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Photo-yellowing of a phenolic anti-oxidant in the presence of various stabilizer/titanium dioxide pigment combinations in polyethylene

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The effect of various stabilizer and titanium dioxide (rutile) pigment combinations on the photo-yellowing and photo-oxidation of commercial polyethylene containing an anti-oxidant, 4,4′-thio-*bis*(6-tert-butyl-*meta*-cresol) is examined. The nature of various interacting mechanisms is discussed.

1. Introduction

Most polymers require additives for various technological applications [1]. For example, the commercial polyolefins have many applications requiring good weathering performance out-of-doors, and for these they must contain various stabilizer combinations [2].

In an earlier paper we examined the weathering performance of commercial polyethylene containing various titanium dioxide (rutile) and anti-oxidant combinations [3]. From this work we found that pigment/anti-oxidant interactions were important in controlling the photo-oxidation of the polymer. However, a further important problem is the unacceptable yellow discoloration produced by certain phenolic anti-oxidants, particularly those containing sulphur atoms [4]. In this paper therefore, we have examined the effect of various stabilizer and uncoated and coated titanium dioxide (rutile) pigment combinations on the photo-yellowing of one such commercial anti-oxidant, 4,4′-thio-*bis*(6-tert-butyl-*meta*-cresol). The rate of photo-oxidation of the polymer has also been examined to obtained information on possible pigment/stabilizer interactions.

2. Experimental

2.1. Materials

Commerical low density polyethylene powder (M.F.I* = 22; density = 0.918 g gm^{-3}) was supplied by ICI (Plastics Division) Ltd. The stabilizers, UV 531 (2-hydroxy-4-n-octoxybenzophenone) and Irgastab 2002 [nickel *bis*(ethyl 3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate] and anti-oxidant, Santanox R [4,4′-thio-*bis*(6-tert-butyl-*meta*-cresol)] were also supplied by ICI Ltd. The hindered amine stabilizer, Tinuvin 770 [*bis* (2,2,6,6-tetramethyl 4-piperidinyl) sebacate] was supplied by Ciba-Geigy Corp., Switzerland. The DABCO [1,4-diazobicyclo (2,2,2)octane] was purchased from Ralph N. Emanual Ltd (London).

The uncoated and coated rutile pigments were supplied by Tioxide International Ltd. The uncoated rutile pigment used was dry-milled (Type I) whereas the coated pigment used was wet-coated and refined and has both an inorganic (~2% of alumina/silica) and organic (~1% silicone) coating (Type II). Further information on the nature of type I and II rutile pigments are given in [5].

2.2. Processing

The anti-oxidant (0.1%), stabilizers (0.05%) and rutile pigments (1%) were incorporated into polyethylene at 150° C for 10 min using a Brabender Plasticorder. The compounded samples were then pressed into film and sheet of 400 μm and 2000 μm thickness respectively at 150° C for 1 min. The Plasticorder mixing head has a capacity of 72 ml and was operated at a mixing speed ratio of 2:3 switch-set at a speed of 100 r.p.m.

2.3. Photo-oxidation

All the polymer films and sheets were irradiated in a Xenotest-150 weatherometer, (Original

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*M.F.I. = melt flow index.

Hanau, Quartzlampen, G.m.b.H.) set up for natural sunlight simulated exposure conditions out-of-doors (45° C-black body, 50% relative humidity).

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

$$\text{Carbonyl index} = [(\log_{10} I/I_t/d]\,\mathrm{m}^{-1},$$

where

I_0 = intensity of incident light

I_t = intensity of transmitted light

d = film thickness in metres.

2.4. Photo-yellowing

The yellow discoloration produced during irradiation was measured using a Colourmaster (Model V) (Mecco Instruments, Pennsylvannia, USA). Using the Adams coordinates recommended for use with the instrument the yellow discoloration or "*b*" value was calculated from the green (G) and blue (B) reflectance values using the relationship:

$$b = (b_G - b_B)$$

where

$b_G = 16.74(G)$

$b_B = 16.74(B)$

3. Results

3.1. Anti-oxidant/stabilizer combinations

Fig.1 shows the degree of photo-yellowing of Santanox R in commercial polyethylene in the absence and presence of stabilizer systems. In the absence of any stabilizer the Santanox R discolours very rapidly during the early stages of irradiation and attains a maxium after about 100 h. After irradiation however, there is a marked reduction in the discoloration and by 500 h the yellow colour attains a lower but stable value. In the presence of the stabilizer systems only the hindered amine, Tinuvin 770, effectively inhibits the yellow discoloration.

The rates of photo-oxiation of all the unstabilized and stabilized polyethylene samples are compared in Fig. 2. It is seen that all the stabilizers

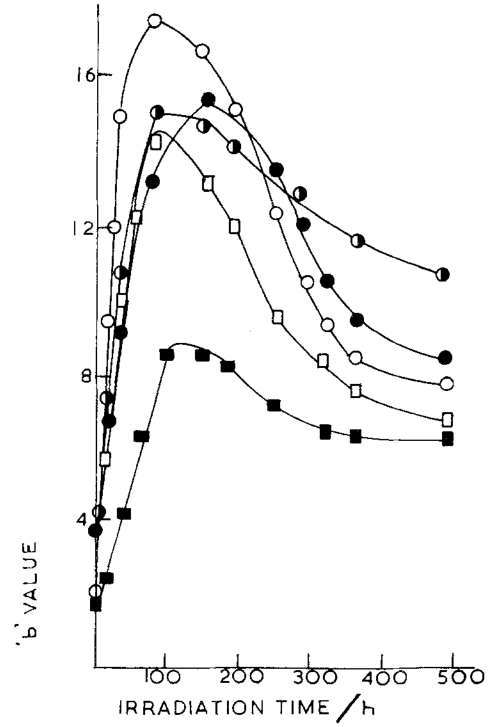


Figure 1 Change in "*b*" value versus irradiation time (h) in a Xenotest-150 weatherometer for Santanox R (0.1%) in polyethylene containing: ○ – no stabilizer; ◑ – UV531 (0.05%); ● – Irgastab 2002 (0.5%); □ – DABCO (0.05%) and ■ – Tinuvin 770 (0.05%).

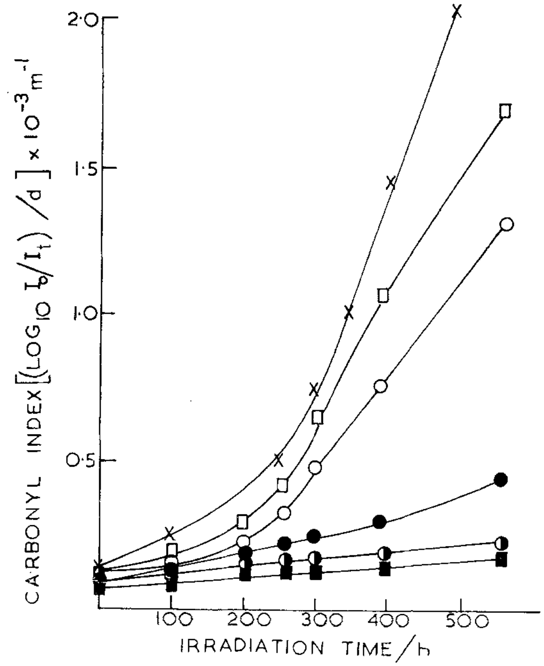


Figure 2 Carbonyl index versus irradiation time (h) in a Xenotest-150 weatherometer for polyethylene containing: X – no additives ○ – Santanox R (0.1%); Santanox R (0.1%) and ◑ – UV531 (0.05%), ● – Irgastab 2002 (0.05%), □ – DABCO (0.5%) and ■ – Tinuvin 770 (0.05%).

except DABCO, inhibit the photo-oxidation of the polymer. The Santanox R also operates as a mild photo-stabilizer.

3.2. Anti-oxidant/stabilizer/rutile combinations

The effect of uncoated and coated rutile pigments on photo-yellowing is shown in Figs. 3 and 4. It is seen from comparing the figures, that the coated rutile markedly inhibts the photo-yellowing. In fact, the coated rutile inhibits the rapid initial increase in yellow discoloration.

Figs. 3 and 4 also show the effect of stabilizer/rutile pigment combinations on the photo-yellowing of Santanox R. In this case it is seen that all the stabilizers are antagonistic with both uncoated and coated rutile pigment and sensitize the yellow discoloration. It should be noted that the "*b*" values for the unpigmented and pigmented polymers cannot be compared directly due to differences in the optical properties of their surfaces.

The rates of photo-oxidation of the stabilized polymers containing uncoated and coated rutile

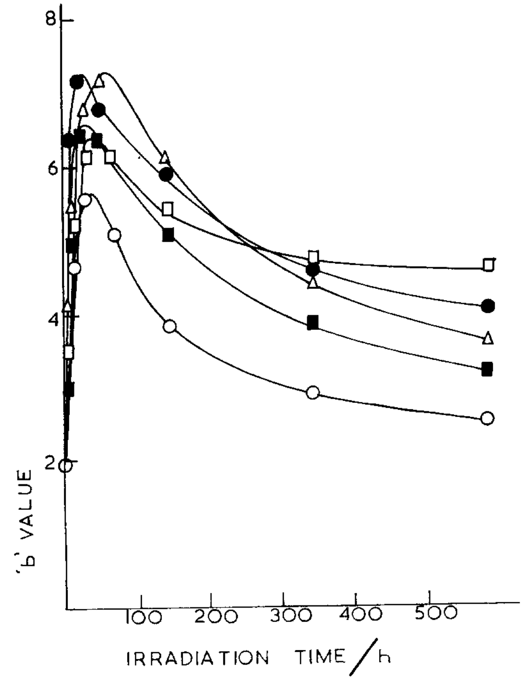


Figure 3 Change in "*b*" value versus irradiation time (h) in a Xenotest-150 weatherometer for Santanox R (0.1)%) in polyethylene containing: ○ – uncoated rutile (1%); uncoated rutile (1%) and ● – UV531 (0.05%), △ – Irgastab 2002 (0.05%), □ – DABCO (0.05%) and ■ – Tinuvin 770 (0.05%).

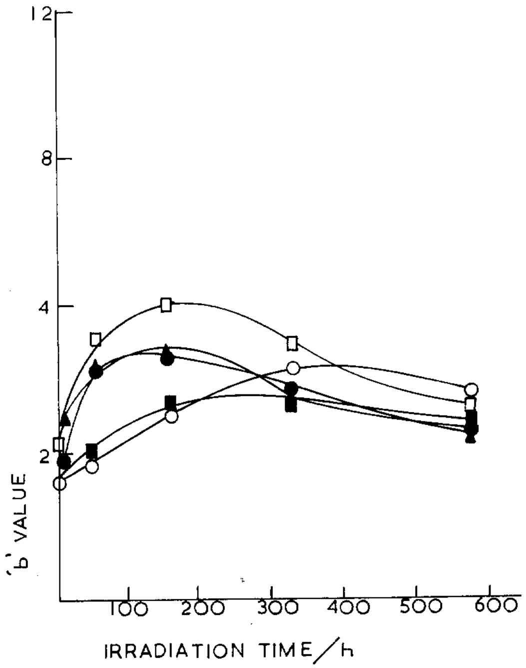


Figure 4 Change in "*b*" value versus irradiation time (h) in a Xenotest-150 weatherometer for Santanox R (0.1%) in polyethylene containing: ○ – coated rutile (1%); coated rutile (1%) and ● – UV531 (0.05%), ▲ – Irgastab 2002 (0.05%), □ – DABCO (0.05%) and ■ – Tinuvin 770 (0.05%).

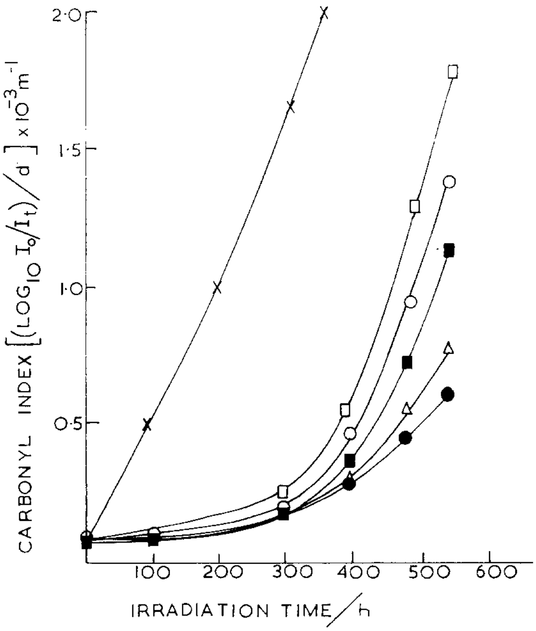


Figure 5 Carbonyl index versus irradiation time (h) in a Xenotest-150 weatherometer for polyethylene containing: × – uncoated rutile (1%); ○ – uncoated rutile (1%) and Santanox R (0.1%); uncoated rutile (1%) and Santanox R (0.1%) and ● – UV531 (0.05%), △ – Irgastab 2002 (0.05%), □ – DABCO (0.05%) and ■ – Tinuvin 770 (0.05%).

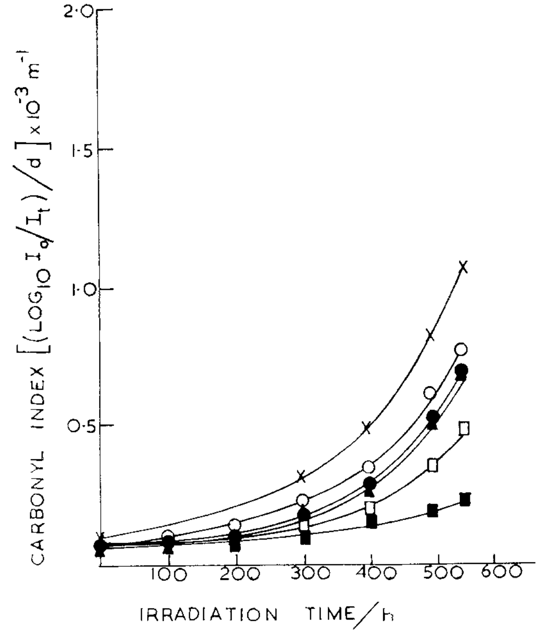


Figure 6 Carbonyl index versus irradiation time (h) in a Xenotest-150 weatherometer for polyethylene containing: X – coated rutile (1%), ○ – coated rutile (1%) and Santanox R (0.1%); coated rutile (1%) and Santanox R (0.1%) and ● – UV531 (0.05%), ▲ – Irgastab 2002 (0.05%), □ – DABCO (0.05%) and ■ – Tinuvin 770 (0.05%).

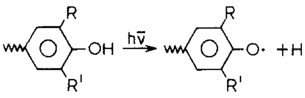
pigments are shown in Figs. 5 and 6. With the uncoated rutile Irgastab 2002 and UV531 are more effective photo-stabilizers than Tinuvin 770 while in the presence of coated rutile the reverse is the case. Finally, in all cases DABCO is the least effective.

4. Discussion

The inhibiting effect of Tinuvin 770 on the photo-yellowing of Santanox R is an important technological result (Fig. 1). Indeed, since Irgastab 2002 and UV531 are generally believed to act as stabilizers by mechanisms involving ultra-violet absorption and/or excited state quenching [6–9] and since neither of these stabilizers inhibits photo-yellowing, then clearly ultra-violet absorption or excited state quenching cannot be the operative stabilizing mechanism for Tinuvin 770. It is of interest therefore that we discuss here possible explanations for this remarkable behaviour of Tinuvin 770.

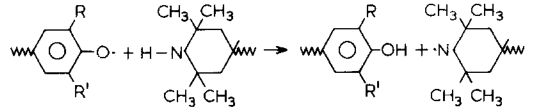
From our earlier work on this stabilizer, two mechanisms could be operative [8, 10 11]. In the first, the stabilizer readily donates a labile hydrogen atom to a propagating free radical, thus inhibiting chain propagation. In the second, the stabilizer acts as a "scavenger" for electronically excited singlet oxygen. Our earlier evidence favours the first mechanism and this is consistent with the further evidence presented here that DABCO, a well-known singlet oxygen quencher [6], has no significant effect on photo-yellowing.

If we assume that the first mechanism is more probable then we can speculate further on the details of the protective action of Tinuvin 770. It is well known that phenolic anti-oxidants, such as Santanox R, are photolysed initially to give a phenoxy radical [6]:



(1)

where R = alkyl group. The hindered amine, Tinuvin 770, may then prevent the Santanox R from undergoing further photo-reaction by transferring its labile hydrogen to the radical site, regenerating the phenol:



(2)

The resulting hindered amine radical is believed to be quite stable. The presence of uncoated pigments however, interferes with the stabilizing mechanism of Tinuvin 770. This could be due to the stabilizer being adsorbed to the surface of the pigment particles during the processing operation. A similar effect was observed in our earlier work on rutile/anti-oxidant systems.

Finally, the results obtained from the photo-oxidation experiments also indicate that some stabilizer/pigment interaction may also occur during processing. For example, the inefficiency of Tinuvin 770 as a photostabilizer in the presence of uncoated rutile (Fig. 5) indicates that it may be adsorbed onto the pigment surface. In the case of UV531 and Irgastab 2002 however, mechanisms of ultra-violet absorption and excited state quenching may still operate in the polymer, even though they may be adsorbed onto the pigment surface. The results in Fig. 6, however, indicate that if this is so then stabilizer adsorption occurs to a lesser extent with the coated rutile pigment.

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