

Mechanisms of Antioxidant Action: Time-Controlled Photoantioxidants for Polyethylene Based on Soluble Iron Compounds

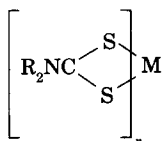
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Synopsis

The effects of two component combinations of soluble iron compounds on the rate of photooxidation and associated embrittlement times of low density polyethylene (LDPE) are examined. It is found that photoantioxidants retard the photo prooxidant effects of iron compounds giving controllable induction periods. In the case of the combination of a nickel dithiocarbamate (photoantioxidant) and an iron dithiocarbamate (photo prooxidant) a very wide range of embrittlement times can be obtained in which the induction period is controlled by the nickel complex and the post-induction period rate by the iron complex.

INTRODUCTION

Dithiocarbamate iron complexes (I, $M = \text{Fe}$, $n = 3$) are the basis of commercial additives for polyolefins with inbuilt but time-variable photostability¹⁻⁴:



Their potential uses range from very short-lived materials such as packaging which is required to degrade in the environment immediately on discard through protective films for annual crops where a lifetime of several months is required to protective mulch young trees which may be required to stand up to 3-4 years in exposed environments before embrittlement.

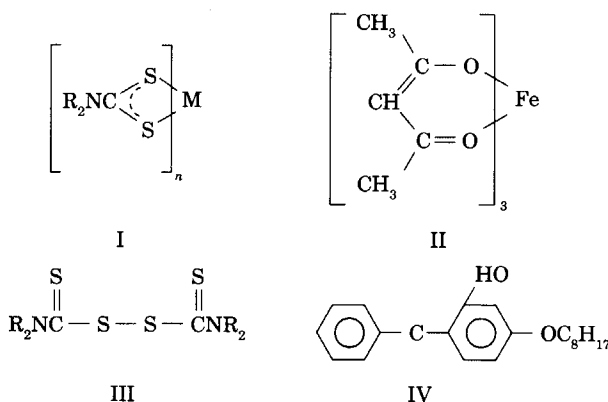
Essential technical requirements for time-controlled degradable materials is that they should be capable of being processed normally; that is the additives should not be prooxidants during processing or in storage.⁵ The iron dithiocarbamates are unique in behaving as effective thermal antioxidants by the peroxidolytic (PD-C) mechanism⁶ while at the same time giving rise to polymer soluble carboxylates during uv irradiation.⁵

The iron dithiocarbamates when used alone impart a range of outdoor lifetimes to polyethylene film in the midlifetime range. They are not, however, as effective photosensitisers as oxygen-chelated iron compounds. For example, the iron acetyl acetonates are known to be highly active photoactivators for polyethylene, but they suffer from the serious practical

deficiency that they are also powerful prodegradants for polyolefins during processing.^{1,2,4}

The purpose of the present investigation is to explore the use of combinations of photo-prodegradants and antioxidants and stabilizers in order to approach more closely the "ideal" degradable polyethylene combinations which will photodegrade rapidly at predetermined times.⁵

Iron dimethyl dithiocarbamate (FeDMC, M=Fe, $n=3$ I) and iron acetylacetonate (FeAcAc, II) were used as photooxidation initiators and zinc diethyl dithiocarbamates (ZnDEC; I, M=Zn, $n=2$), nickel diethyl dithiocarbamate (NiDEC; I, M=Ni, $n=2$), tetramethyl thiuram disulfide (TETD III, R=Et), and 2-hydroxy-4-octyloxy benzophenone (HOBP, IV) were used to modify their behavior during processing and UV exposure:



EXPERIMENTAL

Materials

Unstabilized low density polyethylene was supplied by Imperial Chemical Industries Ltd as Alkathene WJG47, melt flow index (MFI)=2. Metal (M = Fe, Zn, Ni) dithiocarbamates were prepared by addition of metal chloride to the sodium salt of dithiocarbamic acid (ex. Robinson Bros). The precipitates (metal complexes) were washed with water and recrystallised from benzene: melting points and elemental analysis are shown in Table I. Tetraethyl thiuram disulfide was supplied by Robinson Bros. and used without further purification.

Polymer Processing and Testing

The additives were mixed and processed with LDPE in a Hampden-RA-PRA torque rheometer at 160°C, for various times in the presence of limited amount of oxygen (closed mixer, CM) or under oxygen excess (open mixer, OM). The polymer was then compression-molded at 160°C into sheets of thickness 200 μm .

TABLE I
Elemental Analysis, Color, and Melting Points for Some Derivatives of Dithiocarbamic Acid

Compound	Color	Melting point (°C)	C %	H %	N %	S %	
TETD	Pale yellow	70	40.70	7.00	9.20	43.40	Found
			40.54	7.79	9.46	43.24	Calcd
Zn DEC	White	170	33.20	5.70	8.30	36.10	Found
			33.09	5.55	7.90	35.34	Calcd
NiDEC	Green	225	34.00	5.50	7.64	36.40	Found
			33.80	5.67	7.88	36.10	Calcd
FeDMC	Black	> 300	25.60	4.40	10.10	45.00	Found
			25.90	4.35	10.04	46.00	Calcd

These films were irradiated in a UV cabinet in which 8 sunlamps and 24 actinic lamps were arranged in symmetrical sequence.

Screening experiments were carried out by placing LDPE films containing additives 3 mm behind unstabilized (additive free) LDPE films and UV-irradiated as described above. Melt flow index was measured on a Davenport melt flow indexer at 230°C and under a load of 2.16 kg.

RESULTS AND DISCUSSION

Photoantioxidant Behavior of Sulfur Complexes

Figure 1 compares the characteristically different behaviors of FeDMC and NiDEC in LDPE during photooxidation as a function of concentration. The nickel complex becomes progressively more effective as a photoantioxidant with increase in concentration; not only is the induction period extended but the post-induction period rate of photooxidation decreases. By contrast, the iron complex shows an increase in induction period but a commensurate increase in the post-induction period rate with increase in concentration. FeAcAc (II) behaves quite differently. Figure 2 compares the effect of FeAcAc during photooxidation with that of FeDMC under the same conditions. It is clearly a photo prooxidant both during processing (as indicated by the intercept on the carbonyl index axes) and during photooxidation. Figure 3 illustrates clearly the difference in behavior of FeAcAc during processing of LDPE and that of all the sulfur compounds discussed above. A typical 2-hydroxy benzophenone UV absorber (HOBP) has a very weak antioxidant effect during processing. It is evident from Figure 2 that the main difference between FeDMC and FeAcAc during photooxidation lies in the length of the induction period before photooxidation commences.

The rates of photooxidation after the autoaccelerating stage are not very different. ZnDEC, on the other hand, not only effectively inhibits oxidation during processing but also gives an induction period to photooxidation (see

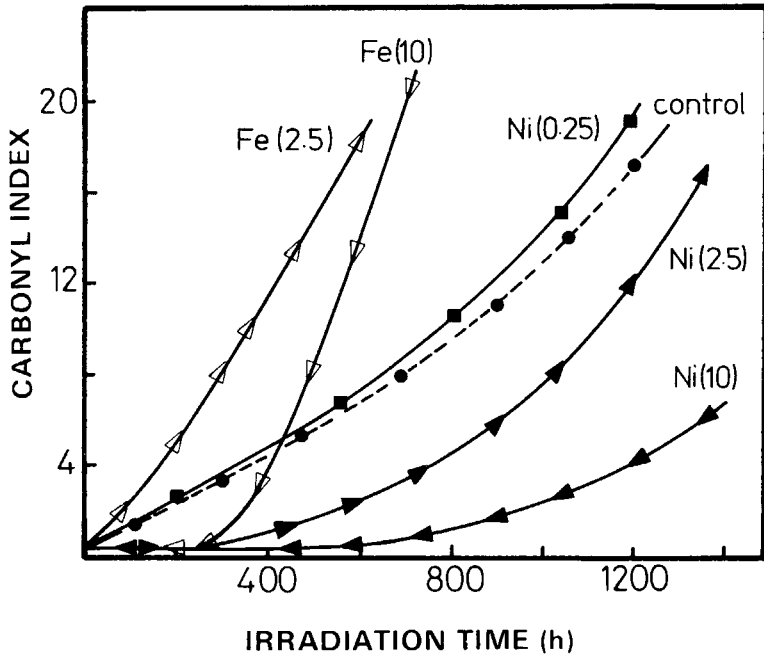


Fig. 1. Effect of concentration of FeDMC and NiDEC on photooxidative stability of LDPE processed for 10 min in CM. Numbers on curves are concentration of additives in mol/100 g $\times 10^{-4}$.

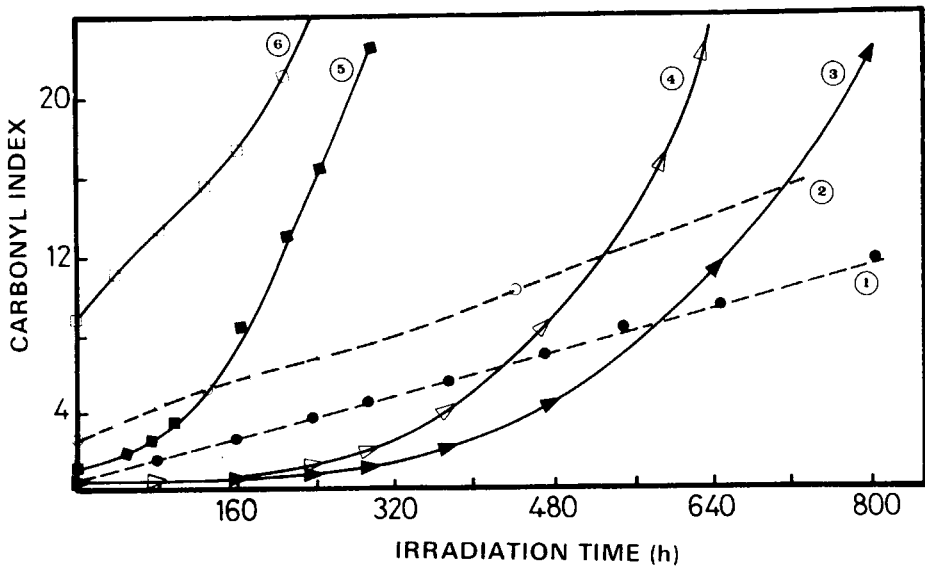


Fig. 2. Effect of processing conditions on photooxidative stability of LDPE containing additives (1×10^{-3} mol/100 g): (1) control processed for 10 min in closed mixer (10,CM); (2) control (30,OM); (3) FeDMC (10,CM); (4) FeDMC (30,OM); (5) FeACAC (10,CM); (6) FeACAC (30,OM).

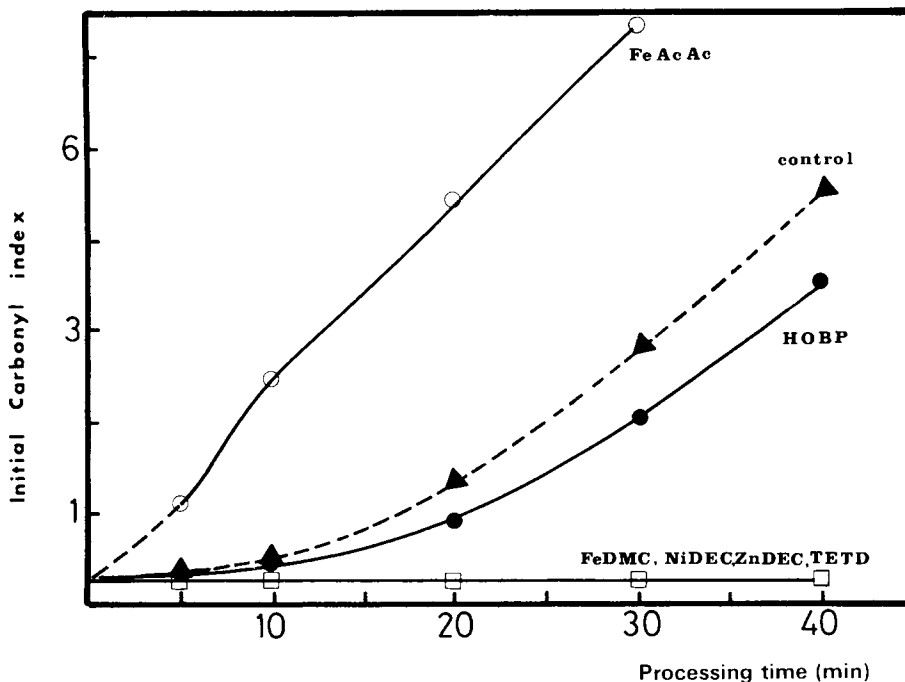


Fig. 3. Effect of additives (2.5×10^{-4} mol/100 g) on carbonyl formation in LDPE during processing in open mixer.

Fig. 4). The disappearance of the ligand as evidenced by the decay of the visible or UV absorbance of the metal complexes (see Fig. 5) corresponds to the induction period. The similarity in behavior of FeAcAc at the end of the induction period to that of the antioxidant, FeDMC, indicates the photochemical liberation of a prooxidant iron compound from the latter at the end of the induction period. There is clear evidence that the antioxidant ligands not only protect the polymer against photooxidation but in some way protect the ligand itself.¹⁷ One possible explanation for autoprotection in the case of the strongly UV absorbing metal chelates is that they may screen out the incident light, thus protecting the metal ligand bond from photolysis. Figure 6 provides clear evidence that this is not the explanation. LDPE films that were physically screened from the UV light by a film containing FeDMC underwent photo oxidation at a similar rate to a control film screened by a film which did not contain FeDMC whereas a film which contained the same concentration of FeDMC as an additive showed first an induction period and then a prooxidant effect. NiDEC has a greater physical screening effect than FeDMC (see Fig. 6), but this was also of marginal importance compared with the induction period it produced as an additive. The main effect of all the dithiocarbamate complexes lies in their peroxolytic activity during the induction period. The post-induction period rate may be higher than (FeDMC), lower than (NiDEC), or not very different (ZnDEC) from that of a control film without additive.

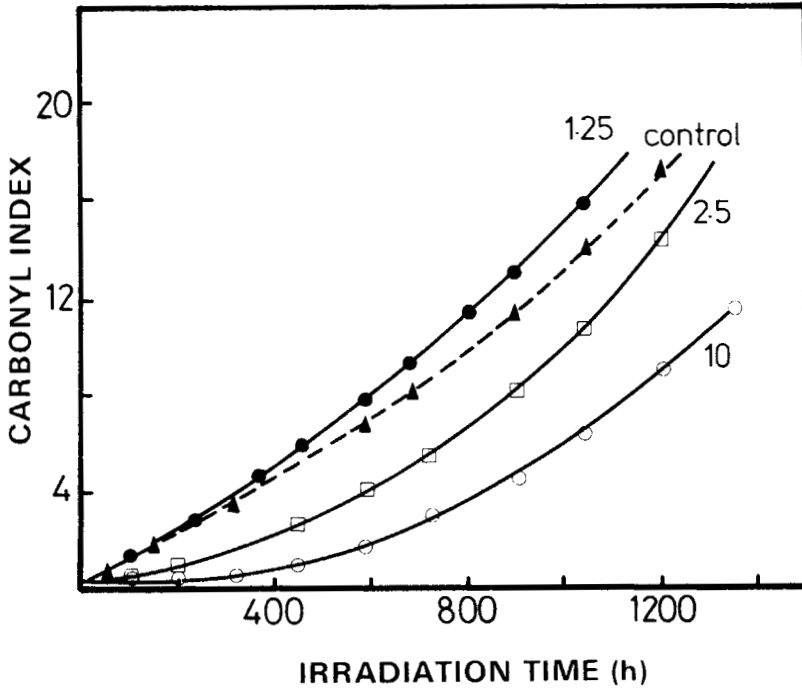


Fig. 4. Effect of concentration of ZnDEC on photooxidative stability of LDPE processed for 10 min in a closed mixer. Numbers on curves are concentrations of additive ($\text{mol}/100 \text{ g} \times 10^{-4}$).

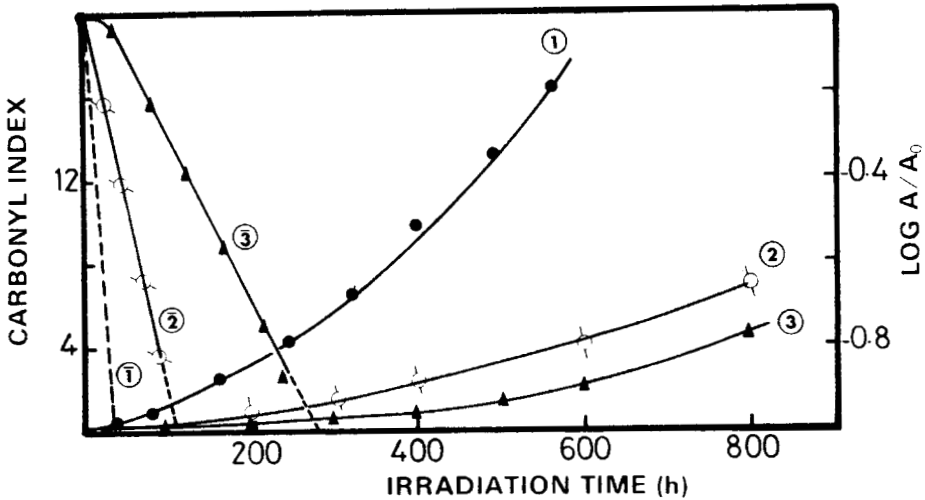


Fig. 5. Kinetics of disappearance of ZnDEC (280 nm), curve 2, and NiDEC (315 nm), curve 3, and disappearance of color of FeDMC, curve 1, in LDPE during photooxidation compared to the changes of carbonyl index of FeDMC (1), ZnDEC (2), and NiDEC (3) under the same conditions (concentration of additives $2.5 \times 10^{-4} \text{ mol}/100 \text{ g}$).

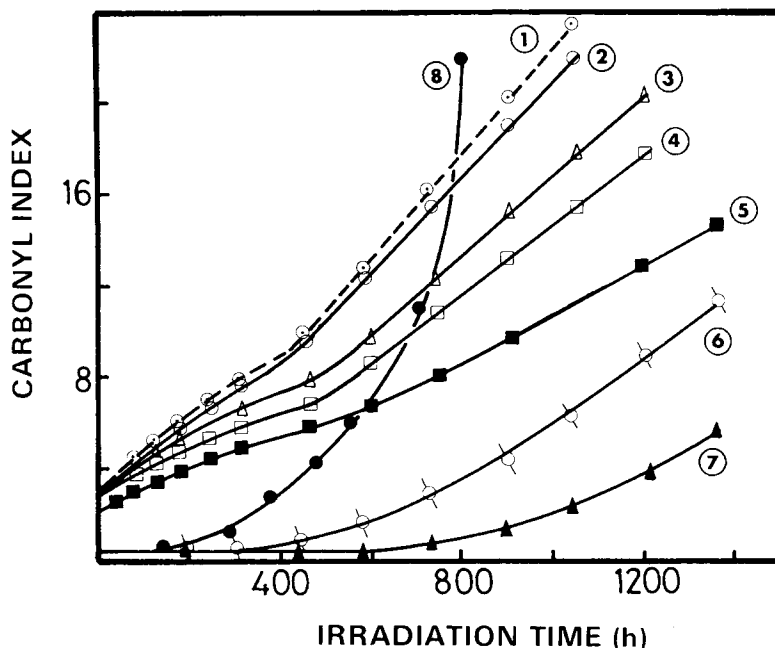


Fig. 6. The effect of metal dithiocarbamates and HOBP (1×10^{-3} mol/100 g) as screens (S) and as additives (A) on carbonyl formation in LDPE during UV irradiation: (1) control screened by control; (2) ZnDEC (S) and FeDMC (S); (3) NiDEC (S); (4) HOBP (S); (5) HOBP (A); (6) ZnDEC (A); (7) NiDEC (A); (8) FeDMC (A).

Combination Effects of Dithiocarbamate Metal Chelates

Figure 7 compares the photo prooxidant effect of FeDMC in the presence and absence of NiDEC. It has been shown previously⁸ that nickel and zinc dithiocarbamates when used together give a synergistic photoantioxidant effect under photooxidative conditions.

The behavior of FeDMC and NiDEC is quite different. At low concentration these additives appear to mutually sensitise each other. Figure 8 shows that much shorter lifetimes can be obtained using this combination than using FeDMC alone. However, the practically useful aspects of the FeDMC system are retained (i.e., reproducible induction period rate). Indeed, the post-induction period rate is actually increased leading to a closer approach to the ideal time controlled photoactivator.⁵

Figure 8 also shows that a relatively small concentration of NiDEC can be used to modify the lifetime of LDPE containing FeDMC over wide concentration ranges. In the absence of NiDEC the embrittlement time of LDPE decreases to about 900 h compared to 2000 h for the control as the concentration of FeDMC increases from 0.01% to 0.05% and then it increases up to 0.2%. In the presence of only 0.025×10^{-4} mol/100 g of NiDEC the lifetime of this LDPE can be varied by 500 h over the same FeDMC concentration range. Furthermore, the lifetime can be reduced considerably compared with the minimum achievable with FeDMC alone. This result is of considerable practical value since it is achieved without any sacrifice in the thermal stability of polyethylene during processing, since both are effective melt stabilisers (see Fig. 4).

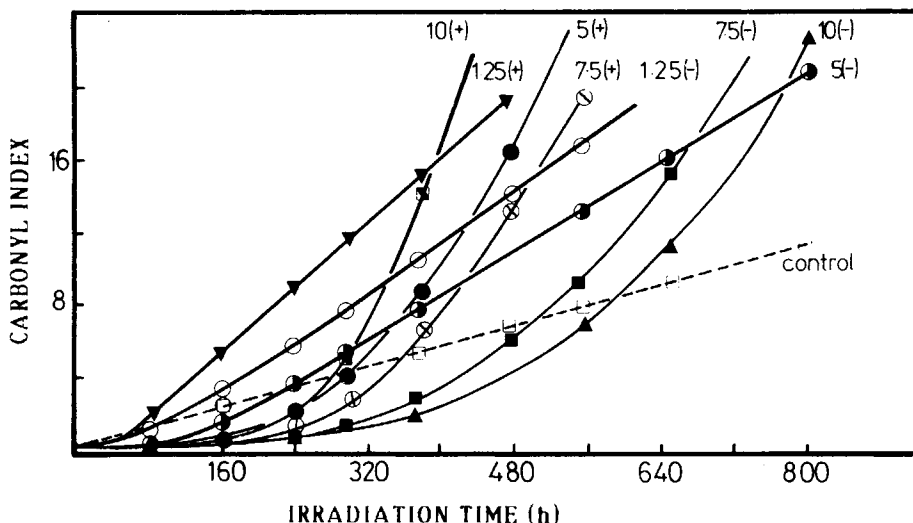


Fig. 7. Effect of concentration of FeDMC on photooxidation of LDPE in the presence (+) and absence (-) of NiDEC (2.5×10^{-5} mol/100 g). Numbers on curves are concentrations of FeDMC (mol/100 g $\times 10^{-4}$).

Similar effects are obtained using a combination of FeDMC and ZnDEC, although in this case the mutual sensitizing effect of the two metal complexes is less obvious (see Fig. 9).

Both Fe/Ni and Fe/Zn systems show interesting reversals of activity at higher iron concentration. All show an increase in stability from a minimum followed by a further decrease as the concentration of iron increases. Both the concentration of the dithiocarbamate ligand and the ratio of (Fe)/(Ni) affect the position and intensity of the peaks and troughs. The depth of the first instability trough at low additive concentration appears to depend primarily on the molar ratio (Fe)/(Ni) or (Fe)/(Zn). The combined sensitization effect of the pairs of additives is most evident at low concentration of both.

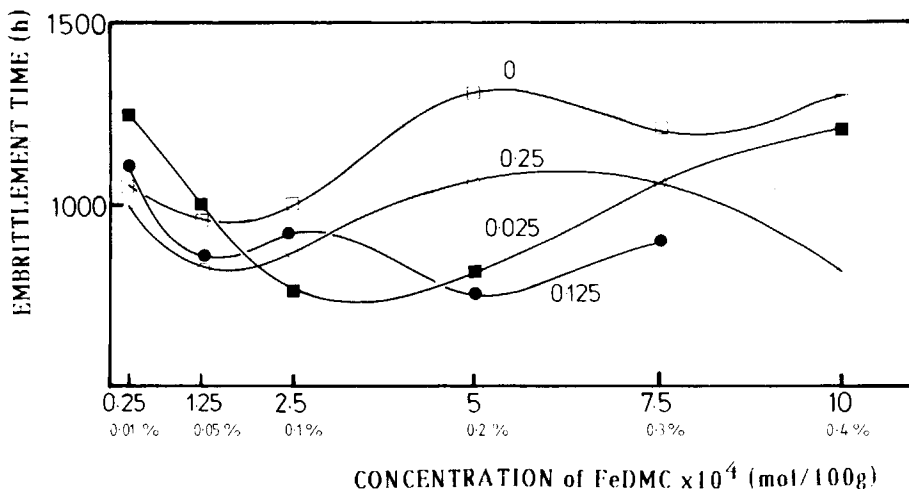


Fig. 8. The effect of combinations of FeDMC and NiDEC on the photooxidative lifetime of LDPE. Numbers on curves are concentrations of NiDEC (mol/100 g $\times 10^{-4}$).

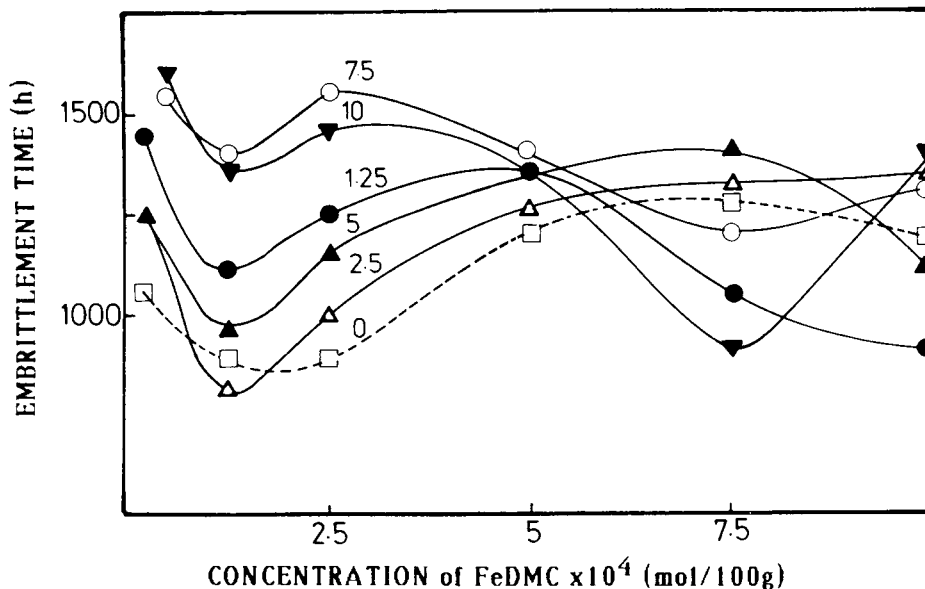


Fig. 9. The effect of combinations of FeDMC and ZDEC on the photooxidative lifetime of LDPE. Numbers on curves are concentrations of ZDEC (mol/100 g $\times 10^{-4}$).

Figures 1 and 4 show that, at low concentration, both NiDEC and ZnDEC alone can behave as mild photosensitizers. Their effects in combination with iron may therefore be regarded as mutual photosensitization. The second synergistic photoactivation trough is less easy to explain. However, it also occurs with the iron complex alone, and it seems likely that derived photolysis products of FeDMC are involved. It has been shown⁹ that primary products of the photolysis of the FeIII dithiocarbamates are the corresponding thiuram disulphides. These are themselves photosensitive, and Figure 10 shows that they are very effective photo prooxidants at low concentration, although at higher concentration they are equally effective photoan-

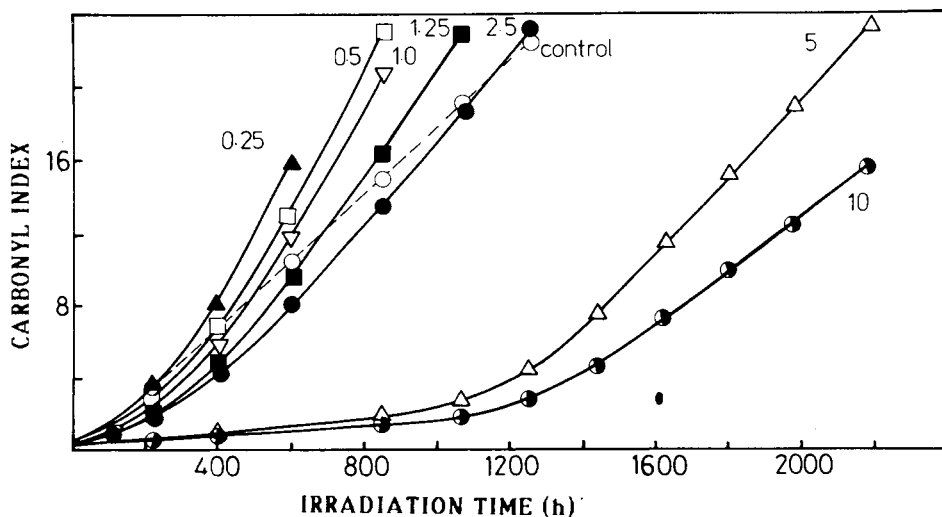
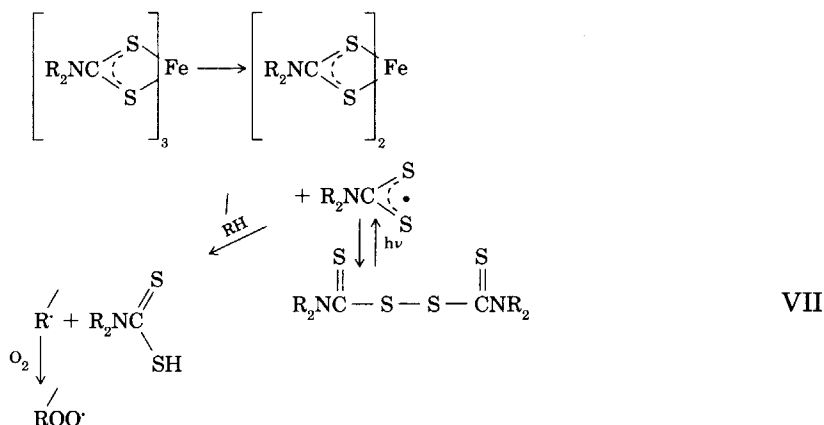


Fig. 10. Effect of concentration of TETD on photooxidative stability of LDPE processed for 10 min in CM. Numbers on curves are concentrations (mol/100 g $\times 10^{-4}$).

tioxidants. The thiurams are thought to be formed within the solvent cage, the reaction being facilitated by oxygen. The probable chemistry of this secondary process is outlined in Scheme 1:



Scheme 1. Sensitization of polyethylene by secondary products derived from dithiocarbamate Fe (III) complexes

The stabilizing role of the second metal complex discussed above is not immediately obvious but may possibly result from their known ability to trap alkylperoxyl radicals.¹⁰

Combination of FeDMC and a Thiuram Disulphide

If the conclusion reached in the last section is correct, then the addition of a thiuram disulphide, VII, at low concentration to FeDMC in LDPE should also give rise to a synergistic photosensitizer. The concentration/activity profile for this combination is shown in Figure 11. Although the behavior is very similar to that of ZnDEC and NiDEC at low concentrations, the second minimum, characteristic of FeDMC when used alone, is missing. This evidence is consistent with the theory propounded above that the second minimum is due to the derived thiuram disulfide formed in low concentration. When used at higher concentration, TETD stabilizes the polymer just as it does in the absence of FeDMC (see Fig. 10).

Combination Effects of a Prooxidant Iron Dithiolate (FeAcAc) with an Antioxidant Dithio Carbamate (ZnDEC)

It is clear from the foregoing that the most important photo-prooxidant species which eventually leads to rapid photodegradation of polyethylene are the organosoluble iron salts (see Fig. 2). However, an ideal system for commercial use should have additional attributes. In particular, it should impart processing and storage stability, a controllable induction period during photooxidation, and a rapid post-induction period rate. It was, therefore, of interest to examine combinations of a typical photoactive iron complex with an effective peroxidolytic antioxidant, which is also known to stabilize polyethylene during processing. ZnDEC satisfies this latter requirement. Figure 12 shows the typical behavior of FeAcAc (VI) in the presence of a small concentration (1.25×10^{-4} mol/100 g) of ZnDEC. All the formulations

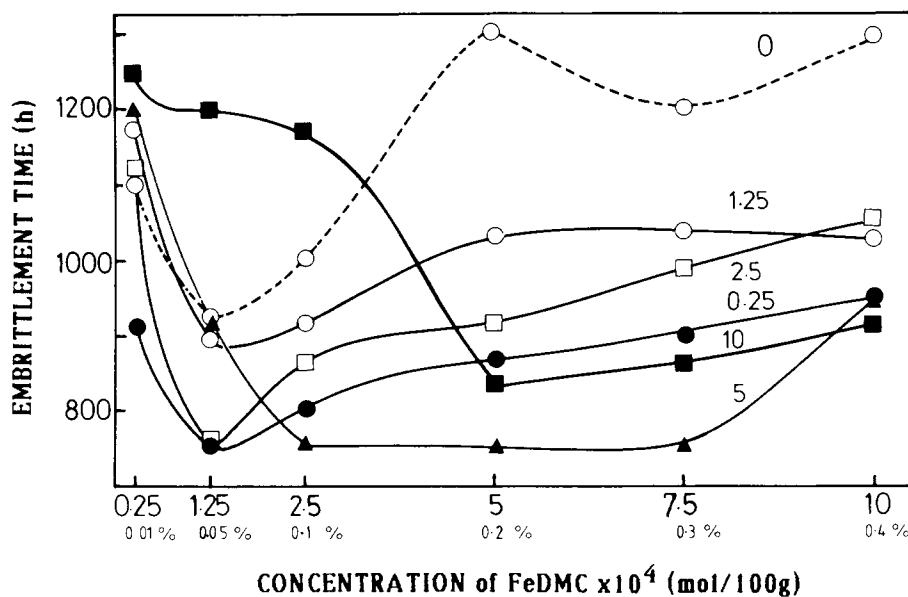


Fig. 11. The effect of combinations of FeDMC and TETD on the photooxidative lifetime of LDPE. Numbers on curves are concentrations of TETD ($\text{mol}/100 \text{ g} \times 10^{-4}$).

were effectively stabilized during processing, even those with a substantial molar excess of FeAcAc (see Table II). Higher FeAcAc concentrations gave longer induction periods to photooxidation. Their behavior is consistent with the postulated metathesis between iron compounds and ZnDEC in the polymer melt during processing.³ The two-component systems therefore behaves basically as though it were FeDEC in the presence of excess FeAcAc, the

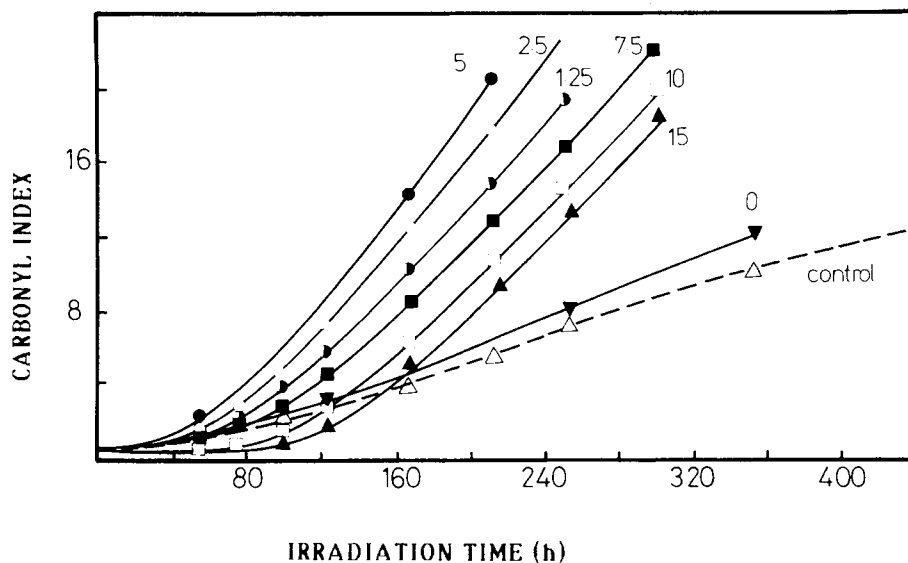


Fig. 12. The effect of ZnDEC ($1.25 \times 10^{-4} \text{ mol}/100 \text{ g}$) in combination with different concentrations of FeACAC on the photooxidative stability of LDPE processed for 10 min in CM. Numbers on curves are concentrations of FeACAC ($\text{mol}/100 \text{ g} \times 10^{-4}$).

TABLE II
Effect of a Small Amount of ZnDEC (1.25×10^{-4} mol/100 g) on the Melt Stability of FeAcAc with Increasing Concentration of the Latter

FeAcAc Conc (10^{-4} mol/100 g)	M:F:I (g/10 min)
1.25	2.34
2.5	2.38
5.0	2.40
7.5	2.40
10.0	2.42
15.0	2.40

dithiocarbamate providing the necessary processing stability. Figure 13 shows that all the FeAcAc/ZnDEC formulations examined were highly effective photo prooxidants for polyethylene. (Compare with FeDMC control in Fig. 11.)

Combination of FeDMC with a Conventional UV Absorber (HOBP)

It might be anticipated that HOBP would retard the photodecomposition of FeDMC in LDPE and hence act as a retarder for the iron catalysed photooxidation. Figure 14 shows that this is only true at relatively high concentrations of HOBP. At lower concentrations it acts as a sensitizer similarly to the antioxidant metal complexes. Unlike the latter, however, it does not show a reversal with increase in concentration of FeDMC but a slight almost linear decrease at all concentrations of HOBP. Photo-prooxidant effects have not previously been reported in the case of the UV absorbers, and it appears that in the presence of FeDMC, at least at low concentrations, HOBP is behaving much more like a typical benzophenone sensitizer.

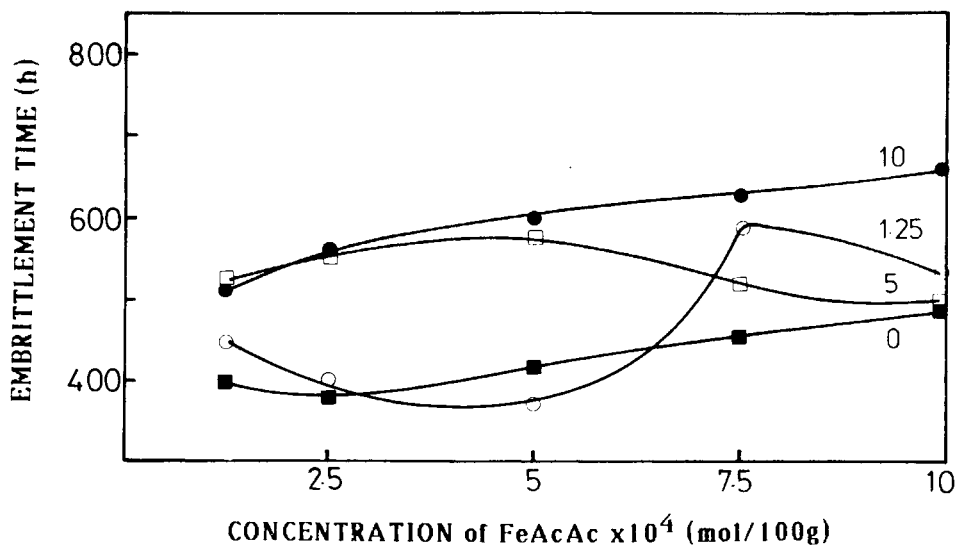


Fig. 13. The effect of combinations of FeACAC and ZDEC on the photooxidative lifetime of LDPE. Numbers on curves are concentrations of ZDEC (mol/100 g $\times 10^{-4}$).

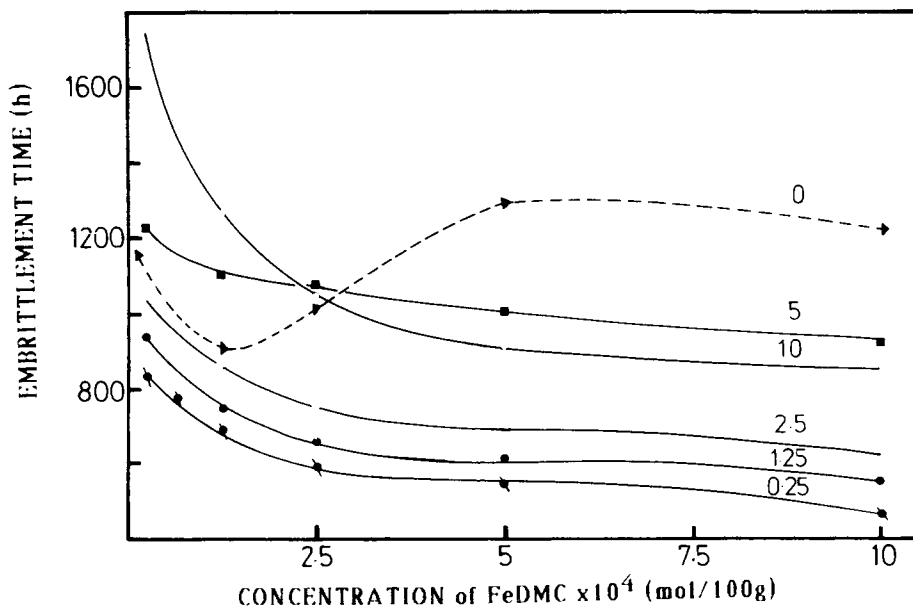


Fig. 14. The effect of combinations of FeDMC and HOBP on the photooxidative lifetime of LDPE. Numbers on curves are concentrations of HOBP (mol/100 g $\times 10^{-4}$).

CONCLUSIONS

Although all the photoantioxidants investigated retard the photoactivating effect of FeDMC, only NiDEC gives the ideal behavior required in time-controlled photodegradable agricultural films. The unique behavior of this system can be categorized as follows:

1. At low concentrations, NiDEC sensitizes FeDMC, whereas at higher concentrations it causes a pronounced but controllable induction period.
2. The presence of NiDEC does not modify the photoactivating effect of the ionic iron liberated from FeDMC so that long induction periods can be obtained followed by a very rapid photooxidation rate.
3. The concentrations of additives required for a delayed action photoactivator are much lower with this system than with other combinations.
4. The combination provides effective melt stabilization of the polymer during processing.

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