

# Photo-oxidation of commercial polyethylene containing titanium dioxide (rutile)/antioxidant systems

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The weathering performance of various grades of untreated (or uncoated) and treated (or coated) rutile pigments in commercial polyethylene in the absence and presence of primary and secondary antioxidants is examined. Using carbonyl index as a monitor of the rate of photo-oxidation, untreated rutile sensitizes the photo-oxidation of polyethylene, whereas the treated grades act as photostabilisers. The photosensitizing effect of untreated rutile is markedly inhibited by a synergistic combination of a hindered phenol (Topanol CA) and a sulphur containing antioxidant (DLTDP). Further, the order of weathering stability of the treated rutile pigments in the absence of any antioxidant in the polymer is altered significantly when an antioxidant system is present. The importance of pigment/antioxidant interactions is discussed. The photo-oxidation of polyethylene containing the treated rutile pigments is also significantly improved by the presence of a primary antioxidant or a primary/secondary antioxidant system compared with a secondary antioxidant alone. These results indicate that peroxides play only a minor role in the photo-oxidation of TiO<sub>2</sub> (rutile) pigmented polyethylene.

## 1. Introduction

In general, pigments rather than dyes are used to colour bulk polymers such as the commercial polyolefins [1-3], however a major technological problem encountered with these pigments is that they may affect the weathering performance of the polymeric material and in certain cases may even act as photosensitizers [1-3]. Studies on the photochemical activity of pigments in commercial polyolefins have been mainly concerned with white pigments, and titanium dioxide (TiO<sub>2</sub>) is the most widely studied of these, since it is technically outstanding in many respects [2].

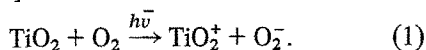
However, it is well known that the two crystalline modifications of TiO<sub>2</sub> can markedly differ in their photodegrading effects. When present in the commercial polyolefins rutile is relatively inactive, while anatase is markedly active in bringing about degradation of the polymer [4-7]. Thus, of the two pigment modifications, the rutile form is more widely used and is available in many grades,

according to its manufacturing history [8, 9]. Also, rutile is used with a range of surface coatings (inorganic and/or organic) that are applied to the pigment particles for various desirable technological reasons [8, 9].

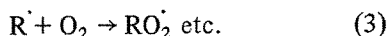
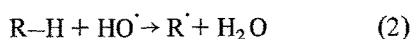
The incorporation of pigments into polyolefins requires long processing times and consequently antioxidants have also to be added to the polymer melt to avoid excessive thermal oxidation [1]. The addition of antioxidants can significantly affect the subsequent weathering performance of the polymer where carbonyl and/or hydroperoxide groups formed during processing are believed to be responsible for sunlight-induced oxidation [3]. The presence of a primary antioxidant (radical scavenger) and/or a secondary antioxidant (hydroperoxide decomposer) can affect the relative concentrations of these oxidation products and hence subsequent light stability [10-12].

The photosensitised degradation of commercial polymers by titanium dioxide pigments is believed

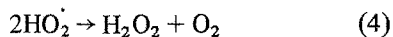
to be related to the formation of an oxygen radical anion  $O_2^-$  and possibly other species by electron transfer from excited state  $TiO_2$  to molecular oxygen [1, 2]



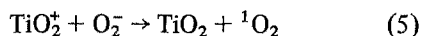
The products of reaction scheme 1 may then react with water to form reactive hydroxyl and perhydroxy radicals. The hydroxyl radicals may then react with the polymer substrate and abstract a hydrogen atom and thus initiate degradation of the polymer by the well-known auto-oxidation chain mechanism for hydrocarbon polymers [1, 2]



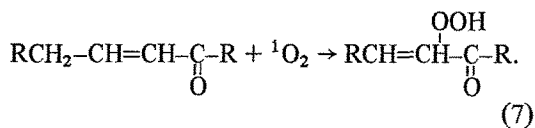
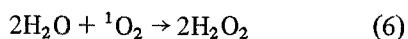
The perhydroxyl radicals recombine to form hydrogen peroxide and oxygen,



A recent modification of this reaction scheme includes the formation of singlet oxygen by ion-annihilation of the radical products of reaction scheme 1 [13] thus;



The singlet oxygen may then react with water to give hydrogen peroxide or alternatively it may attack ethylenic double bonds in the polymer (present as  $\alpha$ ,  $\beta$ -unsaturated carbonyl impurities in polyethylene [14]) to form hydroperoxides.



In this paper we have examined the weathering performance of polyethylene containing various grades of rutile pigments in the absence and presence of primary and secondary antioxidants. This was done by monitoring the build-up of non-volatile carbonylic oxidation products by infrared measurements [7]. From this data the relative merits of a radical scavenger and/or a peroxide decomposer used in combination with rutile pigments were considered. The study also gave some information on the relative importance of carbonyl and hydroperoxide groups, formed during processing, and on the mechanism of the photo-oxidation of polyethylene pigmented by  $TiO_2$ .

## 2. Experimental

### 2.1. Materials

Commercial low density polyethylene powder (M.F.1 = 22; density =  $0.918 \text{ g cm}^{-3}$ ) was supplied by I.C.I. Plastics Division Ltd. Samples of primary antioxidants, Topanol CA (3-methyl-6-tert-butyl-phenol and crotonaldehyde condensate) and Irganox 1010 (pentaerythritol tetra  $\beta$ -(4-hydroxy-3,5-di-tert-butyl-phenyl), propionate and secondary antioxidants, D.L.T.D.P. (dilaurylthio-di-propionate) and Weston 618 (distearyl pentaerythrityl-di-phosphite) were also supplied by I.C.I. Ltd.

All the rutile pigments were supplied by Tioxide International Ltd., and have briefly the following properties. Rutile pigments 1 and 2 are dry-milled or untreated (uncoated) grades, (Types I). Rutile pigments 3 to 6 are all wet-coated and refined grades, having both inorganic (1 to 5% of alumina/silica) and organic (< 1.0%) coatings (Type II). The latter coating is valuable in assisting dispersion of the pigment into the polymer [8, 9]. Information on the manufacturing history of Type I and Type II pigments are given in [9].

### 2.2. Processing

The antioxidants (0.1%) and rutile pigments (1.0%) were incorporated into polyethylene using a Brabender Plasticorder at  $150^\circ \text{C}$  for 10 min. The compounded samples were then pressed into film of about  $250 \mu\text{m}$  thickness at  $150^\circ \text{C}$  for 2 min. The Plasticorder mixing head had a capacity of 72 ml and was operated at a mixing speed ratio of 2:3 switch set at a speed of 100 rpm.

### 2.3. Weathering

All the polymer films were weathered (photo-oxidised) in a Xenotest-150 weatherometer, supplied by Original Hanau, Quartzlampen, G.m.b.H., set up for natural sunlight simulated conditions ( $45^\circ \text{C}$ , 50% r.h.) [1].

### 2.4. Infrared measurements

The rates of photo-oxidation of the polymer films were monitored by measuring the formation of the non-volatile carbonyl oxidation products absorbing at  $1710 \text{ cm}^{-1}$  in the infrared region of the spectrum [7]. Infrared spectra of the carbonyl products were obtained using a Perkin-Elmer Model 157G grating spectrophotometer. The build-up in carbonyl products was measured using an index:

$$\text{Carbonyl Index} = [(\log_{10} I_0/I_t)/d] \text{ m}^{-1}$$

where  $I_0$  = intensity of incident light,  $I_t$  = intensity of transmitted light, and  $d$  = film thickness in metres.

### 3. Results and discussion

Table I shows the carbonyl index values attained for all the unpigmented and pigmented polyethylene films after a period of 500 h in the Xenotest-150. It is seen that in all cases the untreated grade of rutile (1) sensitizes the photo-oxidation of the polymer. The other untreated grade of rutile (2) is also a sensitizer but is less active than (1) and, indeed, in the presence of Topanol CA or Topanol CA + DLTDP, the sensitizing effect is inhibited. A further interesting feature shown by the table is that a combination of Topanol CA and DLTDP significantly suppressed the sensitizing action of

the untreated pigment (1). This combination effect of the two different types of antioxidant may be seen more clearly from Fig. 1. It may be concluded that the combination exhibits a synergistic effect in inhibiting the sensitizing action. It is also apparent from an inspection of the data in Table I, that no other combination of antioxidants clearly exhibit synergism as marked as the Topanol CA-DLTDP combination.

The order of weathering stability of the unpigmented and pigmented polyethylene films is shown in Table II. It is seen that the order for both coated and refined pigments (3 to 6) varies significantly. For example, the stability order in the absence of any antioxidant in the polymer is, in most cases, the reverse of that when an antioxidant system is present. This effect is not

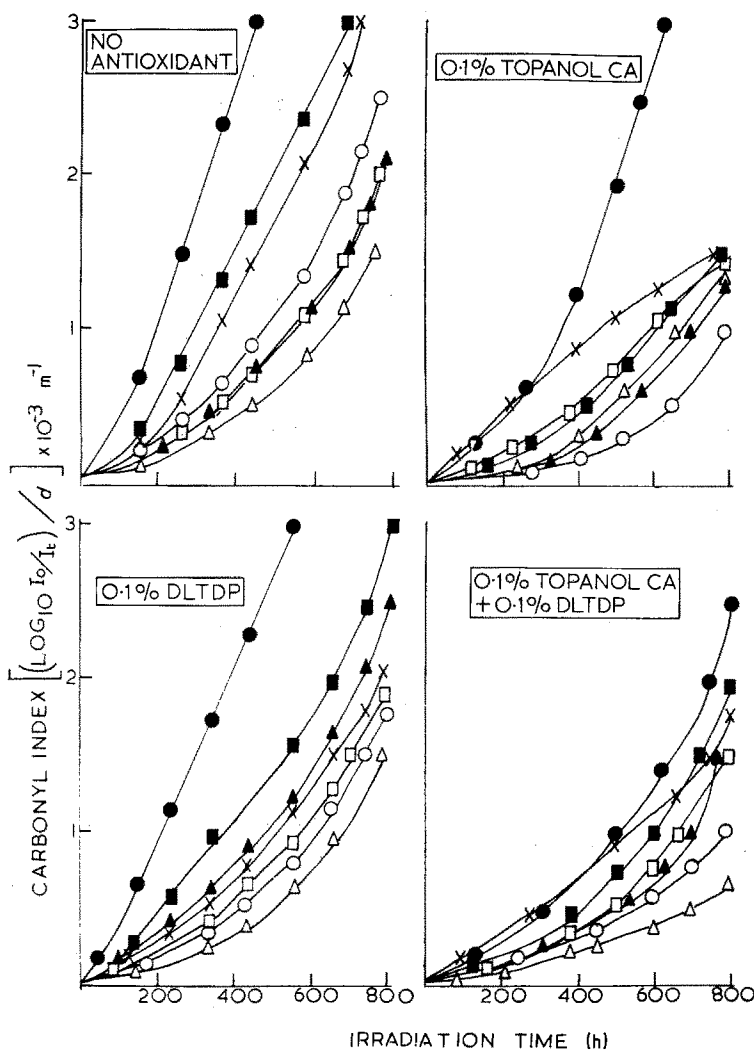


Figure 1 Carbonyl index versus time of irradiation in a Xenotest-150 weatherometer for pigmented polyethylene films (250  $\mu$ m thickness): rutile pigment, None - X, 1 -  $\bullet$ , 2 -  $\blacksquare$ , 3 -  $\circ$ , 4 -  $\square$ , 5 -  $\blacktriangle$ , and 6 -  $\triangle$ .

TABLE I Carbonyl index ( $10^{-3}$ ) after 500 h irradiation in a Xenotest-150.

Antioxidant	Pigment Grade						
	None	1	2	3	4	5	6
None	1.65	3.12	1.88	1.1	0.98	0.88	0.70
Topanol CA	1.20	2.00	0.80	0.37	0.80	0.50	0.55
Irganox 1010	0.95	1.38	0.65	0.14	0.25	0.18	0.20
DLTDP	0.95	2.62	1.40	0.75	0.88	1.14	0.55
Weston 618	0.95	2.12	1.60	0.88	0.90	0.75	0.70
Topanol CA + DLTDP	0.93	0.95	0.80	0.37	0.51	0.50	0.25
Topanol CA + Weston 618	0.95	2.12	1.30	0.35	0.70	0.52	0.40
Irganox 1010 + DLTDP	0.90	1.62	0.95	0.20	0.30	0.25	0.22
Irganox 1010 + Weston 618	1.00	1.25	1.00	0.20	0.32	0.25	0.27

TABLE II Stabilisation efficiencies of unpigmented and pigmented films

Antioxidant	Order
None	6 > 5 > 4 > 3 > CONTROL > 2 > 1
Topanol CA	3 > 5 > 6 > 4 = 2 > CONTROL > 1
Irganox 1010	3 > 5 > 6 > 4 > CONTROL > 2 > 1
D.L.T.D.P.	6 > 3 > 4 > CONTROL > 5 > 2 > 1
Weston 618	6 > 5 = 3 = CONTROL > 4 > 2 > 1
Topanol CA + D.L.T.D.P.	6 > 3 > 5 > 4 > 2 > CONTROL > 1
Topanol CA + Weston 618	3 > 6 > 5 > 4 > CONTROL > 2 > 1
Irganox 1010 + D.L.D.T.P.	3 > 6 > 5 > 4 > CONTROL > 2 > 1
Irganox 1010 + Weston 618	3 > 5 > 6 > 4 > CONTROL > 2 > 1

\* No pigment.

observed for the untreated rutile grades (1 and 2). It would appear that the durability of the coated/refined rutile grades is very sensitive to the presence of antioxidant systems. This indicates that pigment/antioxidant interactions are extremely important. A possible explanation for this is that the coated pigments could be adsorbing the antioxidant from the polymer during processing, although at present we have no further evidence to support this explanation.

Comparing the data in Table I, a further interesting effect is noted: the durability of all the coated and refined rutile grades (3 to 6) are significantly improved in the presence of either a primary or primary/secondary antioxidant system when these are compared with a secondary antioxidant alone. This stabilising effect is, in general, not so marked with the untreated grades, except

for the Topanol CA and DLTDP combination. Thus, secondary antioxidants, which operate as peroxide decomposers, are not as effective as primary antioxidants which operate as radical scavengers [1]. It would appear, therefore, that peroxides do not play a significant role in the photo-oxidation of TiO<sub>2</sub> (rutile) pigmented polyethylene. The synergistic combination of Topanol CA and DLTDP does not contradict this, since sulphur containing antioxidants such as DLTDP only operate as effective peroxide decomposers at processing temperatures [15]. Finally, it is known that phosphite ester antioxidants such as Weston 618 are effective peroxide decomposers at room temperature [15], and thus do not improve the durability of rutile pigmented polyethylene as we have found here.

Finally, recent model system work on the photo-oxidation of primary phenolic antioxidants has shown that some of their oxidation products are efficient quenchers of singlet oxygen [16]. Thus, the variation in the stabilising efficiency of different antioxidant/rutile systems observed here could be due to the ability of the antioxidant to react with or quench singlet oxygen formed by reaction scheme 5. The stabilising action of the inorganic hydrated oxide coatings on the treated pigments is believed to be due to their ability to trap photo-ejected electrons on the surface of the pigment before they can react with oxygen [17].

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