

Mechanisms of antioxidant action: effect of processing conditions on the stabilizing effectiveness of metal xanthates and related dixanthogen in polypropylene

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The effects of processing conditions, on the thermal and photo-oxidation of polypropylene containing different metal octyl xanthates (MOX) and the related dixanthogen (OX) have been examined. It is concluded that in the presence of a limited amount of oxygen the metal xanthates (e.g. nickel and cobalt) are better u.v. stabilizers than the dixanthogen, and their greater effectiveness is attributed to a combination of complementary mechanisms, i.e., peroxide decomposition, u.v. absorption, u.v. screening and radical scavenging. Under severe processing conditions (excess oxygen), the activity of the metal xanthates is reduced and their effectiveness becomes very similar to that of the corresponding dixanthogen in both melt and u.v. stabilization. The main mechanism of action in this case is peroxide decomposition.

(Keywords: antioxidants; polypropylene; u.v. stabilization; xanthates; dixanthogens)

INTRODUCTION

It has been shown¹⁻⁵ that the nickel alkyl xanthates (NiRX) behave similarly as antioxidants to the nickel dithiophosphates. Not only are they effective thermal antioxidants, but they also show a high level of u.v. stabilizing activity. It has been proposed that the general mechanism involved in each case is the oxidation of the nickel complex to the corresponding disulphide and further oxidation products which are effective peroxidolytic antioxidants (PD-C). The purpose of the present investigation is to establish to what extent this occurs during processing and how the conditions affect the subsequent performance of the stabilizers.

EXPERIMENTAL

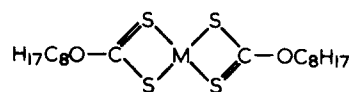
Materials

Unstabilized polypropylene (PP) was supplied by Imperial Chemical Industries Ltd as Propathene HF 20C GV 170.

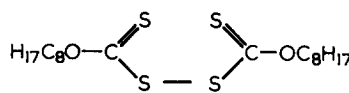
All metal octyl xanthates, MOX where M = K, Ni, Co, Fe and Cu and the corresponding octyl dixanthogen (OX) were prepared by known procedures⁶⁻¹⁰.

Processing of PP

The additives (3×10^{-4} mol/100 g) were mixed and processed with PP in a RAPRA Torquerheometer at 180°C for 10 min in a closed (CM) and open (OM) mixer as described previously¹. The polymer was then



MOX



OX

compression moulded at 180°C into sheets of thickness 200 μm^1 .

Irradiation

Films were irradiated in a u.v. cabinet in which 8 sun lamps and 24 actinic blue lamps were arranged in symmetrical sequence.

Thermal ageing

The accelerated thermal oxidation of the compressed films was carried out in a Wallace oven at 140°C in the presence of air as described previously¹.

Screening

Processed polymer films containing xanthates were mounted in front of unstabilized (additive-free) PP film such as to allow an air gap between the two films i.e. there is no direct physical contact between them. The gap between every set of 2 films was maintained constant at 0.3 cm. These films were u.v. irradiated and changes in

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carbonyl indices of the rear unstabilized PP films were monitored in each case. Unstabilized PP film screened by another unstabilized PP film (with the same air gap between the films) was used as a control for these experiments.

Melt flow index (MFI) measurements

Processed PP samples were extruded in a Davenport melt flow indexer at 230°C and under a load of 2.16 kg. The weight average of at least five samples extruded per fixed time was recorded.

RESULTS AND DISCUSSION

Melt stabilization

Figure 1 compares the MFI's of PP containing different metal octyl xanthates (MOX) and their corresponding disulphide (OX) to those of unstabilized PP control films. Processing was carried out in both open mixer (OM) and closed mixer (CM). It is clear that all the metal complexes and the disulphide are good melt stabilizers for PP. The oxidizabilities of PP control films processed in OM and CM differ by a factor of 10 (Figure 1). On this basis, MFI values for PP films containing xanthates processed in CM and OM can be quantitatively compared. In general, therefore, all the additives were more effective, related to the unstabilized controls, in OM than in CM. A second conclusion from Figure 1 is that the metal centre is relatively less important in OM conditions than in CM.

Figure 2 shows a plot of embrittlement time on u.v. exposure of PP containing metal xanthates and dixanthogen as a function of MFI after processing. It is clear that OM conditions severely reduce the u.v. stabilizing effectiveness of the metal xanthates and the nature of the metal is relatively unimportant. There is a related reduction in activity of the same compounds as melt stabilizers. Further, the disulphides which operate primarily by the peroxidolytic (PD-C) mechanism⁵ show a relatively small difference between CM and OM conditions. It seems clear then, that under OM conditions the PD-C mechanism predominates both in the melt and during u.v. irradiation. Figure 2 shows the same trend in stabilizing effectiveness of the metal complexes (CoOX > NiOX > FeOX) in both open and closed systems.

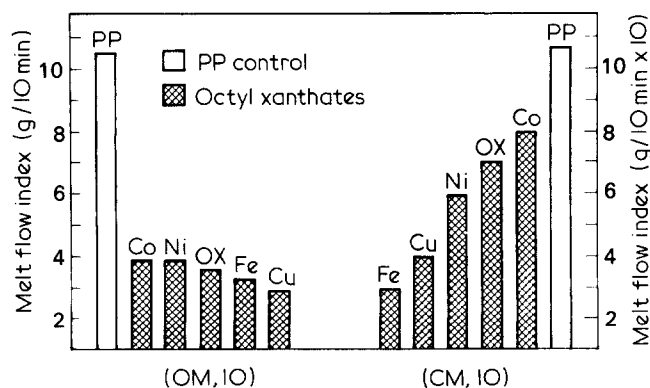


Figure 1 Changes in melt flow index of PP containing different metal octyl xanthates (MOX) and octyl dixanthogen (OX) processed in closed and open mixer for 10 min. Concentration of all additives is 3×10^{-4} mol/100 g

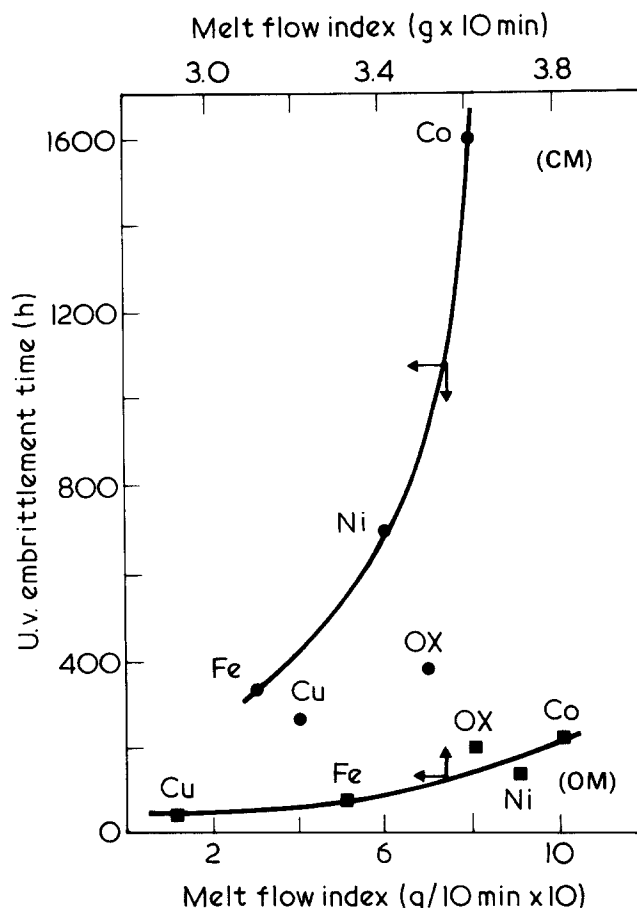


Figure 2 Relation between u.v. embrittlement time and melt flow index (MFI) of PP containing metal octyl xanthates (MOX) and octyl dixanthogen (OX) under severe (OM, 10) and mild (CM, 10) processing conditions. Concentration of all additives is 3×10^{-4} mol/100 g

Two main processes must be considered for the mechanism of melt stabilization; radical scavenging and peroxide decomposition.

The effectiveness of the metal dithiolates as antioxidants is mainly due to their ability to destroy hydroperoxides the most important radical initiators for oxidative degradation^{4,5}. Nickel and copper dithiolates have in addition been shown^{1,12} to act by the chain-breaking (CB) mechanism. However, the relative contribution of these processes is greatly influenced by the ratio of sulphur compound to peroxide¹ and consequently on the availability of oxygen¹³. In general copper dithiolates have been shown to be relatively more effective as radical scavengers than the other metal dithiolates¹⁴. The disulphides, however, have been shown⁵ to act mainly as peroxide decomposers and their radical scavenging ability is only limited.

Photo and thermal stabilization of xanthates

Figure 3 and Table 1 show that under mild processing conditions (CM, 10), all the xanthates except KOX are effective u.v. stabilizers. Mildly processed (CM) FeOX and OX, although they show an initial pro-oxidant effect during the early stage of u.v. irradiation, autoretard to give an induction period before further oxidation.

It has been shown¹⁶ that iron dithiolates (e.g. iron dithiocarbamates) photolyse giving rise to the corresponding disulphides along with other oxidation

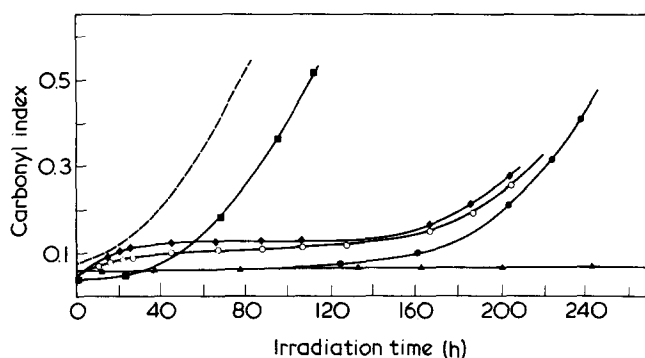
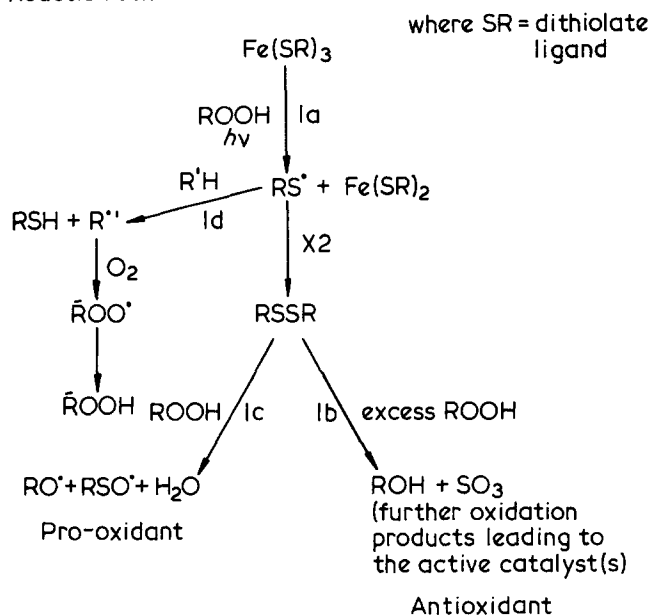


Figure 3 Effect of metal octyl xanthates (MOX) and octyl dixanthogen (OX), 3×10^{-4} mol/100 g, on photo-oxidation of PP. All samples are processed in a closed mixer for 10 min. ----, PP; ■, KOX; ◆, FeOX; ○, OX; ●, CuOX; ▲, NiOX and CoOX

products. The disulphides themselves photolyse giving rise to both antioxidant species (reaction scheme 1a) and pro-oxidant products (reaction 1b). The more the former process is favoured the higher the concentration of peroxides. The dixanthogen is relatively unstable to u.v. light compared with the nickel and cobalt xanthates (see Figure 4). The iron xanthate was so unstable to u.v. light that its decomposition kinetics could not be followed under the same conditions. It seems then, by analogy with the iron dithiocarbamates (Scheme 1), that the reason for

Reaction scheme 1



the initial rapid rise in carbonyl concentration in the polymer (Figure 3) is associated in both cases with the formation of pro-oxidant thiyl radicals. During later stages of photo-oxidation the disulphides (formed as primary intermediates) are further oxidized to the antioxidant species responsible for the peroxide decomposition⁴. The slow generation of sulphur acids is consistent with the observation of an induction period at this stage of photo-oxidation. In all other cases an induction period is observed from the start of u.v. exposure and the pro-oxidant step is missing.

Stability to photo-oxidation is a primary requirement

of the metal complex u.v. stabilizers⁴. This condition is satisfied by the xanthate complexes of nickel, cobalt and copper whereas the photo-oxidative stabilities of the corresponding disulphides and the iron complex are low (at the same molar concentration). Figure 4 shows the decay of the u.v. absorption bands for nickel ethyl xanthate and the corresponding dixanthogen in solution and for NiOX, CoOX and OX in PP under photo-oxidative conditions.

Figure 5 indicates that screening by CoOX contributes at least in part, to the higher effectiveness of the cobalt as compared to the nickel complex, probably by protecting photosensitive oxidation⁵ products. However, neither iron nor copper xanthates, nor the dixanthogen, exhibit

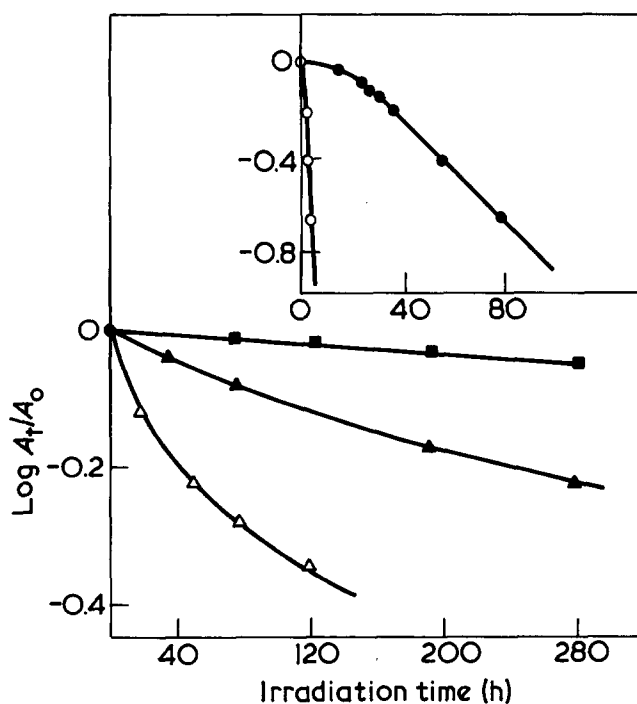


Figure 4 Kinetics of disappearance of CoOX (325 nm), NiOX (316 nm) and OX (285 nm) in PP samples (processed in CM) during photo-oxidation. Inset shows kinetics of disappearance of NiEX (316 nm) and EX (285 nm) in hexane during photo-oxidation. Concentration of all additives is 3×10^{-4} mol/100 g. ●, NiEX; ○, EX; ■, CoOX; ▲, NiOX; △, OX

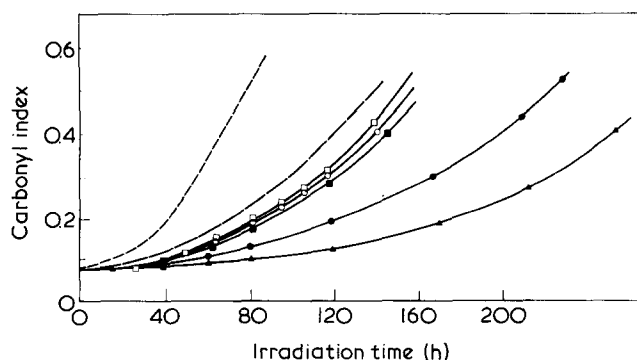


Figure 5 Effect of metal octyl xanthates (MOX) and octyl dixanthogen (OX), 3×10^{-4} mol/100 g, as screens on the photo-oxidation of PP. All films are processed in CM for 10 min. ----, PP; ·····, PP screened by PP; □, OX; ○, FeOX; ■, CuOX; ●, NiOX; ▲, CoOX

Table 1 U.v.-embrittlement times of PP films containing xanthates processed in CM and OM for 10 min at 180°C

Additive (3×10^{-4} mol/100 g)	U.v. - EMT (h) ^a	
	(CM,10)	(OM,10)
PP(control)	80	40
Co ^{III} OX	1600	330
Ni ^{II} OX	700	130
Fe ^{II} OX	330	60
Cu ^I OX	250	45
KOX	120	65

^a U.v. EMT = u.v. embrittlement time

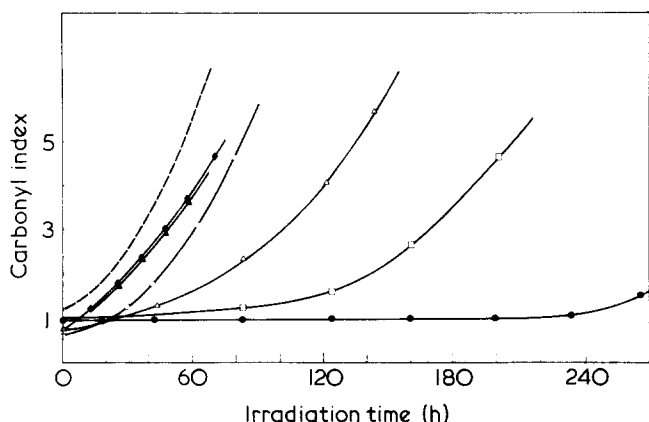


Figure 6 Effect of metal octyl xanthates (MOX) and octyl dixanthogen (OX), 3×10^{-4} mol/100 g, on photo-oxidation of PP (processed in OM for 10 min). ---, PP; ◆, CuOX; ▲, FeOX; ○, KOX; △, NiOX; □, OX; ●, CoOX

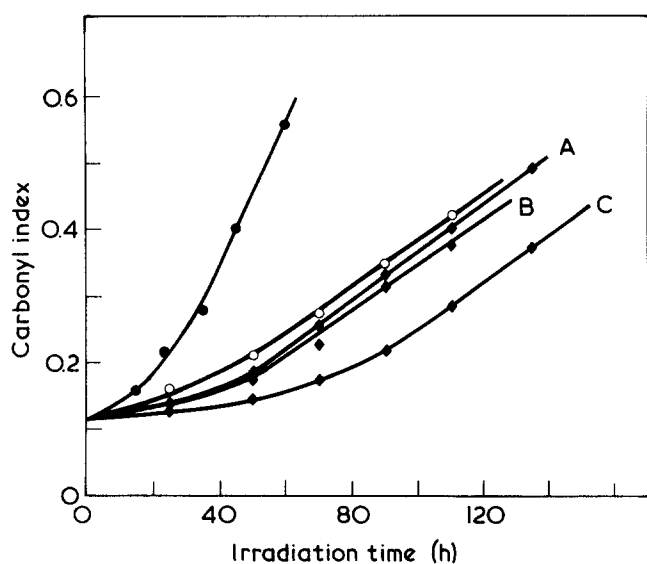


Figure 7 Effect of metal octyl xanthates (MOX) and octyl dixanthogen (OX) as screens on the photo-oxidation of PP. All films are processed in OM for 10 min. ●, PP; ○, PP screened by PP; A, OX; B, NiOX; C, CoOX

significant screening ability. Xanthates of nickel and cobalt, therefore, impart stabilization through a combination of complementary mechanisms: radical scavenging, peroxide decomposition and u.v. screening. Iron xanthate (at the concentration used) and the dixanthogen, however, function almost exclusively as peroxide decomposers.

The presence of a substantial amount of oxygen during processing (OM) markedly reduces the u.v. stabilizing

effectiveness at the metal xanthates (see Table 1 and compare Figure 3 and Figure 6). The u.v. stabilizing effect of the dixanthogen, however, remains relatively unaffected, but the rapid oxidation which occurs during the early stages of u.v. irradiation when processed in CM (see Figure 3) is virtually eliminated. This must be due to the fact that processing in OM leads to a higher concentration of oxidation products, and indeed no characteristic disulphide u.v. absorption can be observed in films processed in OM. Consequently, during photo-oxidation where both reactions 1c and 1b (Scheme 1) occur, there is a net shift towards reaction 1b. Retardation rather than a real induction period is observed under these conditions. More metal xanthates is lost during OM processing due primarily to chemical transformation and to a lesser extent to a physical loss. This is supported by comparing Figure 7 with Figure 5 which shows that the screening effect of the different metal xanthates was reduced when this experiment was carried out for PP films containing metal xanthates processed in OM. Figure 7 suggests, therefore, that the primary stabilizing mechanism is peroxide decomposition and that the performance of nickel and cobalt xanthate under open mixer conditions become similar to that of the dixanthogen (see Figure 2).

Figures 8 and 9 show the thermal stabilization of PP by

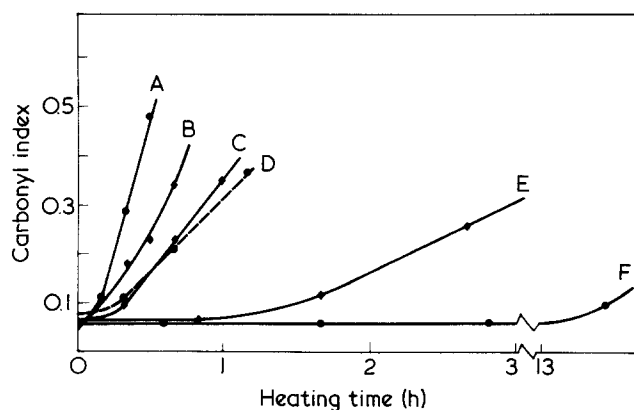


Figure 8 Effect of metal octyl xanthates (MOX) and octyl dixanthogen (OX), 3×10^{-4} mol/100 g, on the thermal oxidation of PP. All films are processed in CM for 10 min. A CuOX; B, FeOX; C, CoOX; D, PP; E, OX; F, NiOX

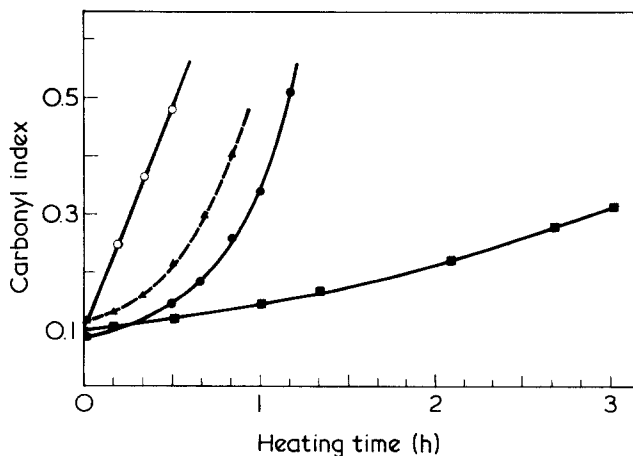


Figure 9 Effect of metal octyl xanthates (MOX) and octyl dixanthogen (OX), 3×10^{-4} mol/100 g, on thermal oxidation of PP. Films are processed in OM for 10 min. ○, CoOX; ▲, PP; ●, NiOX; ■, OX

xanthates under both CM and OM processing conditions. Both NiOX and the corresponding dixanthogen have the greatest effect. The other metal xanthates exhibit a pro-oxidant effect except CoOX which shows some initial stabilization. In an open mixer, dixanthogen was even more effective than nickel xanthate (Figure 9), whereas cobalt xanthate was a pro-oxidant. These observations provide strong support for the view that in the presence of excess oxygen, the disulphide is converted to an effective peroxidolytic antioxidant.

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