC)₄.

Figure 4 compares the photoantioxidant activity of Te(DEC)₄ and Te(DEC)₂ at different concentrations and processing times. This shows that Te(DEC)₄ is clearly more effective than Te(DEC)₂, and that the incremental effect of concentration increase is higher with the former than with the latter. Other chelates show similar photoantioxidant activities, but, surprisingly, Te(DBzC)₄ and Te(DiBC)₄, which are much more effective thermal antioxidants than

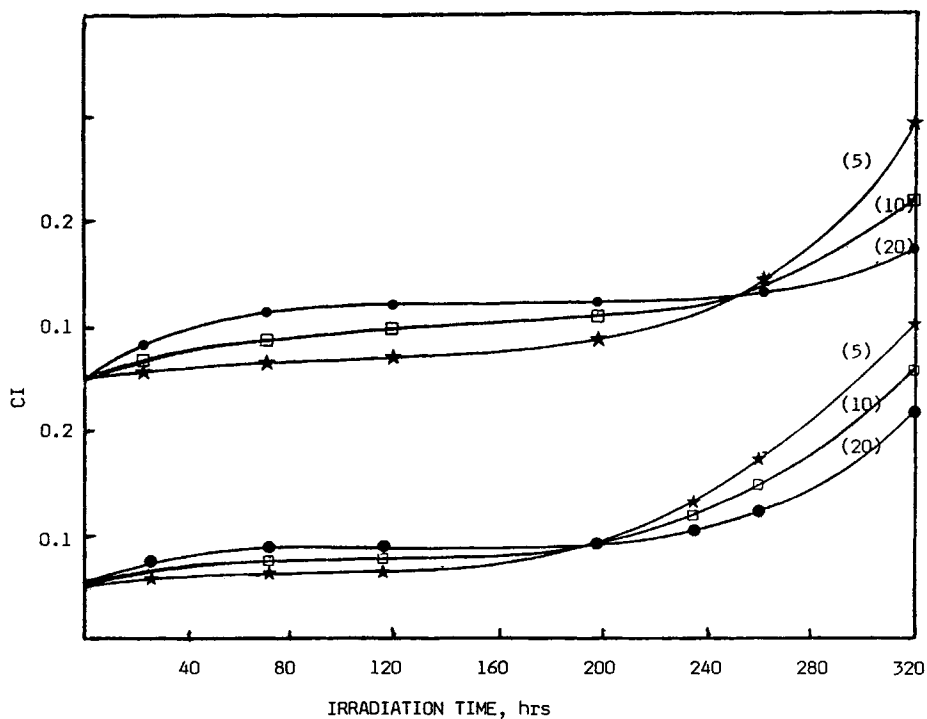


Fig. 5. Comparison of the photoantioxidant activity of Te(DEC)₄ with a synergistic mixture of Te(DEC)₂ and TETD (lower curves) at the same total molar concentration (1.4 × 10⁻⁴ mol/100 g). Numbers in parenthesis are processing times at 180°C (min).

their ethyl analogue (see Fig. 3), do not show a similar superiority in photoantioxidant activity (see Table III). Extended processing has a very favorable effect on the photoantioxidant activity of all the tetrakis(dithiocarbamate)s and this is most marked with $\text{Te}(\text{DEC})_4$. A more detailed investigation of the whole course of photooxidation as indicated by carbonyl index (see Fig. 5) shows that the more severe the processing operation, the greater is the initial prooxidant effect during photooxidation but the better is the long term stabilizing effect. Solution studies showed that both $\text{Te}(\text{DEC})_4$ and $\text{Te}(\text{DEC})_2$ are photounstable in the presence of oxygen, and in this respect they appear to behave like the group II metal complexes rather than the nickel chelates which are relatively photostable.⁸ $\text{Te}(\text{DEC})_4$ is only about one third as effective as bis(dinonyldithiocarbamate)Ni(II), Ni(DNC)₂ as a photoantioxidant.⁴

DISCUSSION

Previous studies have shown¹² that the nature of the *N*-alkyl group has a dominating influence on both thermal and photoantioxidant activity of the dithiocarbamate chelates. This was shown to be due to differences in the solubilities of the additives in the polymer. The same trend is observed in the present study, although a more systematic investigation of the photoantioxidant activity of the tellurium chelates would be necessary to establish whether solubility of the additive in the polymer or photostability is the determining factor under conditions of UV irradiation.

The tellurium dithiocarbamates follow the pattern of the group II dithiocarbamates in their lability to light. However, oxidation during processing has a more complex effect in that the bischelate $\text{Te}(\text{DEC})_2$ becomes less efficient with processing severity whereas $\text{Te}(\text{DEC})_4$ becomes more efficient. The latter behavior is characteristic of thiocarbamoyl disulfides (thiuram disulfides) and thiophosphoryl disulfides,¹³⁻¹⁵ which, in oxidized form, synergize effectively with the parent metal complexes in the photostabilization of polypropylene.² Since in the present studies it is shown that $\text{Te}(\text{DEC})_4$ disproportionates thermally, it seems clear that the increased photoantioxidant activity on severe processing is due to synergism between the oxidation products of TETD and the bischelate or residual tetrachelate. The same phenomenon is observed during thermal oxidation (Table II) and almost certainly accounts for the quite exceptional thermal antioxidant activities of $\text{Te}(\text{DBzC})_4$ and $\text{Te}(\text{DiBC})_4$ at 140°C (see Fig. 3).

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