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INTERACTION BETWEEN TITANIUM DIOXIDE PIGMENTS AND HINDERED PIPERIDINE/ANTI-OXIDANT COMBINATIONS IN THE PHOTOSTABILISATION OF POLYPROPYLENE

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SUMMARY

The complex interaction between titanium dioxide pigments, a primary anti-oxidant and a hindered piperidine compound in the photostabilisation of polypropylene has been examined using infrared absorption spectroscopy. The hindered piperidine compound, Tinuvin 770, was found to be ineffective in protecting the polymer against the photocatalytic action of anatase. In the case of rutile good photoprotection of the polymer was observed, the effect being greater for a coated pigment. However, the presence of the anti-oxidant, Irganox 1010, antagonised the stabilising action of the hindered piperidine compounds, the effect being greater in the presence of an uncoated pigment. The results are discussed in terms of additive adsorption onto the pigment particle surface versus the photocatalytic activity of the pigment. The effects were also found to be dependent on the ultraviolet content of the light source.

1. INTRODUCTION

The interaction between anti-oxidants and light stabilisers and their influence on the photostabilisation of polyolefins is currently a topic of considerable scientific and technological interest. Many early studies in this area showed a favourable

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interaction between, for example, phenolic anti-oxidants and ultraviolet stabilisers based on 2-hydroxybenzophenone.[1] Nickel chelate stabilisers also interact favourably with many types of anti-oxidants, except those containing sulphur atoms.[2,3] In this case, discoloration due to nickel sulphide formation can occur on processing.

However, the relatively new types of stabilisers based on the hindered piperidine structure have been found to interact unfavourably with a number of anti-oxidants, particularly those containing sulphur atoms.[4-8] In this case strong antagonism is observed. Certain types of phenolic anti-oxidants have also been found to be antagonistic.[4,7,8]

Whilst there have been many studies dealing with the interaction between processing additives and light stabilisers, there have been relatively few dealing with the even more complex interaction involving pigments. Since most commercial polymers are used in a pigmented form their influence on photostabilisation is obviously more important from a commercial as well as from a scientific point of view.

Studies on the photochemical behaviour of pigments in polyolefins have been mainly concerned with white pigments and of all the white pigments used the oxides of titanium have attracted the most interest.[3,9-11] It is well known that the two crystalline modifications of titanium dioxide (TiO_2) exhibit markedly different photoactivities in polyolefins and this adds a further complication to stabilisation.[12] Early studies in this area have shown that while ultraviolet stabilisers based on 2-hydroxybenzophenone are ineffective in inhibiting the photocatalytic activity of titanium dioxide pigments, nickel chelates appear to be quite effective.[13-15] Information on the behaviour of the hindered piperidines, however, is limited. Patel and Usilton[16] have shown that the hindered piperidine compound known commercially as Tinuvin 770 exhibits good photostabilisation with the rutile form of TiO_2 in polyethylene. Allen *et al.*,[17] on the other hand, have shown that the same compound is not as effective in inhibiting the photocatalytic oxidation of polyethylene by uncoated rutile as certain types of nickel chelates. With coated rutile pigments, however, good photostabilisation was observed.

In view of the widespread interest and use of these hindered piperidine compounds in polyolefins, we have examined in detail the photostabilisation of polypropylene by uncoated and coated forms of anatase and rutile in the absence and presence of various combinations of a phenolic anti-oxidant, Irganox 1010 (Ciba–Geigy AG), and the hindered piperidine stabiliser, Tinuvin 770 (Ciba–Geigy AG). The formula of these commercial additives are given later in the experimental section. The results provide valuable information on the importance of additive adsorption versus the photocatalytic activity of the pigments. In this work, we have also used two different light sources for exposure, one of which possesses emission lines at 313 and 334 nm. This comparative study provides useful information on the influence of the ultraviolet content of the light sources.

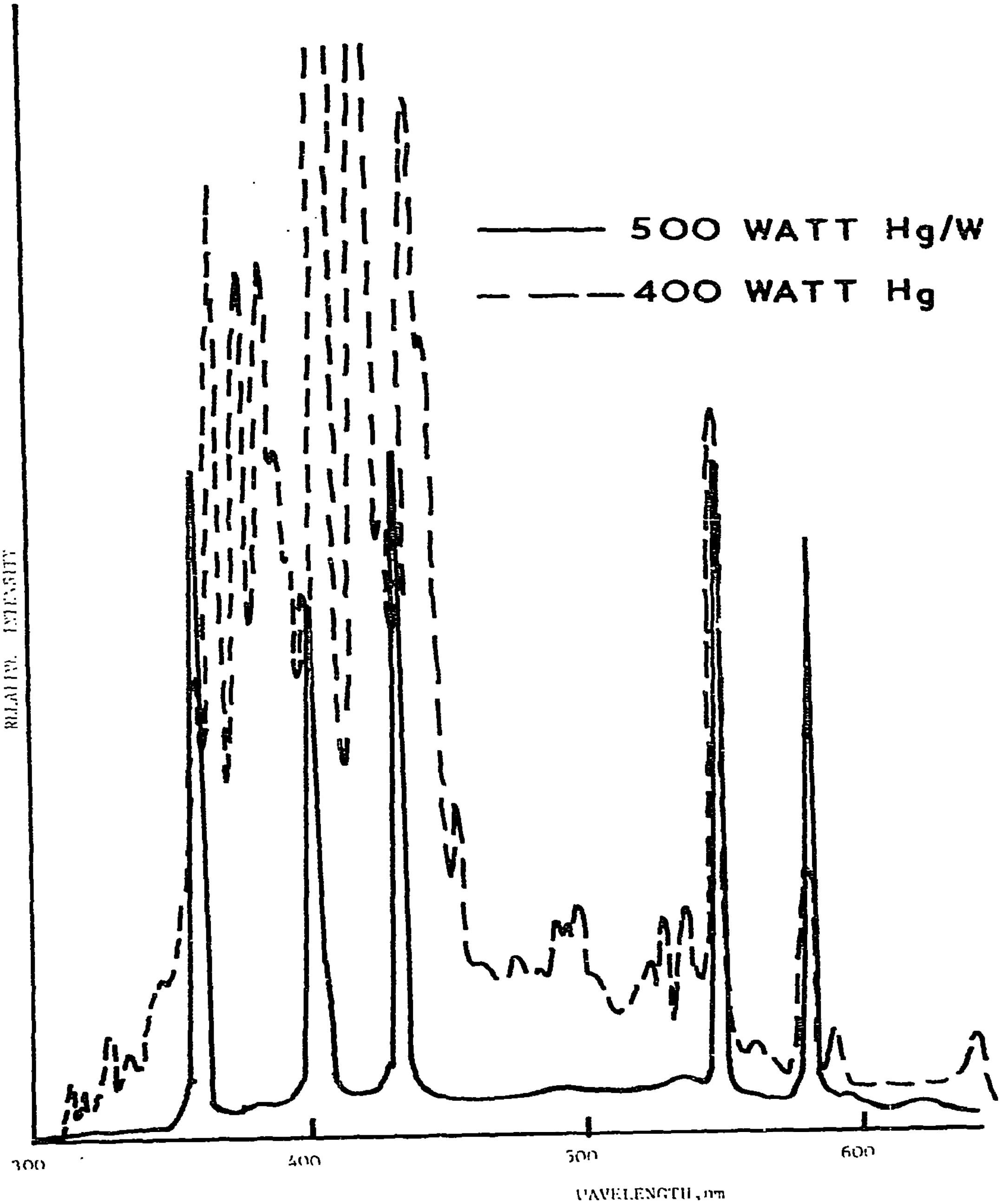

Fig. 1. Comparison of the spectral distribution of a 500 W high pressure mercury/tungsten fluorescent lamp with that of a 400 W medium pressure mercury lamp, used in the Microscal and SEPAP exposure units respectively.

2. EXPERIMENTAL

2.1. *Materials*

Polypropylene powder containing no commercial additives was supplied by ICI (Plastics Division) Ltd, UK. The anti-oxidant, pentaerythrityl tetra-β-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate, known commercially as Irganox 1010, and the light stabiliser, bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate, known commercially as Tinuvin 770, were supplied by Ciba-Geigy Ltd, Manchester, UK. The absorption spectra of these compounds are well known.[18] Tinuvin 770 is a hindered amine exhibiting no absorption above 200 nm.

The uncoated and coated anatase and rutile pigments were supplied by Tioxide International Ltd, Stockton-on-Tees, UK. The coated pigments were treated with alumina/silica ($\sim 1\%$).

The additives (0·1 %) and pigments (1·0 %) were incorporated into the polymer by processing in a Brabender Plasticorder (Duesburg, W. Germany) for 10 minutes at 190 °C. Polymer films (100 μm thick) were prepared by heat pressing at 200 °C for 2 minutes, followed by quench cooling in water.

2.2. *Photo-oxidation*

Polymer films were exposed in a Microscal lightfastness apparatus at Manchester Polytechnic (Microscal Ltd, UK) employing a 500 W high pressure HgW fluorescent lamp (50 °C; 20 % relative humidity).

Films were also exposed in a SEPAP 30·24 apparatus at University of Clermont II[6] employing a 400 W medium pressure mercury lamp filtered by a Pyrex envelope (55 °C; 20 % relative humidity).

The spectral distribution of both light sources are compared in Fig. 1. The SEPAP unit possesses emission lines at 313 and 334 nm which are absent in the Microscal, due to its fluorescent coating absorbing most of the ultraviolet emission below 340 nm. The coating also serves to reduce the irradiance, thus compensating for its higher power.

The rates of photo-oxidation of the polymer films were monitored by measuring the build-up in the concentration of the non-volatile carboxylic oxidation products absorbing at 1712 cm^{-1} in the infrared region. Infrared spectra were recorded using two instruments, a Perkin-Elmer Model 180 (University of Clermont II) and a Perkin-Elmer 457 (Manchester Polytechnic). Oxidation was monitored quantitatively using a well-established carbonyl index method.[3–5,7] The polymer films were flexed periodically to test for embrittlement.

3. RESULTS

3.1. *Exposure in Microscal unit*

(*i*) *Titanium dioxide/anti-oxidant combinations:* Figure 2 shows the influence of uncoated and coated anatase and rutile pigments on the rate of photo-oxidation of

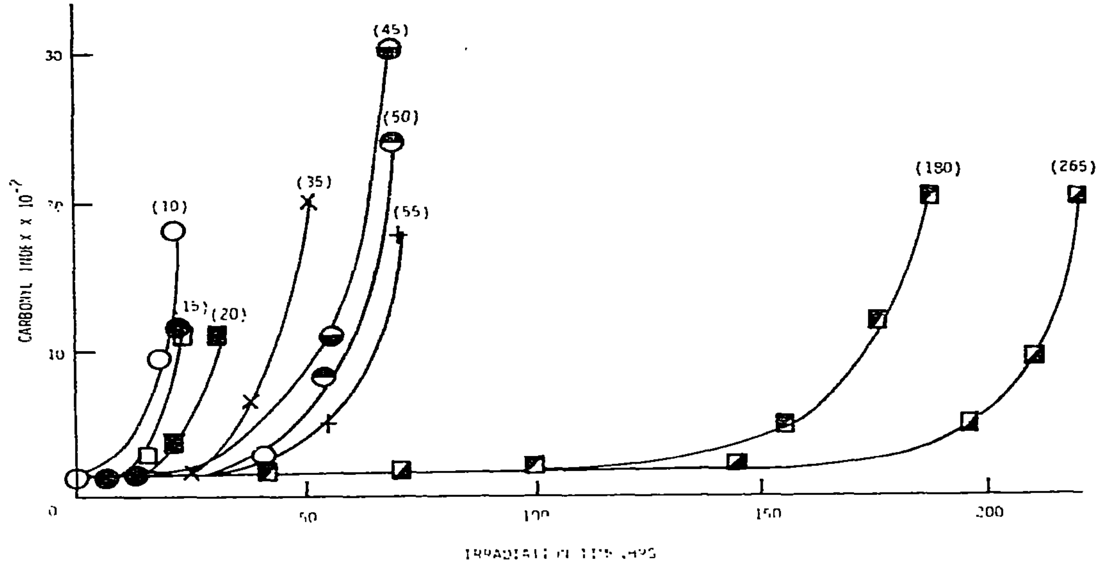

Fig. 2. Rate of photo-oxidation of polypropylene film (100 μm thick) containing: ×, no additives; +, 0·1 % Irganox 1010, ○, 1 % uncoated anatase; ●, 1·0 % coated anatase; ◒, 1·0 % uncoated anatase + 0·1 % Irganox 1010; ◓, 1·0 % coated anatase + 0·1 % Irganox 1010; □, 1·0 % uncoated rutile; ■, 1·0 % coated rutile; ◩, 1·0 % uncoated rutile + 0·1 % Irganox 1010; ◪, 1·0 % coated rutile + 0·1 % Irganox 1010. Embrittlement time (h) is given in parentheses. Microscal unit irradiation.

polypropylene with and without the anti-oxidant, Irganox 1010. It is seen that all four pigments catalyse the photo-oxidation of the unstabilised polymer, their catalytic activity decreasing in the order uncoated anatase > coated anatase > uncoated rutile > coated rutile. In polypropylene containing anti-oxidant, there is quite a different pattern of behaviour. For example, while both anatase pigments catalyse polymer photo-oxidation, the rutile pigments are stabilisers. In fact, there is strong synergism between the rutile pigments and the anti-oxidant which dominates the photocatalytic activity. In the case of the anatase pigments their photocatalytic activity appears to have a detrimental effect on the anti-oxidant.

(*ii*) *Titanium dioxide/hindered piperidine combinations:* The influence of the anatase and rutile pigments on the rate of photo-oxidation of polypropylene stabilised with the hindered piperidine compound, Tinuvin 770, is shown in Fig. 3. Again there is a marked difference in photochemical behaviour between the two modifications of TiO_2. In comparison with a stabilised control film, it is seen that while both uncoated and coated anatase pigments are powerful catalysts of polymer photo-oxidation, both rutile pigments are powerful stabilisers. In fact, there is strong synergism between the rutile pigments and the Tinuvin 770. In the case of anatase there is very little protection by the stabiliser. Here the photocatalytic activity of the pigment is detrimental to the stabilising action of the Tinuvin 770.

However, one other noticeable effect for both crystalline modifications is the marked difference in stabilisation between the uncoated and coated pigments. This effect is far greater than the differences in catalytic activity and can only be explained on the basis of adsorption of stabiliser onto the surface of the uncoated pigment particles. It is well known that uncoated pigments exhibit a higher chemi-adsorption than coated pigments.[18]

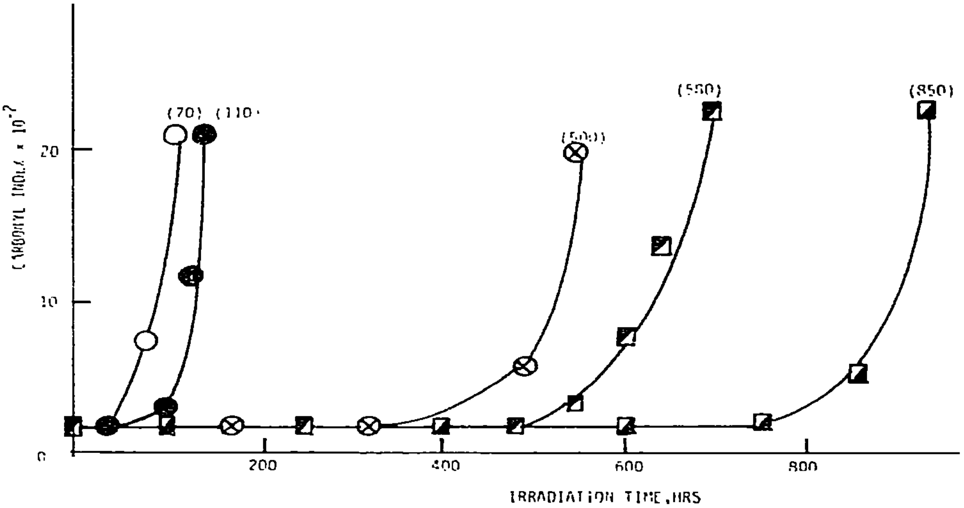

Fig. 3. Rate of photo-oxidation of polypropylene film (100 μm thick) containing: ⊗, 0·1 % Tinuvin 770 with ○, 1 % uncoated anatase; ●, 1 % coated anatase; ◩, 1 % uncoated rutile; ◪, 1·0 % coated rutile. Embrittlement time (h) is given in parentheses. Microscal unit irradiation.

(*iii*) *Titanium dioxide/anti-oxidant/hindered piperidine combinations:* The influence of anatase and rutile pigments on the rate of photo-oxidation of polypropylene containing both an anti-oxidant and light stabiliser is shown in Fig. 4. Here it is seen that the presence of the anti-oxidant produces a strong antagonism when compared with the stabilisation imparted by the TiO_2/Tinuvin 770 systems shown in Fig. 3. In fact, when compared with the unpigmented control films, it is seen that the antagonism is enhanced by the presence of anatase and rutile, the effect being greater for an uncoated than for a coated pigment. The detrimental effect of the uncoated pigments on photostabilisation of the polymer can only be explained in terms of adsorption of the anti-oxidant and light stabiliser on to the surface of the pigment particle. In this case any interaction between the anti-oxidant and light stabiliser will be enhanced and the photostabilisation would be considerably reduced. The function of the anti-oxidant as a process stabiliser, however, would not be inhibited.

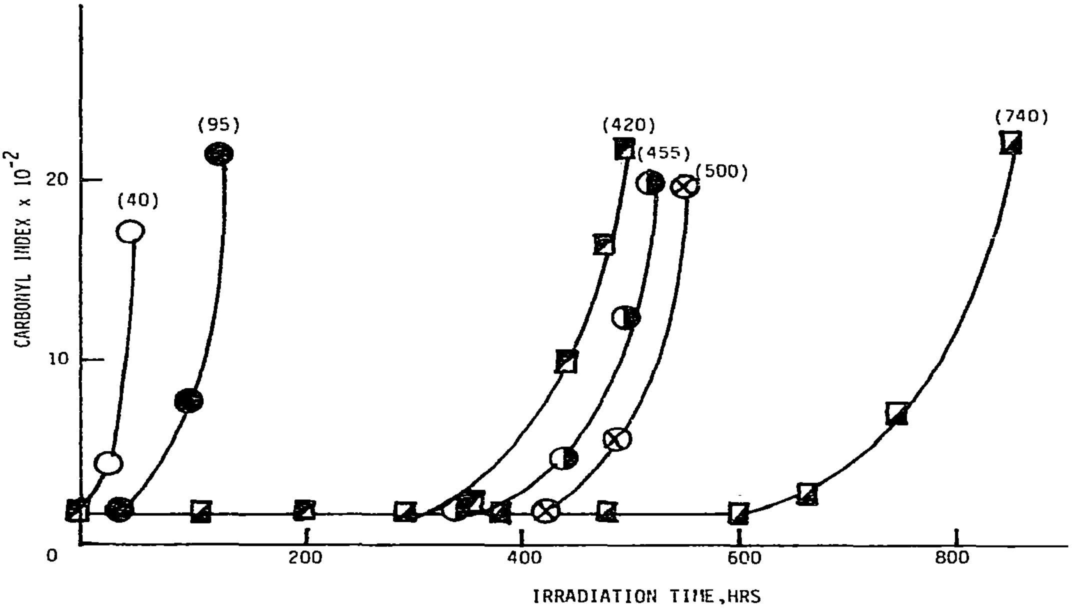

Fig. 4. Rate of photo-oxidation of polypropylene film (100 μm thick) containing: ◑, 0·1 % Irganox 1010 + 0·1 % Tinuvin 770 with ○, 1·0 % uncoated anatase; ●, 1 % coated anatase; ▨, 1 % uncoated rutile; ◪, 1·0 % coated rutile; ⊗, 0·1 % Tinuvin 770 control. Embrittlement time (h) is given in parentheses. Microscal unit irradiation.

3.2. *Exposure in SEPAP 30.24 unit*

(*i*) *Titanium dioxide:* It is seen that in the absence of any additives the two crystalline forms of TiO_2 exhibit similar effects on the light stability of the polymer (Fig. 5). Also, the nature of the surface treatments on the pigment particles appears to be of little importance. In fact, compared with the unstabilised control, both pigment modifications have a stabilising effect, their activity following the order quoted in section 3·1(*i*). The stabilising effect of the pigment in this exposure unit is evidently due to the ability of the pigments to absorb the ultraviolet light present in the source.

(*ii*) *Titanium dioxide/anti-oxidant combinations:* Figure 5 also shows the results obtained when an anti-oxidant is present in the polymer–pigment system. Here it is seen that the crystalline forms and nature of the surface treatments are of low importance. In fact, the same order in protecting ability as before is noted. The main observation here, however, is the marked difference between unpigmented and pigmented polymers. In this case the inductive effect of the anti-oxidant is inhibited by the pigments when compared with the unpigmented polymer. Again the ultraviolet absorbing properties of the pigments are responsible for this effect.

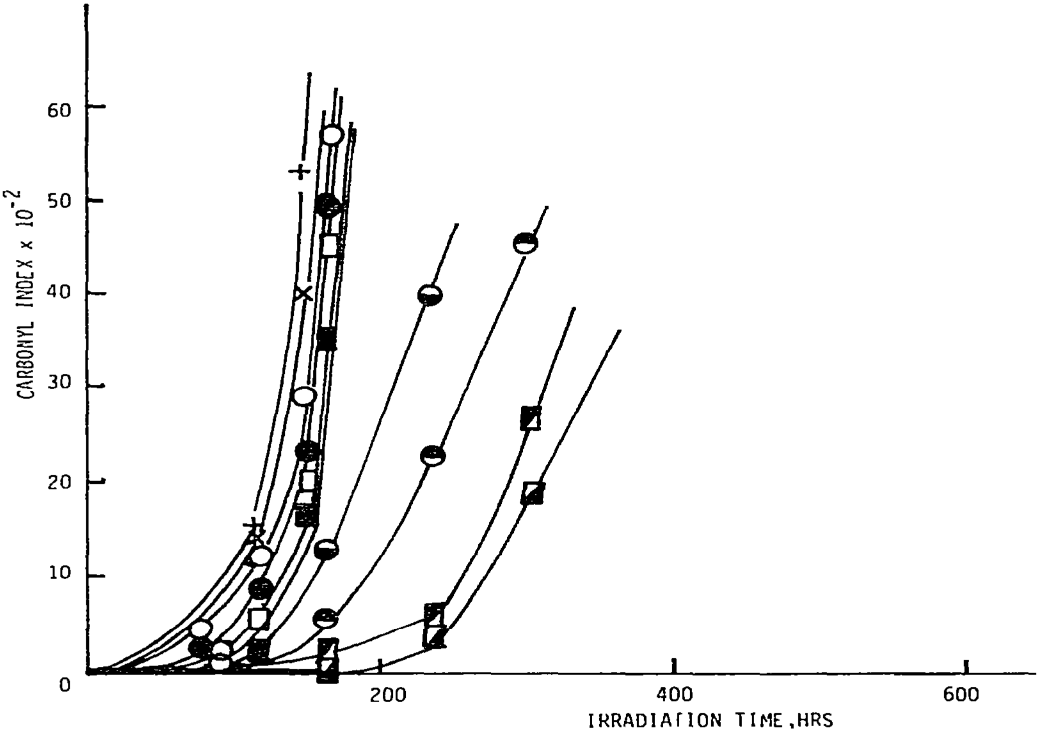

Fig. 5. Rate of photo-oxidation of polypropylene film (100 μm thick) containing: ×, no additives; +, 0·1 % Irganox 1010; ○, 1 % coated anatase; ●, 1 % coated anatase; ◒, 1 % uncoated anatase + 0·1 % Irganox 1010; ◓ 1 % coated anatase + 0·1 % Irganox 1010; □, 1 % uncoated rutile; ■, 1 % coated rutile; ◩, 1 % uncoated rutile + 0·1 % Irganox 1010; ◪, 1 % coated rutile + 0·1 % Irganox 1010. SEPAP 30·24 unit irradiation.

(*iii*) *Titanium dioxide/hindered piperidine combinations:* Figure 6 shows the influence of the TiO_2 pigments on the rate of photo-oxidation of polypropylene stabilised with the hindered piperidine compound, Tinuvin 770. The results found here, apart from one exception, confirm those observed in section 3.1(*ii*) with the Microscal unit. Both crystalline modifications exhibit a marked difference in activity in the presence of Tinuvin 770. For example, while the rutile modification exhibits strong stabilisation, the anatase form is an antagonist. The presence of surface treatments gives a small improvement in stabilisation. The one difference, however, is that the presence of rutile strongly antagonises the stabilising action of the Tinuvin 770.

(*iv*) *Titanium dioxide/anti-oxidant/hindered piperidine combinations:* Figure 7 shows the behaviour of samples containing both the anti-oxidant and Tinuvin 770. Again there is a marked difference in photocatalytic activity between the anatase and

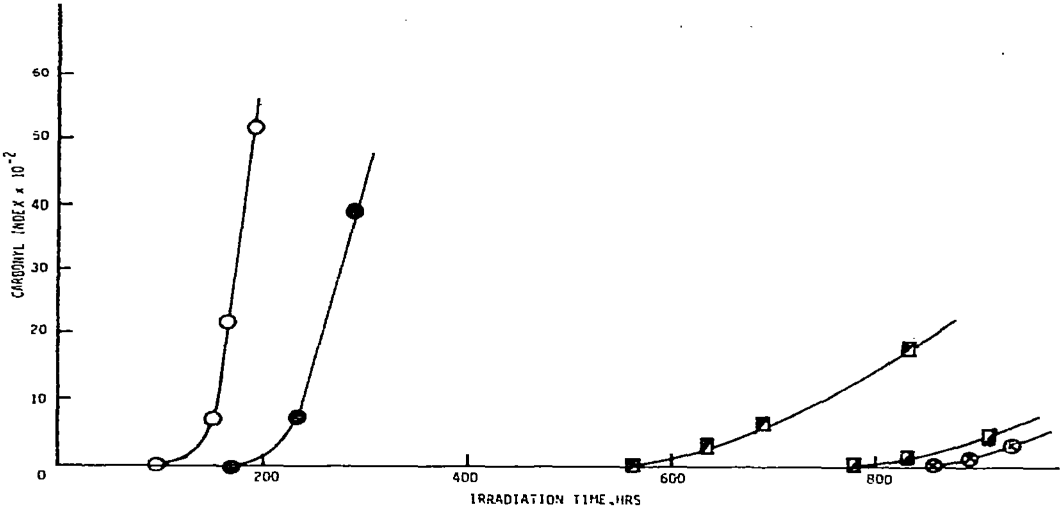

Fig. 6. Rate of photo-oxidation of polypropylene film (100 μm thick) containing: ⊗, 0·1 % Tinuvin 770 with ○, 1 % uncoated anatase; ●, 1 % coated anatase; ◩, 1 % uncoated rutile; ◪, 1 % coated rutile. SEPAP 30·24 unit irradiation.

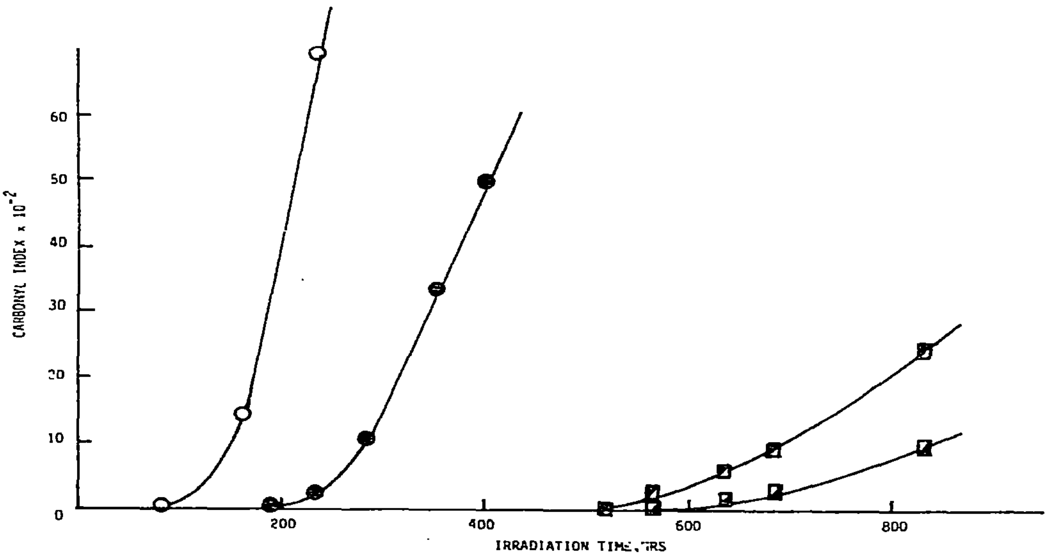

Fig. 7. Rate of photo-oxidation of polypropylene film (100 μm) containing: 0·1 % Irganox 1010 + 0·1 % Tinuvin 770 with ○, 1 % uncoated anatase; ●, 1 % coated anatase; ◩, 1 % uncoated rutile; ◪, 1 % coated rutile. SEPAP 30·24 unit irradiation.

rutile modifications. Also, as found with the Microscal exposure results, antagonism is displayed by the anti-oxidant with both rutile pigments. However, no antagonism is observed with anatase.

4. CONCLUSIONS

The results of this joint programme of work are, as would be expected from the commercial nature of the materials studied, quite complex. However, a careful analysis of the data enables us to draw on some important conclusions which can be related to the difference in the ultraviolet light content (300–350 nm) of the exposure sources. These are as follows:

(a) In the Microscal unit both pigment modifications exhibit a catalytic effect whereas in the SEPAP unit they exhibit a stabilising effect. In the latter exposure unit the pigments are capable of absorbing the harmful ultraviolet light that would otherwise be also absorbed by the polymer chromophores.

(b) In the SEPAP unit the phenolic anti-oxidant will absorb the ultraviolet light directly whereas in the Microscal unit there are fewer photons below 350 nm and hence a lower possibility of absorption. In the latter case the anti-oxidant will exhibit a protective effect through a radical scavenging process whereas in the former case it will be destroyed by direct photo-oxidation.

(c) In the Microscal unit there is a strong synergistic effect between rutile and the hindered piperidine stabiliser, whereas in the SEPAP unit antagonism is observed. In this case there would appear to be a smaller photocatalytic effect than in the SEPAP unit.

(d) In the SEPAP unit there is no antagonism between the anti-oxidant and Tinuvin 770 in the presence of anatase, an effect opposite to that observed in the Microscal. Here the difference in photocatalytic activity of the anatase in the exposure units could be responsible for this difference in behaviour provoking a fast disappearance of the anti-oxidant. This is only a minor problem since overall the presence of Tinuvin 770 has virtually no protective effect in the presence of anatase pigments.

Finally, it is important to note that differences in the reflectance spectra of uncoated and coated pigments[20] cannot account for the marked differences observed here in light stability.[19,21]

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