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Photodegradation: A Solution for the Shopping Bag "Visual Pollution" Problem?

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SUMMARY: Plastic bags pose a "visual pollution" problem as they have a high surface-to-volume ratio and because they are often brightly coloured. Enhanced photo-oxidation is a possible route to accelerate the mineralisation of such litter. Thus we evaluated the effect of selected metal complexes and an anti-oxidant on the accelerated weathering of blown polyethylene and polypropylene films in a QUV tester. It was found that the additives were more effective in polypropylene than in polyethylene. The transition metal complexes, particularly ferric stearate, were very effective photodegradants. Copper stearate provided a measure of UV protection to polyethylene but not to polypropylene. Poly (1,2-dihydro-2,2,4-trimethylquinoline), a commercial anti-oxidant, also caused accelerated UV degradation. This is significant as its use as a prodegradant is not expected to adversely affect the recyclability of the polymers.

Introduction

Plastic shopping bags have become an integral part of the South African life-style. Most retailers supply them free of charge to their customers.[1,2] Previously such bags were recovered and recycled after use. Flexible, black plastic irrigation pipe was a typical re-use application. Unfortunately, progress in film blowing and resin technology has now made it possible to produce bags that are so thin that post-consumer recycling has become impractical. Furthermore, our public is not yet sensitised with respect to environmental issues. Littering is therefore a major problem.

Plastic shopping bags are fairly resistant to degradation, are often brightly coloured and have a high surface-to-volume ratio. This leads to such a substantial "visual" pollution problem that they have been dubbed the "New National Flowers" of South Africa. The South African Government is exploring various ways of solving this problem. Increasing film thickness to encourage re-use and recycling is a strategy that is being considered. Despite these efforts, it is anticipated that the littering problem will continue for some time in the future.

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Photodegradation[2-7] can aid rapid disintegration of polymers into a powdery residue with a much-reduced visual impact. It is a strategy used in Israel for controlled mineralisation of polymer films used in agricultural applications.[8] The problem with this approach is that it often precludes subsequent recycling. The photodegradants, once activated, also enhance thermo-oxidative degradation. This means that the polymer will also degrade faster during reprocessing in extruders.

In this study we investigate the use of metal complexes and antioxidants that, while showing photodegradation activity, have minimal effect on thermo-oxidative degradation under plastic processing conditions.

Oxidative Degradation in Polymers

Organic polymers are subject to degradation by atmospheric oxygen. This process is an autocatalytic, free radical chain reaction.[7] The effects vary from simple discoloration, through a reduction in gloss, to cracking and embrittlement. Eventually complete loss of mechanical integrity results. The degradation reaction leads to the formation of carbonyl (>C=O) bonds. They show a strong infrared band at ≈ 1710 cm^{-1}. The progress of the oxidative degradation reaction can therefore be followed spectroscopically.[7]

Antioxidants are used to prevent or retard the autoxidation of polymers in order to minimise the associated damage. The mechanism of thermal oxidation of organic polymers occurs via the free-radical chain reaction outlined in Scheme 1.

1. Initiation	Initiator $\rightarrow$ Free Radicals ($R^\bullet$)
2. Propagation	$R^\bullet + O_2 \rightarrow ROO^\bullet$
	$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$
3. Autocatalysis	$ROOH \rightarrow RO^\bullet + HO^\bullet$
4. Termination	$R^\bullet + R^\bullet \rightarrow R\text{-}R$
	$ROO^\bullet + R^\bullet \rightarrow ROOR$

Scheme 1. Simplified model of the autoxidation of organic polymers.[7]

Initiation can be mediated by impurities or by thermal; mechanical or light induced degradation of the polymer. Hydroperoxide impurities are recognised as the principal free radical initiators. However, absorption of UV light can also produce radicals by the cleavage of hydroperoxides and ketones. Furthermore, homolytic chain cleavage can result from the mechanical stress experienced by the polymer during processing. Trace levels of transition metal ions such as copper, iron, cobalt and manganese accelerate the rate of oxidation by catalysing the decomposition of hydroperoxides into free radical species (Scheme 2). Depending on the polymer substrate and the reaction conditions, the termination reactions may give rise to chain scission, e.g. as in polypropylene, or crosslinking, e.g. as in polyethylene.

$$\begin{array}{lcl}
\mathrm{ROOH} + \mathrm{M}^{+} & \rightarrow & \mathrm{RO}^{\bullet} + \mathrm{HO}^{-} + \mathrm{M}^{2+} \\
\mathrm{ROOH} + \mathrm{M}^{2+} & \rightarrow & \mathrm{ROO}^{\bullet} + \mathrm{H}^{+} + \mathrm{M}^{+} \\
\hline
2\mathrm{ROOH} & \rightarrow & \mathrm{RO}^{\bullet} + \mathrm{ROO}^{\bullet}
\end{array}$$

Scheme 2. Metal ions catalysing the decomposition of hydroperoxides to produce alkoxy and peroxy radicals.[7]

Commercial photodegradants include organic compounds such as substituted benzophenones that act as photoactivators.[4,5] Metal-organic compounds are also employed and play a catalytic role in the degradation mechanism.[6,7] For this study we chose to compare the photocatalytic activity of a series of metal complexes to that of the commercially applied iron (III) stearate.

Oxidative film embrittlement is primarily the result of the clipping of tie-molecules between crystallites.[7] At an early stage the material can, in principle, still be reprocessed into a useful material. Reprocessing forms new crystallites connected by new tie-molecules. It is clear that this is only possible if the photodegradants used do not affect thermal degradation in the recycling extruder. It was therefore decided to also investigate the possibility of using suitable anti-oxidants as UV prodegradants.

In this respect the oligomers of 1,2-dihydro-2,2,4-trimethylquinoline (OTMQ) are of special interest. OTMQ is a well-established anti-oxidant for cross-linked polyethylene.[9-12] Literature[12] also mentions synergistic interactions between OTMQ and other classes of antioxidants, e.g. hindered phenols.

The amine functionality in OTMQ is very similar to that of Hindered Amine Light Stabilisers.[13] It might therefore be expected that it could act as a light stabiliser for polymers. Such activity was indeed reported by Laurenson *et al.*[14] for polyethylene and Saure[15] for epoxy resins. On the other hand Toyoshima *et al.* [16] report that OTMQ acts as a catalytic photodegradant for polypropylene. We therefore decided to re-evaluate the performance of OTMQ in both polyethylene and polypropylene.

Experimental

Materials

Table 1 lists the compounds used in this study. Unstabilised samples of low-density polyethylene (LDPE) and polypropylene homopolymer were obtained from Polifin.

Table 1. Compounds used as additives in the polymer films

Compound	**CAS No.**
poly (1,2-dihydro-2,2,4-trimethylquinoline) (OTMQ)	[26780-96-1]
2,6-di-*tert*-butyl-4-methylphenol	[128-37-0]
tetrakis[methylene (3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamate)] methane	[6683-19-8]
tris(2,4-di-*tert*-butyl-phenyl) phosphite	[2082-79-3]
phenolphthalein	[77-09-8]
Iron (III) 2,4-pentanedione	[14024-18-1]
Titanyl 2,4-pentanedione	[14024-64-7]
Zirconyl 2,4-pentanedione	[17501-44-9]
Magnesium 2,4-pentanedione	[6488-07-3]
Vanadyl 2,4-pentanedione	[3153-26-2]
Copper 2,4-pentanedione	[13395-16-9]
Calcium 2,4-pentanedione	[19372-44-2]
Aluminium 2,4-pentanedione	[13963-57-0]
Nickel dimethylglyoxime	[13478-93-8]
Calcium stearate	[1592-23-0]
Iron (III) stearate	[2980-59-8]

The commercially available stabiliser additives were masterbatched (10% actives level by mass) into a 20 MFI polyethylene resin on a laboratory extruder. The other additives were incorporated into the polymer resin in powder form by high speed mixing.

Ferric stearate was prepared as follows. Potassium hydroxide (0,165 mol) was dissolved in 1 litre of distilled water. A total of 46.94 g (0,165 mol) stearic acid was added in small portions while stirring. The next quantity was only added upon complete dissolution of the previous quantity. To this solution was then added a total of 26,94 g (0,055 mol) ferric sulphate pentahydrate. The resultant precipitate was recovered by filtration. The filter cake was washed with copious quantities of distilled water to remove the soluble potassium sulphate. The product was dried for 24 hours at 60°C in a convection oven. The yield was 48,6 g (96,7%).

Anti-oxidant Properties

The oxidation induction temperature (OIT) was used as a measure to determine the effect of the additives on the thermal stability of the polymers. A high OIT value implies high antioxidant activity. The technique provides a rapid screening procedure for comparison purposes. OITs were obtained by Differential Scanning Calorimetry (DSC) on a Perkin Elmer DSC 7 at a scan rate of 2°C/min in a stream of air or at a scan rate of 10°C/min in oxygen flowing at 20 ml/min.

The effect of some additives on the process stability of the polymers was also evaluated using the method of repeated extrusion. In this method the change in Melt Flow Index (MFI) of the polymer is monitored. The MFI corresponds to the mass of polymer that passes through a standard capillary, in a time interval of 10 minutes, at a specified applied pressure. The applied pressure is such that the resulting shear rate in the MFI tester is low enough for the typical polymer melt to show Newtonian behaviour. The MFI is therefore inversely proportional to the zero-shear viscosity (η_o). η_o has a strong molecular mass dependence: $\eta_o \approx kM^{3,4}$. Oxidative degradation in polypropylene leads primarily to chain scission whereas in polyethylene, during the initial stages, cross-linking occurs. One therefore expects the MFI for polypropylene to increase and that of polyethylene to decrease during the initial phases of oxidative degradation.

The experimental procedures and conditions were as follows.

Polypropylene. Grade 1100K unstabilised homopolymer powder (ex Polifin), with a nominal MFI of 3,5 g/10 min @ 230°C/2,16 kg was used. Test mixtures were prepared by dry blending the polypropylene powder with the required amounts of stabilisers in a coffee grinder. The standard recipe was 0,2 % calcium stearate together with 0,1 % antioxidant blend. These mixtures were then extruded directly.

Polyethylene. Since oxidative degradation initially leads to an increase in melt viscosity, it was decided to use LDPE grade WNG 14 ex Polifin. The initial melt flow index of this resin was 7,0 g/10 min @ 190°C/2,16 kg. In this case 0.1% stabiliser blend was incorporated via the 10% masterbatches. No calcium stearate was used with the polyethylene.

Extrusion. A RAPRA 25 mm laboratory tandem extruder set-up was used for this purpose. For polypropylene the temperature profiles were set as follows (from hopper towards die). Primary extruder: 190°C /215°C /215°C; secondary extruder: 215°C /220°C /220°C and die temperature: 230°C. The screw speeds were 200 and 210 rpm for the primary and secondary extruders, respectively. Corresponding settings used with the polyethylene samples were 136 °C /162°C/174°C in the primary extruder; 175°C /180°C /180°C in the secondary extruder and a die temperature of 200°C. Screw speeds were 135 and 145 rpm, respectively.

Before each test the extruder was purged with virgin material. This was followed by a second purging with the unstabilised resin. Approximately 2 kg samples were then extruded, cooled in a water bath and re-pelletised before being re-extruded. Samples were taken after the first, third and fifth pass. The melt flow indexes (MFI) of these samples were determined using a weight with a mass of 2,16 kg. The measurement temperature was 190°C for the polyethylene samples and 230°C for the polypropylene samples. Table 2 lists the formulations that were investigated.

Accelerated UV Ageing

Low-density polyethylene (MFI 2,0) and polypropylene film samples (MFI 1,8) were blown on a laboratory film blower. The ca. 40 μm thick films samples were weathered in a QUV fitted with A340 UV lamps for up to 1200 hours. A dry cycle was used with the temperature set at 45°C.

Mid-infrared absorption spectra samples were recorded of mounted on plastic squares to fit into the sample holder of a Bruker® 113V FTIR spectrometer. The sample chamber of the instrument was evacuated during the recordings to minimise any effects caused by water vapour and carbon dioxide. The resolution was $2cm^{-1}$ and 32 scans were signal-averaged in each interferogram. The recorded spectra were baseline corrected. The Carbonyl Index (CI)[7] used here is defined as the ratio of the intensities of the C=O band at 1710 cm^{-1} to the C-H rocking band at 729 cm^{-1} for polyethylene films and the band at 972 cm^{-1} for polypropylene films. The latter peaks remained unchanged during the degradation process, while the >C=O peak increased with time. In our study the C-H stretch vibration band at 2820 cm^{-1} could not be used as the film thickness of the samples was sufficient to cause the intensity of this band to be so high that it was cut off, i.e. it was saturated. A specific fixed Carbonyl Index value may be used to define a failure criterion for use in photo-stabilisation studies of polymers. A value of $CI = 0{,}1$ was arbitrarily chosen in this study.

Results and Discussion

Accelerated Weathering

Figure 1 shows the effect of metal 2,4-pentanedione complexes on UV ageing of LDPE film. With the possible exception of the titanyl complex, all additives show the typical incubation period before oxidation commences. The observed photodegradation efficiency of the metals decreased in the following order:

$$Ti > Al > Zr > VO >> Cu.$$

The high photoactivity of the aluminium complex is encouraging, as it reportedly does not appreciably effect the oxidative degradation in polyolefins.[6] Copper, a well-known and potent thermo-oxidation promoter actually acts as an UV stabiliser in polyethylene. Ozawa *et al.*[6] previously noted similar behaviour. They studied the effect of metal stearates on the degradation of polyethylene and polypropylene. The photo-stabilising activity of copper stearate was attributed to an UV absorption mechanism.

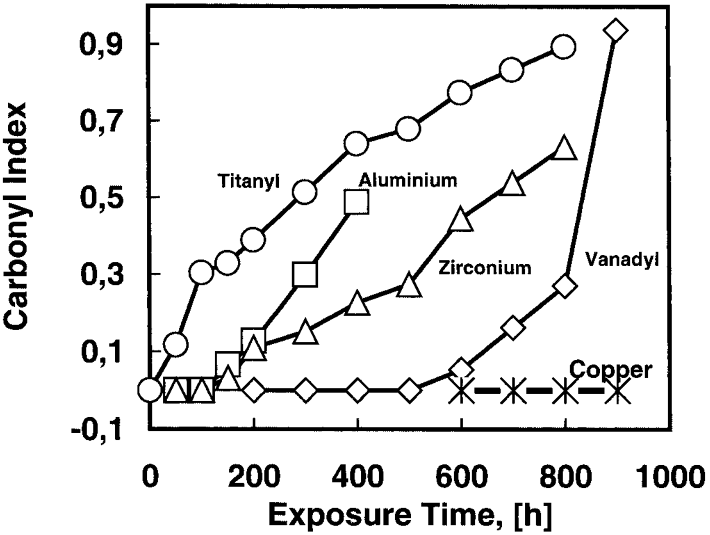

Fig. 1. Effect of metal 2,4-pentanedione complexes on the UV degradation of LDPE film. Additives dosage was 0,5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

Table 2. Effect metal 2,4-pentanedione complexes (1%) on the accelerated UV ageing of polypropylene films. The degree of ageing is quantified in terms of the carbonyl index.

2,4-Pentanedione complex	**Irradiation time in QUV weatherometer, [h]**				
	100	**200**	**300**	**400**	**500**
Fe (III)	0.4	embrittled			
Titanyl	0.25	0.54	embrittled		
Zirconium	0.14	0.33	embrittled		
Magnesium	0.09	0.28	0.55	embrittled	
Vanadyl	0	0	0.61	embrittled	
Copper	0	0	0.48	embrittled	
Calcium	0	0	0.18	0.47	embrittled
Aluminium	0	0	0.16	0.31	embrittled

Table 2 shows the effect of metal 2,4-pentanedione complexes on UV ageing of PP film. The ferric complex has the highest photo-activity of all metal complexes. The photodegradation efficiency of these metals decreased in the following order:

Fe > Ti > Zr > Mg > V > Cu > Ca > Al.

The vanadyl and copper complexes showed a distinct induction time followed by rapid oxidative degradation. Interestingly, even the calcium and magnesium complexes showed photoactivity. It is suspected that for these complexes it derives from the carbonyl functionality of the organic residue rather than from the activity of the metal.

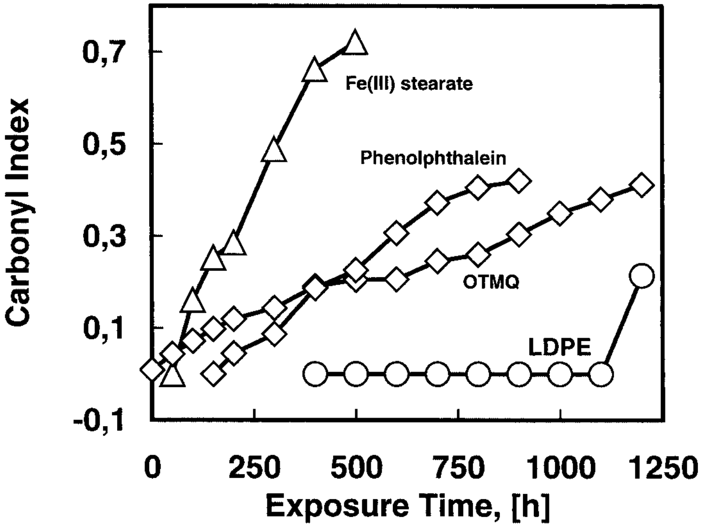

Fig. 2. Effect of ferric stearate and OTMQ on the UV degradation of polyethylene film. Additives dosage level was 0,5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

In Figures 2 and 3 the photo-activity of molecules with potential anti-oxidant properties are compared with that of ferric stearate in LDPE and polypropylene. While ferric stearate is much more efficient, it is clear that OTMQ does show promising photo-degradation properties. Figure 4 shows the effect of dosage level of the anti-oxidant, OTMQ, on the time to reach a Carbonyl Index of 0,2 for polyethylene film. By comparison, films containing ferric stearate reached this level at irradiation times of less than 150 hours.

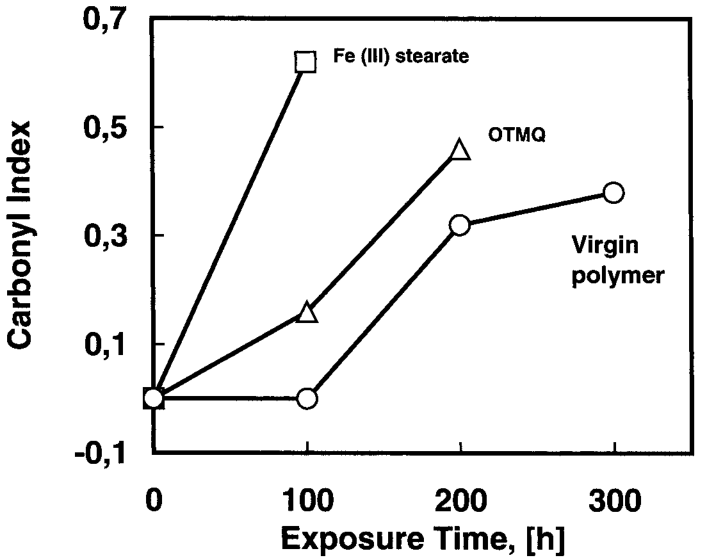

Fig. 3. Effect of ferric stearate and OTMQ on the UV degradation of polypropylene film. Additives dosage level was 1,0 %. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

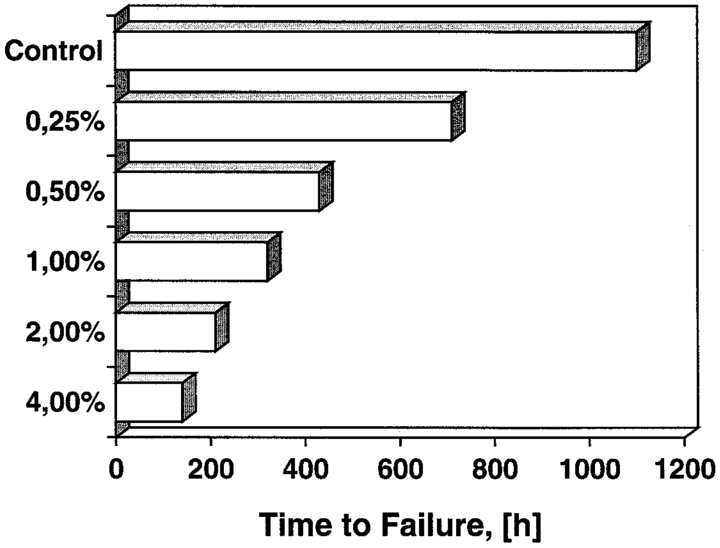

Fig. 4. QUV photo degradation of LDPE film: Effect of the OTMQ dosage level on the time to reach a Carbonyl Index of 0,2 in polyethylene film.

Multiple Extrusion Tests

The MFI of both the polymers increased with extruder pass, indicating that chain scission dominated over cross-linking as the main degradation reaction.

Polyethylene. Only small changes in MFI were observed for the polyethylene samples. This suggests that the extrusion conditions were not very severe for this polymer. The standard commercial blend of hindered phenol (AO-3) with a phosphite (AO-4) was used as reference. It was a very effective stabiliser; this formulation showed the least change in MFI with extruder pass. The data for OTMQ (AO-1) and its blend with BHT (AO-2) showed a drop in MFI after the third extruder pass, followed by an increase after the fifth pass. The initial drop suggests that some cross-linking might have occurred.

Polypropylene. The results for polypropylene are presented graphically in Figure 5. The fact that the MFI increased steadily with extruder pass suggests that the test conditions were more severe for the polypropylene sample. Both stabiliser systems reduced the rate of MFI increase.

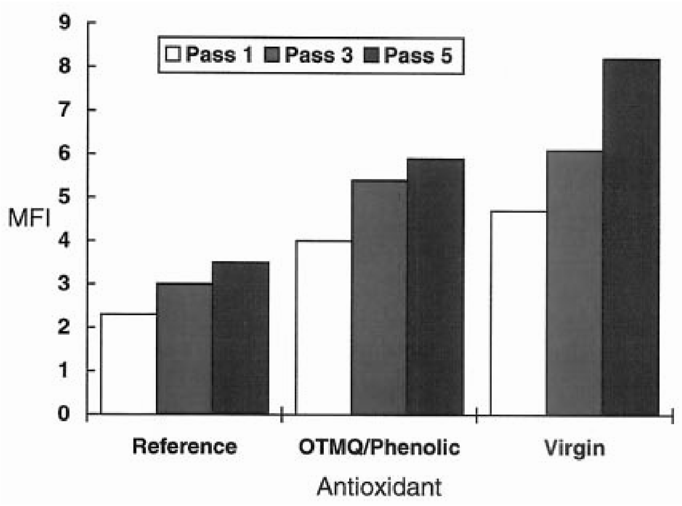

Fig. 5. Measured MFI's (g/10 min @ 230°C/2,16 kg) for polypropylene formulations following repeated extrusions

Oxidation Induction Temperature (OIT)

Measured OITs for the polypropylene and polyethylene samples are given in Table 3 for oxygen and Table 4 for air. These results suggest that OTMQ (AO-1) in combination with calcium stearate and AO-3 is an excellent antioxidant combination for polypropylene.

Table 3. Effect of various additives on the OIT of polyethylene and polypropylene films.

Measured oxidation induction temperature at a scan rate of 10°C/min in oxygen flowing at 20 ml/min.	**LDPE (XJF 46/60)**	**PP (1102H)**
Additive (0,5% unless stated otherwise)	**OIT, [°C]**	
1. None	217	177
2. OTMQ (poly (1,2-dihydro-2,2,4-trimethylquinoline))	255*	202
3. Nickel dimethylglyoxime	230	179
4. Phenolphthalein	199	-
5. Aluminium 2,4-pentanedione	189	175
6. Iron (III) stearate	164	164
7. Copper 2,4-pentanedione	177	154

*Concentration in polyethylene 0,4%

Table 4. OIT measured in air for stabiliser formulations used in repeated extrusions tests.

Measured oxidation induction temperature at a scan rate of 2°C/min in air flowing at 20 ml/min.	**LDPE (WNG 14)**	**PP (1100K)**
Stabiliser Formulation	**OIT, [°C]**	
1. None (polyethylene) or calcium stearate 0,2% only (polypropylene)	191	184
2. Reference: 1:1 Blend of Tetrakismethylene (3,5-di-t-butyl-4-hydroxy-hydrocinnamate) methane and tris (2,4-di-t-butyl-phenyl) phosphite	225	206
3. 1:1 Blend of OTMQ and Tetrakismethylene (3,5-di-t-butyl-4-hydroxy-hydrocinnamate) methane (Anox 20)	-	218
4. 1:1 Blend of butylated hydroxytoluene (BHT) and OTMQ	217	-

Conclusions

Aluminium 2,4-pentanedione has little effect on thermo-oxidative stability but shows considerable photodegradation activity in polyethylene and polypropylene films under accelerated weathering conditions. Poly(1,2-dihydro-2,2,4-trimethylquinoline) is an effective antioxidant yet accelerates photodegradation behaviour. Thus these compounds are expected to aid rapid degradation under the action of solar radiation without significantly affecting the recyclability of these polymers. They therefore have potential for controlling the mineralisation of plastic shopping bag litter.

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