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An ESR study on the photoreactivity of TiO_2 pigments

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The photoreactivity of commercial TiO_2 pigments has been studied by monitoring the generation of radicals at the TiO_2–water interface upon illumination with ultraviolet light. The ESR spin-trapping technique has been employed, using 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) as spin trap. In illuminated TiO_2 dispersions the only radical species identified has been the $OH^\cdot$. The amount of radicals generated was found to depend upon the surface properties of the pigment, such as impurities and surface treatments, and upon the oxygen concentration in the slurry. A feasible mechanism for radical generation, involving O_2 adsorption is proposed. The initial rate of radical generation has been found to be in good agreement with other methods commonly used to characterize the photostability of paints.

1. Introduction

Titanium dioxide is a white pigment widely used in the paint industry. Among other outstanding physical properties, one of them, i.e. its ability to absorb light in the ultra-violet region, causes serious troubles in the resistance of paint towards weathering, specially in outdoor conditions. Attempts made to clarify the mechanism of paint photodegradation [1, 2] have stressed the fundamental role played by water in such reactions.

It is well known that n-type TiO_2 (rutile) semiconductor has a band-gap of 3.05 eV [3]. Thus interaction with photons having a wavelength less than 400 nm excites electrons from the valence to the conduction band. As a consequence, irradiation with ultra-violet light of any particulate system containing TiO_2, dispersed in aqueous or organic media can lead to many photochemical reactions such as photodecomposition of water [4–6], photo-assisted synthesis of organic molecules [7, 8] and photodegradation of paints [9].

A large number of papers has been published on the photo-electronic processes at the oxygen–TiO_2 interface [10–12], while less knowledge seems to exist on the water–TiO_2 interface.

The aim of the present work was to study the reactions occurring at the water–TiO_2 interface upon ultra-violet irradiation and to make correlations with the photostability of paints. Electron spin resonance (ESR) was used to identify the radicals generated. Since the lifetime of the free radicals produced is very short, the "spin-trapping" method was used [13, 14]. In this technique, "spin-trap" molecules, which have unsaturated functions designed to give persistent free radical adducts by reaction with the short-lived radicals, are added to the system. These adducts show characteristic ESR patterns from which the short-lived radicals can often be identified. A widely known nitrone spin-trap which was used in the present investigation is 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) [14].

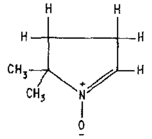

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TABLE I Post-treatment compositions and weathering index values (W_i) for TiO_2 commercial pigments

Sample	Post-treatment	W_i	
		Enamel	Latex
C1	Al_2O_3–SiO_2	–	92
C2	Al_2O_3–SiO_2	–	72
C3	Al_2O_3	58	–
C4	Al_2O_3	13	–

2. Experimental details

DMPO was obtained from Ega Chemie and was used without further purification.

Two series of rutile TiO_2 samples, obtained from the sulphate process [15] and kindly provided by SIBIT, were investigated. The first series consisted of uncoated TiO_2 products (Samples A, B1, B2, B3). Samples labelled B differ from Sample A as they contain different amounts of zinc oxide (1.1 %, 0.7 % and 0.5 % in Samples B1, B2 and B3 respectively), which was added, before calcination, in order to improve the durability of the final pigment. Small amounts of potassium and sulphate ions were released by their surface in aqueous solution.

Samples C1 to C4 (second series) are commercial post-treated rutile pigments. Table I shows the surface-coating compositions and the relative weather resistance of these products. The latter property, expressed by a weathering index value (W_i), was determined using an artificial weathering test (Weather Ometer intrument) which accelerates the material destruction by exaggerating the real outdoor conditions (radiation power, humidity, temperature, etc.). The W_i values were determined on samples as enamels or latexes as a weighted average of the losses in colour, gloss, or chalk resistance [16] of the pigmented film after 200 h accelerated weathering. Owing to possible fluctuations in the treatment, two samples of known low and high weather stability were used as internal 0 and 100 standards. Lower W_i values are typical of a poorly stable pigment.

ESR spectra were obtained at X band on a Bruker 200tt model spectrometer at room temperature. A concentrated aqueous slurry (40% by weight), containing 0.1 mol/l DMPO, was introduced into an ESR quartz sample cell. The cell was then horizontally positioned into the ESR resonance cavity, by simply modifying the connecting waveguide, in order to minimize sedimentation effects during the irradiation and recording of the spectrum. The position of the cell in the resonance cavity was also carefully controlled in order to obtain the best reproducibility of the spectra intensity. Irradiation was carried out in the microwave resonance cavity by means of a Philips SP 500W SPEC 21 mercury lamp. The curves of ESR spectral intensity against time were plotted with the kinetic setting of the instrument positioned at a magnetic field corresponding to the maximum height of one hyperfine line of the spectrum. Changes in concentration of molecular oxygen in the solution could affect the peak-to-peak linewidth which, however, is probably dominated by some unresolved hyperfine splitting from γ-protons [17].

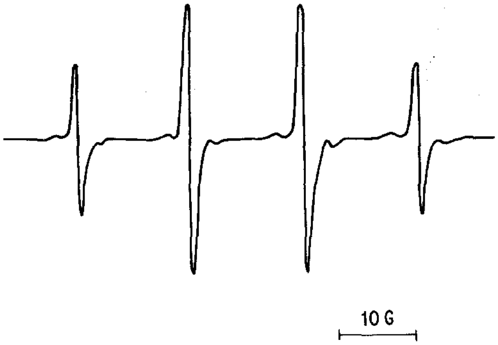

Figure 1 Electron spin resonance spectrum obtained upon ultra-violet illumination of TiO_2 rutile water suspension in the presence of DMPO.

Since no absolute spin concentration measurements were made, this feature was not further taken into account.

3. Results and discussion

Ultra-violet irradiation of aqueous suspension of rutile TiO_2 containing DMPO gives the ESR spectrum shown in Fig. 1, with $g = 2.0060$ and coupling constants $a_H = a_N = 14.9$ G. The two coupling constants are accidentally equal so that the spectrum appears as 1:2:2:1 pattern. This spectrum has been previously identified by Harbour and co-workers [17, 18] and by Sargent and Gardy [19], respectively, by ultra-violet irradiation of H_2O_2 solution and ZnO suspension and during radiolysis of water by 3 MeV electrons in the presence of DMPO. It seems well established that it arises from the $OH^{\cdot}$/DMPO radical adduct.

By contrast, ultra-violet illumination of cadmium sulphide aqueous suspension gave only a spectrum attributable to the O^{2-}/DMPO adduct [20, 21]. In our case, neither this spectrum nor

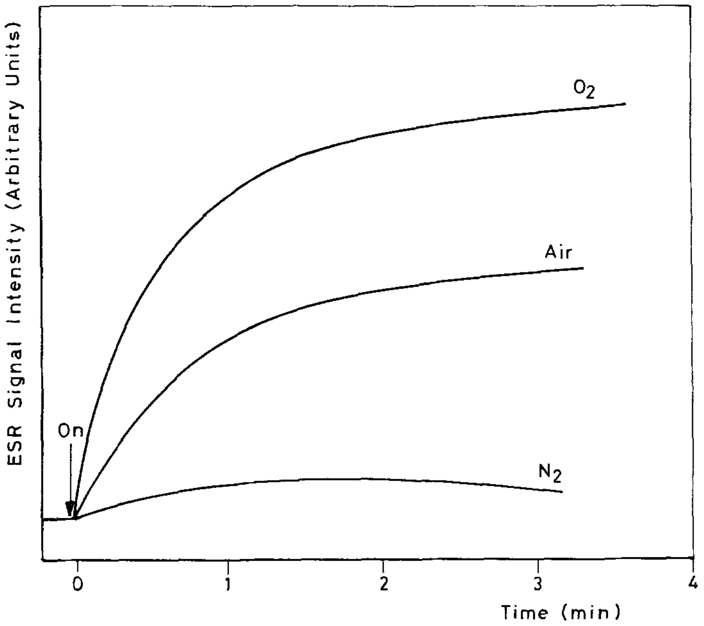

Figure 2 ESR signal intensity of the OH˙/DMPO adduct as a function of time of ultra-violet illumination for TiO_2 water suspension saturated with oxygen, air or nitrogen. The magnetic field was maintained constant at a position corresponding to the maximum height of one hyperfine line.

spectra belonging to reduced titanium species were recorded.

In TiO_2 studies the OH˙ free radical intermediate was only identified during photodecomposition of water by ultra-violet irradiation of de-aerated TiO_2 (anatase) suspensions by using α-phenyl *N*-tert-butyl nitrone (PBN) and α-(4-pyridyl *N*-oxide) *N*-tert-butyl nitrone (4-POBN) as spin traps [22]. In this case other spectra were also simultaneously detected, one of which was attributed to the $HO_2^{\cdot}$ radical. Rutile TiO_2 was not found to give any spectrum under the same experimental condition.

Fig. 2 shows the overall kinetics of radical formation; molecular oxygen dissolved in the solution seems to play a determining role in the formation of the OH˙ radical. In fact, suspensions purged with pure nitrogen showed only a very weak spectrum, while upon bubbling with pure oxygen the intensity significantly increased with respect to air-saturated suspensions. This observation is in agreement with a recent study by Harbour and Hair [18] concerning radical intermediates in the photosynthesis of H_2O_2 in aqueous ZnO dispersions. After the initial rise, the signal intensity suddenly levels off, presumably when all molecular oxygen in the sample cell has been consumed. The maximum intensity reached is thus a function of the amount of oxygen availabe during illumination and seems, therefore, variable depending on pigment concentration, rate of radical decomposition, diffusion and other setting conditions. The photo-activity of pigments upon ultra-violet illumination should, instead, be related to the rate of radical generation, expressed by the initial slope of the curve of intensity against time. In fact, such a rate was found to depend only upon the reactivity of the dispersed phase, provided that the oxygen concentration remained constant (samples equilibrated with air). Fig. 3 shows results obtained with the first series of untreated pigments. In all cases the initial slope is in good agreement with the expected photostability of the products [15], attributed to the zinc ion concentration, mainly present at the TiO_2 particle surface. Fig. 4 shows the ESR signal intensity as a function of time for commercial TiO_2 pigments of known photostability in paints. Again the good correspondence is to be noted between initial slope and photostability values obtained by the weathering test. Such a correlation has to be considered semi-quantitative since the W_i determination depends upon the standards used.

The results reported above provide clear evidence for the formation of an OH˙ radical during the irradiation of TiO_2 rutile in the presence of water and molecular oxygen. This can be interpreted in terms of a general mechanism based on the band model for semiconductors.

The adsorption of a quantum of light of energy greater than the semiconductor E_{gap} excites an electron from the valence to the conduction band giving rise to an electron-hole pair (exciton) in the lattice:

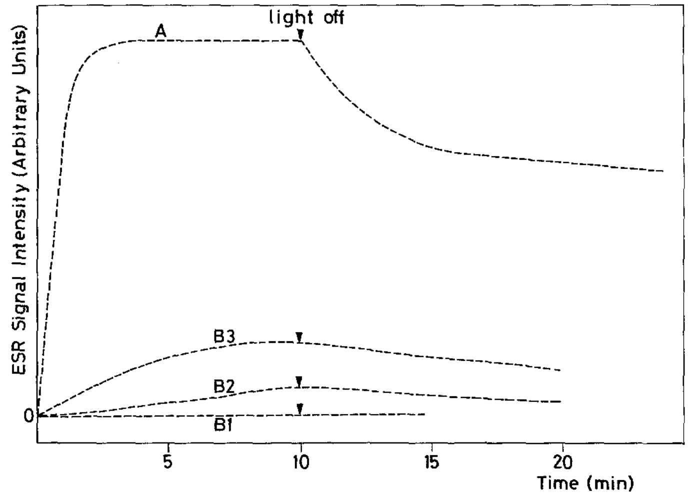

Figure 3 ESR signal intensity of the OH·/DMPO adduct as a function of time of ultra-violet illumination for TiO_2 (first series) water suspensions. The powders are uncoated products which differ in zinc oxide content: 1.1%, 0.7%, 0.5% and 0.0% in Samples B1, B2, B3 and A, respectively.

$$TiO_2 + \text{light}\ (h\nu) \rightarrow h - e\ (Ti^{3+}O^-). \qquad (1)$$

The excitons generated in a few sub-surface atomic layers might diffuse to the surface and react with adsorbed species. The oxidation potential of OH^- adsorbed species to $OH^{\cdot}$ radical lies above the valence band edge of TiO_2, so that a photogenerated hole is expected to be sufficiently energetic to produce the radical species [22].

$$OH^-_{ads} + h \rightarrow OH^{\cdot}_{ads} \qquad (2)$$

The $OH^{\cdot}$ radicals initially formed must then react with either oxidizable products and/or "spin-trap" molecules (DMPO) [18, 23].

$$OH^{\cdot}_{ads} + \text{oxidizable products} \rightarrow \text{oxidized products} \qquad (3)$$

$$OH^{\cdot}_{ads} \rightleftarrows OH^{\cdot}_{free} \qquad (4)$$

$$OH^{\cdot}_{free} + DMPO \rightarrow OH^{\cdot}/DMPO \quad \text{(when DMPO is present)} \qquad (5)$$

On the other hand, in order to maintain the electroneutrality within the semiconductor, the free electron must react with molecular oxygen at the surface:

$$O_{2\,ads} + e^-_{free} \rightarrow O^-_{2\,ads} \qquad (6)$$

the superoxide radical ion may react further [18] according to

$$O^-_{2\,ads} + e^-_{free} + 2H^+ \rightarrow H_2O_{2\,ads} \qquad (7)$$

$$H_2O_{2\,ads} \rightleftarrows H_2O_{2\,free}\,. \qquad (8)$$

As an alternative to Equation 4, an $OH^{\cdot}$ radical could also be formed by homolytic cleavage, under ultra-violet illumination, of H_2O_2 produced by Equation 8. In fact, it is known that ultra-violet

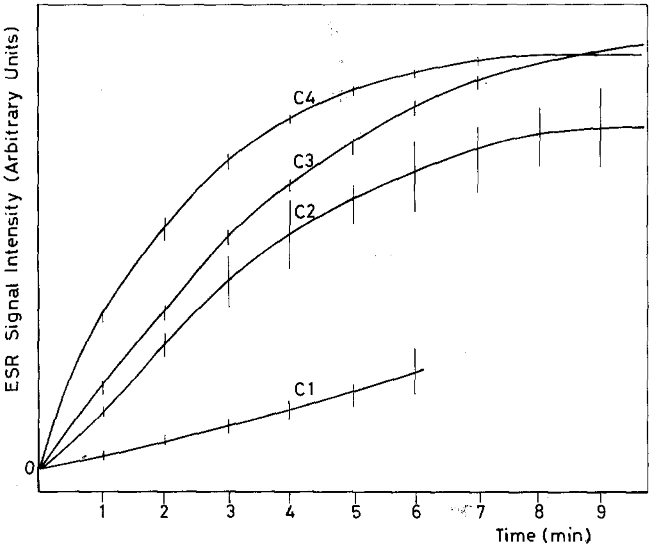

Figure 4 ESR signal intensity of the OH·/DMPO adduct as a function of time of ultra-violet illumination for TiO_2 (second series) water suspensions. The samples are commercial post-treated pigments (see Table I).

photolysis of aqueous hydrogen peroxide, in the presence of DMPO, gives a spectrum identical to that of Fig. 1 [17]. The observed $OH^{\cdot}$/DMPO radical adduct could thus, in principle, arise from the simple reaction

$$H_2O_2\ (\text{solution}) \xrightarrow{h\nu} 2OH^{\cdot} \qquad (9)$$

Superoxide radical adducts have been observed when CdS water suspensions or concentrated hydrogen peroxide solution are irradiated with ultra-violet light [17, 20, 21]. In our experiments only the $OH^{\cdot}$ radical adduct has been detected; this probably means that O_2^- is not desorbed or that it reacts quickly towards other products (e.g. H_2O_2). On the other hand, the fact that in the absence of molecular oxygen no $OH^{\cdot}$ radical is observed could be attributed to the recombination reaction

$$e^-_{\text{free}} + OH^{\cdot}_{\text{ads}} \rightarrow OH^-_{\text{ads}} \qquad (10)$$

which shows that free electrons, not reacting with molecular oxygen according to Equation 6, withdraw $OH^{\cdot}$ radicals from the $OH^{\cdot}$/DMPO formation equilibrium. In the absence of oxidizable molecules, Equation 5 accounts for the observed ESR signal. The close correspondence between rate of $OH^{\cdot}$ radical formation and photoactivity of TiO_2 pigment in paint degradation upon ultra-violet illumination suggests that $OH^{\cdot}$ is a true intermediate radical in a much more complex reaction, when the particulate system is dispersed in a polymeric vehicle. This result is in good agreement with the conclusions by Voltz *et al.* [1, 2] which showed that chalking of rutile pigmented films was caused by hydroxyl radicals.

Hydrogen extraction processes are known to proceed easily with oxygen centred radicals such as hydroxyles. The formation of radical adducts such as $^{\cdot}CH_2OH$ [24] and $^{\cdot}CO_2^-$ [18] with DMPO has already been detected, arising from simple reactions of $OH^{\cdot}$ with methanol, and formate or oxalate ions, present in water solution. This kind of reaction is the first step of the possible mechanism by which photodegradation in paints occurs. Unfortunately, our preliminary results, in the presence of polymeric species or in vehicle media, gave complex spectra in which the identification of well-defined radical species was not achieved.

5. Conclusions

It has been shown that spin trapping is a useful technique for the photoreactivity studies of TiO_2 water dispersions.

The hydroxyl radical, detected using the spin-trap DMPO, has been the only species observed, upon ultra-violet illumination.

A good correlation was found between the initial rate of radical generation and the degradation of pigmented films determined by an artificial weathering method. This shows that the hydroxyl radical is a true active intermediate in the photodegradation process.

A mechanism of $OH^{\cdot}$ radical generation, which involves O_2 adsorption, has been discussed in terms of the band model for semiconductors.

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