

Luminescence properties and photo-activity of sulphate-processed rutile (titanium dioxide) pigments in commercial polyethylene

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The low temperature infra-red emission spectra of five commercial rutile pigments prepared by the sulphate process have been recorded and compared with that of a pigment prepared in the laboratory by the same method. All the pigments, dispersed in low density polyethylene, exhibit emission at 815 nm whereas a different type of emission is observed from the laboratory prepared pigment. The photoactivity of all the commercial rutile pigments in polyethylene have been examined and found to correlate well with their corresponding emission intensities at 815 nm.

1. Introduction

In earlier papers we reported on the low temperature emission properties of the anatase and rutile modifications of titanium dioxide in commercial polymers and related the energy of these emissions to the photo-activity of the pigments in the polymers [1-3]. For example, the more photo-active anatase pigments gave strong green emission with a wavelength maximum at 540 nm on exciting with light of 340 nm, whereas the less photo-active rutile pigments gave only a weak infra-red emission with a wavelength maxima at 815 nm and 1015 nm on exciting with light of 375 nm. More recently we reported some preliminary results on the luminescence properties of rutile pigments manufactured by different processes [4]. Only rutile pigments produced by the "sulphate" process gave the emission band at 815 nm whereas the rutile pigments produced by the "chloride" process gave a broad emission band with a maximum at 1015 nm. We have also found that the intensity of the emission at 815 nm was related to the photo-activity of the rutile pigment in commercial polyethylene [5].

The nature of the species responsible for the infra-red emission from rutile has been the subject of much attention [6-9]. In general, the major species are believed to be either interstitial Ti^{3+}

ions present as imperfections in the rutile crystal lattice or impurities such as Cr^{3+} ions. In this paper the luminescence properties of five commercial, "sulphate produced", uncoated and coated rutile pigments have been examined and compared with those of a rutile pigment produced in the laboratory by the same route to provide further information on the nature of the species responsible for the infra-red emission at 815 nm. All the pigments were dispersed in commercial low density polyethylene. Finally, the photo-activity of the commercial rutile pigments in the polymer have been examined and compared with their emission properties.

2. Experimental

2.1. Materials

Commercial low density polyethylene powder (Melt Flow Index = 22; density = 0.918 g cm^{-3}) was supplied by ICI (Plastics Division) Ltd. and contained no commercial additives. The uncoated (pigment 1) and coated (pigments 2 to 5) rutile pigments prepared by the common commercial sulphate process were supplied by Tioxide International Ltd. A rutile pigment prepared in the laboratory (6) by the sulphate process was also supplied. Details on the manufacturing processes for titanium dioxide pigments are given in [10].

The uncoated pigment (pigment 1) was dry-milled (type I) whereas the coated pigments (pigments 2 to 7) were wet-coated and refined and have an inorganic (2% of alumina/silica) coating (type II) and the coated pigment (pigment 5) had only an organic (1% silicone) coating (also type II). Further information on the nature of type I and II rutile pigments are given in [11].

2.2. Processing

The commercial rutile pigments (1%) were incorporated into polyethylene using a Brabender Plasticorder at 150°C for 10 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 r.p.m. The polymer was then pressed into film (200 μm thick) at 150°C for 1 min.

2.3. Photo-oxidation

All the polymer films were irradiated in a Xenotest-150 weatherometer, (Original Hanau, Quartzlampen, G.m.b.H) set up for natural sunlight simulated exposure conditions out-of-doors (45°C black body, 50% relative humidity) [12].

The rates of photo-oxidation of the polymer films were monitored by measuring the formation of the non-volatile carbonylic products absorbing at 1710 cm⁻¹ in the infra-red region of the spectrum using a Perkin Elmer 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,

d = film thickness in metres.

2.4. Luminescence measurements

The low temperature luminescence spectra were recorded using a compensated double grating (1200 lines mm⁻¹) Hitachi-Perkin-Elmer MPF-4 spectrofluorimeter equipped with two R-446F photomultiplier tubes containing an S1 photocathode. The lifetime of the infra-red emission from rutile is very short (~10⁻⁵ sec) [9] and therefore the rotating chopper was removed from the phosphorescence accessory in order to observe the emission.

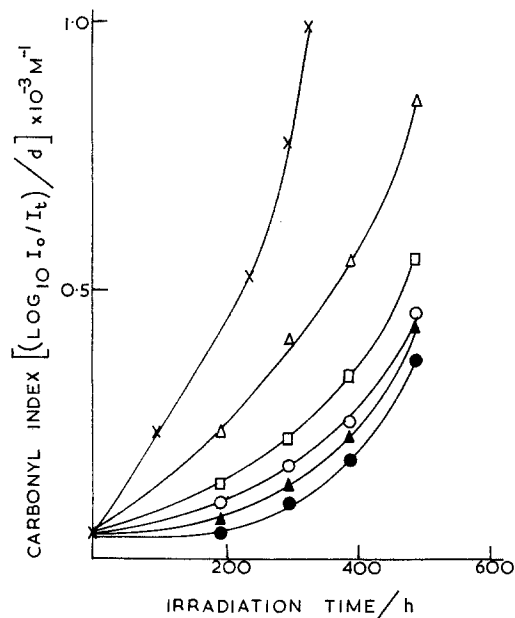


Figure 1 Rate of photo-oxidation in a Xenotest-150 weatherometer of commercial unstabilized polyethylene film (200 μm thick) containing: X no pigment; Δ pigment 1; ▲ pigment 2; ○ pigment 3; □ pigment 4; and ● pigment 5. The pigment concentrations were all 1%.

3. Results

3.1. Pigment photo-activity

The rates of photo-oxidation of the polyethylene films containing the commercial rutile pigments are shown in Fig. 1. It is seen that all the pigments inhibit photo-oxidation of the polymer to varying degrees. The stabilizing efficiency of the pigments increase in the order 5 > 2 > 3 > 4 > 1.

3.2. Pigment luminescence

Fig. 2 compares the infra-red emission spectra of the commercial rutile pigments with that of the laboratory prepared pigment. It is seen that all the commercial pigments exhibit an emission band at 815 nm with a much weaker emission band at 1015 nm whereas the laboratory grade pigment exhibits a broad emission spectrum with wavelength maxima at 815, 890, 930 and 1015 nm. There is also a significant variation in the intensity of the emission at 815 nm with the pigment grade. The strongest emission is observed from the uncoated pigment 1 whereas the weakest emission is observed from the silicone-coated pigment 5. The other pigments with inorganic coatings exhibit emissions of intermediate intensities, the pigment

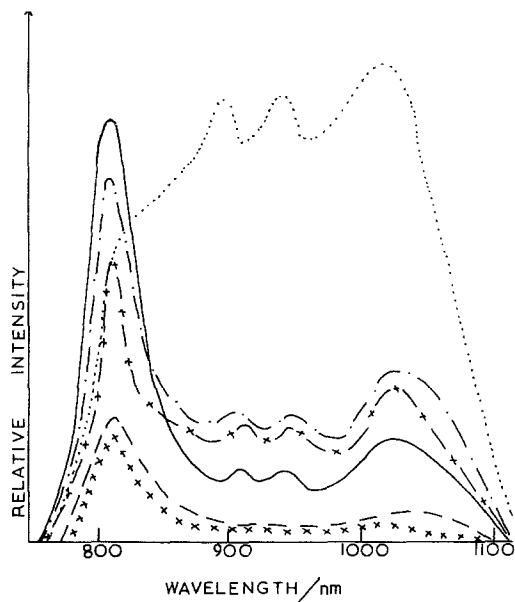


Figure 2 Corrected low temperature infra-red emission spectra at 77 K of commercial rutile pigments: — pigment 1; - - - pigment 2; - · - pigment 3; -x-x-x pigment 4; and xxxxx pigment 5; and laboratory grade pigment · · · · · pigment 6 in low density polyethylene (200 μm thick). Excitation wavelength = 375 nm.

with the heaviest coating (pigment 2) exhibiting the weakest emissions. Thus, the emission intensities of the commercial pigments decrease in the order $1 > 3 > 4 > 2 > 5$ which correlates with the corresponding increase in their stabilizing efficiency in the polymer, apart from one exception.

4. Discussion

An interesting feature of the results is the correlation between the photo-activity of the pigment in the polymer and the emission intensity. The lower the emission intensity the less active the pigment and this is shown in Figs. 1 and 2. Fig. 2 also shows the further interesting feature that there is a marked difference in the emission spectra of the commercial and laboratory grade rutile pigments.

In studies on single crystals of rutile other workers have observed a broad infra-red emission with a wavelength maximum at 850 nm. The maximum of this emission is thus marginally different from that observed here. A likely explanation for this difference in the wavelength maxima may be due to the following factor. The workers [7-9] using single crystals used as their excitation source the 365 nm line of a high

pressure mercury lamp. This is far more intense than the 375 nm excitation beam from the xenon arc lamp in our work with the spectrofluorimeter. Also, in the former arc the more intense excitation light will travel deeper into the rutile crystal lattice, and therefore excite other impurities or defects to give a much broader emission. In our experiments the much weaker excitation light will excite only impurities or defects on the surface of the pigment particle.

Studies on the thermoluminescence of rutile crystals [7-9] have attributed the emission centre to the presence of defect Ti^{3+} sites in the rutile crystal lattice. In our study on the steady state photoluminescence of commercial rutile pigments, although other processes may well interfere, our results also suggest that the emission at 815 nm may originate from Ti^{3+} ions. The observation of emission at 815 nm from the laboratory grade pigment would tend to support this conclusion. Further, Ti^{3+} ions are believed to be important in the photosensitized oxidation of polymers by titanium dioxide pigments [13].

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