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Photo-Chemistry of Pigments

Studies on the Mechanism of Chalking

S. PETER PAPPAS and RICHARD M. FISCHER*
North Dakota State University†

Studies are presented which demonstrate that: (1) irradiation of titanium and zinc oxide pigments produces singlet oxygen; (2) irradiation of titanium dioxide pigments in water yields hydrogen peroxide; and (3) the formation of singlet oxygen and hydrogen peroxide correlates with chalking tendencies of the pigments. These findings, together with the results of quenching studies, are interpreted in terms of a working hypothesis, for the generation of reactive oxidants, which ties together previous work into a unified scheme. The relative chalking rates of anatase and rutile titanium dioxide, as well as the improvement of chalk resistance by surface treatment, are discussed within the framework of this scheme. The role of singlet oxygen in the chalking process, the importance of its presence with regard to the control of chalking, and possible mechanisms for its formation are also discussed.

KEY WORDS: Chalking; Energy transfer; Hydrogen peroxide in chalking; Singlet oxygen in chalking; Photo-chemistry; Photo-sensitization; Weathering.

INTRODUCTION

OUR interest in chalking developed from a primary concern in the photo-chemistry of pigments. We were particularly intrigued by the prospect of pigments acting as photo-sensitizers,[1] and by the application of this concept to the utilization of UV radiation for curing pigmented coatings (UV curing). In view of the considerable effort that has been devoted to the problem of chalking, it was inevitable that even a cursory view of the literature on pigment photo-chemistry would lead us to a consideration of the chalking phenomenon.

In initiating a research project on chalking, we received considerable encouragement and inspiration from Dr. Alfred E. Rheineck,[2] to whose memory this paper is dedicated.

Chalking is a common problem of exterior paints which involves degradation of the organic polymer part of the paint (i.e., the binder), thereby exposing the pigment, which appears on the surface as a chalk-like substance. With regard to the mechanistic aspects of chalking, a recent review on the weatherability of TiO_2-containing paints[3] is particularly informative and presents two modern views: (1) that polymer degradation is related to the formation of superoxide ion (or oxygen radical anion), $O_2^{\cdot-}$, produced by electron transfer from excited-state TiO_2 to molecular oxygen, and (2) that the degradative species is hydroxyl radical, $HO^{\cdot}$, postulated[4] to arise by electron transfer from water to excited-state TiO_2. Earlier studies had implicated oxygen atoms as the reactive oxidant.[5] In view of our interest in photo-sensitization, we were particularly intrigued by the suggestion[6] that electronically excited oxygen molecules may be produced on irradiation of the semi-conducting white pigments, by analogy with dye sensitization.

In the way of background, two excited states of oxygen are of interest (both of which are singlet states in contrast to the triplet ground state of oxygen): (1) the sigma singlet state, which possesses 37.5 kcal/mol above the ground state and is predicted to have free radical reactivity, and (2) the delta singlet state, which possesses 22.5 kcal/mol above the ground state and has been characterized as a reactive dienophile.[7] Although higher in energy, the sigma state is considerably shorter lived, and, in fact, rapidly deactivates to the delta state, which has been identified or implicated in many important chemical processes, including polymer degradation[8,9] and autoxidation of drying oils.[10]

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* Present address: 3M Co., 3M Center, St. Paul, Minn. 55101.
† Dept. of Polymers and Coatings, Fargo, N. D. 58102.

Thus, it appeared worthy of study to investigate whether singlet oxygen might be involved in the chalking process.

EXPERIMENTAL

Microwave Synthesis of 2-Methoxy-5-oxo-2, 5-dihydrofuran (I)

Singlet oxygen was produced in a flow system with a Raytheon microwave power generator,[8] model PGM-10, 2450 mc, as an excitation source. With the system under a vacuum of less than 1 mm, the microwave discharge was ignited with a Tesla coil and the oxygen flow was increased until the system pressure was 3 mm. Furan vapor was released into the system until a pressure of 5 mm was attained. A total of 30 ml of furan was introduced into the system over a period of 6 hr.

The reaction products and unreacted furan were collected in a liquid nitrogen cold trap. Vanadium pentoxide (1 g) and 80 ml of methanol were added, and the mixture was refrigerated for 36 hr. After filtration of the vanadium pentoxide, the methanol and furan were removed from the higher boiling products by rotary evaporation at room temperature. The residue (0.4 g) was decolorized with charcoal and fractionated by gas-liquid chromatography (glc), using a Varian-Aerograph 1740 instrument with flame ionization detector and disc integrator. The major product (73%) was collected and identified as 2-methoxy-5-oxo-2, 5-dihydrofuran[11] by infrared and mass spectral analysis. The infrared spectrum, obtained in chloroform, exhibited the characteristic carbonyl absorbances at 5.57 and 5.68 μ. The mass spectrum, obtained on a Hitachi Perkin-Elmer, RMU-6E, spectrometer, exhibited a prominent molecular ion at m/e 114, and fragment ions corresponding to losses of H, CH_3, CH_3O, and CO_2.

Irradiation of the Furan-Pigment System

Irradiations were carried out in a 2000-ml beaker modified with a condensor, sampling port, and oxygen inlet. A General Electric Par-38, H100PSP38-4, 100-w black light source was mounted above the beaker and the light was filtered through a 2-mm Pyrex cover glass, to eliminate wavelengths shorter than 300 nm.

Titanox® A-MO and Titanox 2005, obtained from N L Industries, Inc., Ti-Pure® R-901, obtained from E. I. du Pont de Nemours & Co., Inc., and zinc oxide XX-602, obtained from the New Jersey Zinc Co., were utilized individually as sensitizers. Characterization of the TiO_2 pigments is presented in *Table* 1. In each case, the pigment (20 g) was allowed 24 hr to settle on the bottom of the reactor, which contained 400 ml of reagent-grade methanol. Furan (4.8 g) and ethylene glycol (100 mg), the internal standard for glc analysis, were added to the reaction mixture just prior to irradiation. Oxygen was passed over the system at a flow rate of 10-15 ml/min. The reaction temperature was maintained at about 15°C by placing the beaker in a water bath with a coil for the continuous passage of tap water. Aliquots (20 ml) were removed every 24 hr. These were rotary evaporated, diluted with 0.25 ml of acetonitrile, and analyzed by glc. The desired product, 2-methoxy-5-oxo-2, 5-dihydrofuran, was identified in the glc traces by peak matching with authentic material from the microwave synthesis.

Table 1—Characterization of the Titanium Dioxides

Titanium Dioxide	Type	Chalking Ability	Surface Treatment
Titanox A-MO[a]	Anatase	High	Light
Titanox 2005[b]	Rutile	Medium	Minimum
Ti-Pure R-901[c]	Rutile	Low	Treated

(a) ASTM D476-70, Type I.
(b) Type II.
(c) Type III.

The peak matching was performed under five different sets of conditions, including the utilization of three different column-packing materials: 5% Carbowax 1500 on 80/90 Anakrom U, 5% isooctylphthalate on 60/80 Chromosorb G, and 1.5% Versamid 900 on 80/90 Chromosorb G. The system of choice was 5% Carbowax 1500 on 80/90 Anakrom U in an 8 ft × ⅛ in. column at 128°C, with carrier gas flow rate of 10 ml/min. Under these conditions, the retention time of the desired product was 11.1 min. This product was not formed in the absence of pigment over a 5-day irradiation period. Preliminary studies had demonstrated that the product is formed on sensitization with the dye, Eosin Y.

Representative results with the pigments are presented in *Table* 2 and *Figure* 1. Studies were also carried out which demonstrated that neither the singlet oxygen product nor the internal standard, ethylene glycol, are differentially adsorbed on the TiO_2 pigments examined. A sample of known product ratio was added to a suspension of the pigment in methanol and allowed to equilibrate for 24 hr. The pigment was removed by filtration through a bed of Celite 545, the methanol was removed by rotary evaporation, and the resulting sample was re-analyzed

Table 2—Formation of 2-Methoxy-5-oxo-2, 5-dihydrofuran (I)

Irradiation Time (days)	Product/Internal Standard[a] Titanox A-MO	Titanox 2005	Ti-Pure R-901	Zinc Oxide XX-602
0	—	—	—	—
1	0.028	Trace	—	0.017
2	0.09	0.022	—	0.028
3	0.105	0.038	—	0.035
4	0.118	0.055	Trace	0.042
5	0.15	0.061	0.012	0.049

(a) Glc response ratio; internal standard: 4 mM.

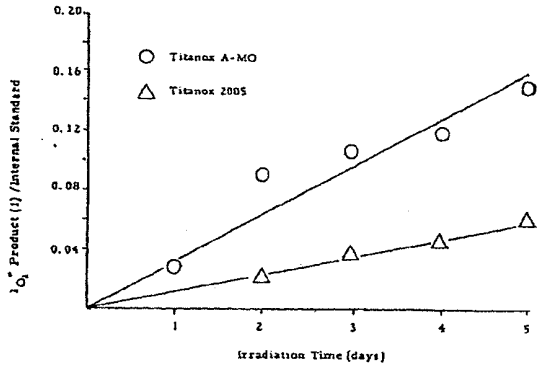


Figure 1—Graphic comparison of singlet oxygen product formation for Titanox A-MO and 2005

by glc. For each of the TiO_2 pigments, the ratio of singlet oxygen product to internal standard remained unchanged, thereby eliminating selective adsorption as a possible explanation for the results.

Several experiments were performed on the effect of *p*-benzoquinone (1.90×10^{-4} to 2.57×10^{-2} *M*) and triethylamine (4.0×10^{-2} *M*) on the formation of the singlet oxygen product, I, utilizing Titanox A-MO as sensitizer. In each case, the formation of singlet oxygen product was verified by glc prior to introducing the additive. The results of these studies are presented in *Figures* 2 and 5.

Irradiation of the Water-Pigment System

The apparatus was identical to that utilized in the furan system. Titanox A-MO, Titanox 2005, and Ti-Pure R-901 were utilized individually as sensitizers. In each case, the pigment (20 g) was dispersed with distilled water (300 ml) by magnetic stirring, and subsequently was allowed to settle on the bottom of the beaker. Unwetted pigment was skimmed off the surface prior to irradiation. During the irradiation, aliquots were removed periodically and filtered through a 5-mm bed of silicic acid to remove any suspended pigment particles. The aliquots were assayed for hydrogen peroxide content by the following method.[12]

To 3.9-ml aliquots are added: (1) 0.5 ml of 0.3 *M* potassium phosphate buffer, pH 7.8, (2) 0.5 ml of 0.6 m*M* *o*-dianisidine dihydrochloride, and (3) 0.1 ml of a 0.01% aqueous solution of horse radish peroxidase, buffered with potassium phosphate. The presence of hydrogen peroxide was qualitatively indicated by the formation of reddish color in the sample immediately after the addition of the peroxidase solution to the irradiated samples. Quantitative measurements were made with a Bausch and Lomb Spectronic 20 at 450 nm. Optical density at this wavelength was converted into hydrogen peroxide concentration by reference to a standard curve. The results are presented in *Figure* 3.

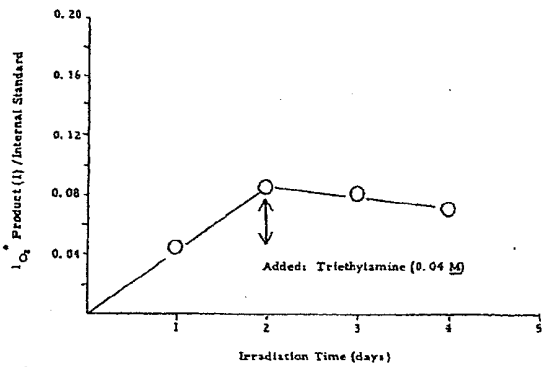


Figure 2—Effect of triethylamine on singlet oxygen product formation with Titanox A-MO

The effect of *p*-benzoquinone (2.3×10^{-4} *M*) and triethylamine (4.0×10^{-2} *M*) on the stationary concentration level of hydrogen peroxide, utilizing Titanox A-MO as sensitizer, was investigated. The results are presented in *Figures* 4 and 6. Control experiments were also carried out which demonstrated that the assay system is not adversely affected by the presence of the inhibitors at the concentrations utilized. Furthermore, the stability of hydrogen peroxide toward triethylamine in the absence of pigment was demonstrated under the irradiation conditions.

RESULTS

Singlet Oxygen Production

Our initial approach to the problem was to determine whether delta singlet oxygen is produced on irradiation of TiO_2, by exploiting its known specific reactivity with unsaturated compounds.[13] After considerable experimentation with several systems, we settled on the use of furan, which, in the presence of methanol, is known to produce 2-methoxy-5-oxo-2,5-dihydrofuran (I) by dye-sensitized oxygenation.[14] The established mechanism of this process is outlined in Scheme I, the critical feature being electronic energy

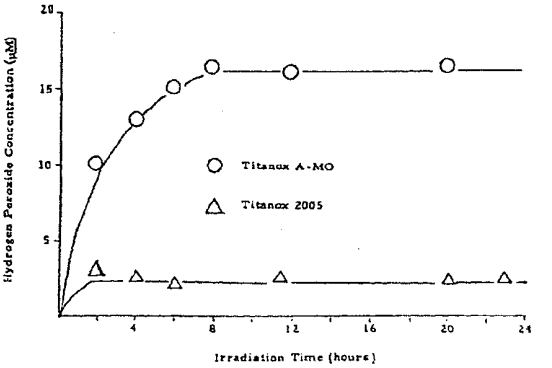


Figure 3—Comparison of hydrogen peroxide formation for Titanox A-MO and 2005

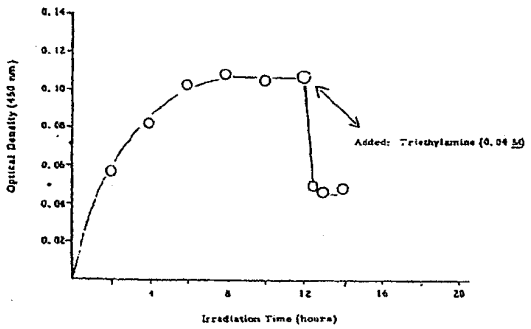


Figure 4—Effect of triethylamine on hydrogen peroxide formation with Titanox A-MO

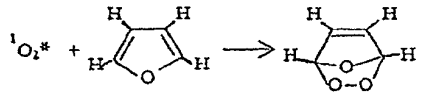
transfer (Equation 3) from the excited triplet-state dye ($^3D^*$) to ground-state oxygen ($^3O_2$), to produce ground-state dye (D_0) and excited singlet-state oxygen ($^1O_2^*$).[15,16] The singlet oxygen undergoes a Diels-Alder reaction with furan to produce a peroxide (Equation 4), which may be isolated at low temperature, but reacts with methanol under ambient conditions to produce I.

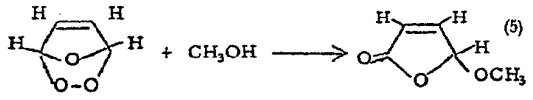
SCHEME I

$$D_0 \xrightarrow{h\nu} {}^1D^* \quad (1)$$

$$^1D^* \rightarrow {}^3D^* \quad (2)$$

$$^3D^* + {}^3O_2 \rightarrow D_0 + {}^1O_2^* \quad (3)$$


(4)


(5)

I

It was our intent to determine whether TiO_2 could function in place of the dye in the energy transfer step. For the purpose of identifying and monitoring the formation of I by glc, this compound was prepared independently by reaction of furan with singlet oxygen generated in a microwave discharge,[8] followed by work-up with methanol. Preliminary studies were also performed utilizing dye sensitization. Irradiations with pigments as sensitizers were carried out in a beaker with side arms for oxygen intake and exhaust. The pigment was deposited on the bottom of the beaker, which also contained the furan-methanol solution and ethylene glycol as an internal standard for glc analysis. The system was irradiated from the top through a Pyrex cover glass to exclude wavelengths shorter than 300 nm. The initial results with a chalking anatase, Titanox A-MO, were encouraging, as shown in *Figure* 1, since no singlet oxygen product was obtained in the absence of pigment. These findings prompted the investigation of a medium-chalking rutile, Titanox 2005, which produced significantly less product (see *Figure* 1), and of a more chalk-resistant rutile, Ti-Pure R-901, which generated only a trace of product after irradiation for 4 days. These pigments are described in *Table* 1. A zinc oxide pigment, XX-602, which was also examined, produced the singlet oxygen product I to the same extent as did Titanox 2005. These results were found to be reproducible, and representative data are presented in *Table* 2.

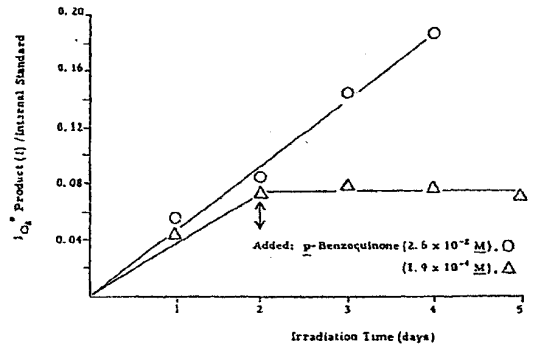


Figure 5—Effect of p-benzoquinone on singlet oxygen product formation with Titanox A-MO

The formation of product I constitutes strong evidence for the intermediacy of singlet oxygen. Further support was acquired by demonstrating that triethylamine (4×10^{-2} *M*), a known singlet oxygen quencher,[17] effectively quenches the formation of I, as shown in *Figure* 2. The possibility that the relative extents of formation of I reflected differential adsorption of either product I or the internal standard on the pigments was also ruled out. Thus, the results demonstrate that: (1) irradiation of titanium and zinc oxide pigments produces singlet oxygen, and (2) the extent of formation of singlet oxygen correlates with the chalking tendencies of the TiO_2 pigments examined.

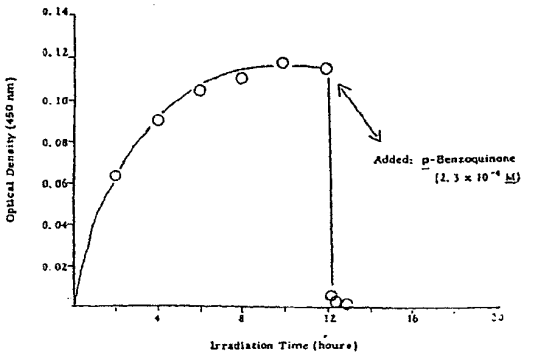


Figure 6—Effect of p-benzoquinone on hydrogen peroxide formation with Titanox A-MO

Hydrogen Peroxide Formation

In view of the possible relationship of these results to chalking, consideration was given to the role of water, since there appears to be no question that moisture accelerates the chalking process.[3] This is particularly emphasized in a recent study which clearly implicates the involvement of hydroxyl radicals (HO·).[4] The formation of HO· was proposed to occur by oxidation of water adsorbed on the surface of excited TiO_2 with concomitant reduction of titanium to the +3 state. However, this mechanism has been questioned on thermodynamic grounds.[3] An alternative source of HO· which should be considered is hydrogen peroxide.

Photolysis of hydrogen peroxide is known to produce hydroxyl radicals, and this process appears to be catalyzed by TiO_2.[18] Furthermore, hydroxyl radicals are produced in a redox reaction between hydrogen peroxide and Ti (III),[19] which is known to be present in the TiO_2 lattice.[20] Thus, hydrogen peroxide represents an attractive precursor for hydroxyl radicals. However, the formation of H_2O_2 on irradiation of TiO_2 pigments has not been clearly demonstrated and, consequently, its possible involvement in the chalking process has remained an open question.[3] This situation is contrasted by the well-documented formation of hydrogen peroxide[21] on irradiation of ZnO, and its recognized relationship with chalking in zinc oxide systems.[22] For these reasons, it was decided that further investigation on the possible formation of hydrogen peroxide with TiO_2 pigments was warranted.

Irradiations were carried out in the same apparatus utilized for the singlet oxygen experiments, except that the methanol-furan solution was replaced by water. Anticipating that levels of H_2O_2 would, if produced, be low, a highly sensitive and specific enzymatic-spectroscopic assay method,[12] rather than the conventional iodide titration, was utilized. The assay system is based on the reaction of hydrogen peroxide with the enzyme, horse radish peroxidase, which, in the presence of *o*-anisidine, may be quantitatively monitored at 450 nm. As illustrated in *Figure* 3, the formation of hydrogen peroxide was readily demonstrated with the chalking anatase, Titanox A-MO, and lower levels were obtained with the medium-chalking rutile, Titanox 2005. Hydrogen peroxide could not be detected with Ti-Pure R-901. Thus, in accordance with the singlet oxygen results, the formation of hydrogen peroxide correlated with chalking tendencies of the pigments.

Further Quenching Studies

The production of a steady-state concentration of hydrogen peroxide is also characteristic of the zinc oxide system, for which it has been demonstrated by isotopic labeling that both oxygens of the hydrogen peroxide are derived from molecular oxygen.[23] With the hope of providing further insights into the possible relationships between singlet oxygen and hydrogen peroxide formation, some common quenching experiments were also carried out. Of particular significance, the addition of 4×10^{-2} *M* triethylamine, which totally quenched singlet oxygen product formation with Titanox A-MO, reduced the corresponding stationary level of hydrogen peroxide by about 50%, as shown in *Figure* 4. Appropriate control experiments were performed which demonstrated that hydrogen peroxide solutions were stable toward triethylamine in the absence of pigment under the irradiation conditions. The addition of 2×10^{-4} *M* *p*-benzoquinone efficiently quenched both the formation of singlet oxygen product and hydrogen peroxide, as shown in *Figures* 5 and 6. It is interesting to note in *Figure* 5 that singlet oxygen production is not quenched by 10^{-2} *M* *p*-benzoquinone. This apparent anomaly arises from the production of singlet oxygen, not from the pigment, but by energy transfer from *p*-benzoquinone which exhibits substantial absorption in the 300 to 400 nm region at concentrations above 10^{-3} *M*. This result is presented to illustrate one of the complexities of the quenching studies.

DISCUSSION

Generation of the Reactive Oxidants

Our first reaction to the results is the basic similarity in the photo-chemistry of titanium and zinc oxide pigments, as measured by singlet oxygen and hydrogen peroxide formation. Thus, Scheme II, which is offered as a working hypothesis for relating the present findings to previous results, may apply, basically, to both pigment types, although specific reference is made to TiO_2.

SCHEME II

$$TiO_2 + O_2 \xrightarrow{h\nu} \underset{\text{II}}{TiO_2^{+\cdot} \ldots O_2^{-}} \quad (6)$$

$$\text{II} \rightarrow TiO_2 + {}^1O_2{}^* \quad (7)$$

$$\text{II} + H_2O \rightarrow TiO_2 + HO\cdot + HO_2\cdot \quad (8)$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \quad (9)$$

$$H_2O_2 + Ti\ (III) \rightarrow Ti\ (IV) + HO^- + HO\cdot \quad (10)$$

$$H_2O_2 \xrightarrow[TiO_2]{h\nu} 2HO\cdot \quad (11)$$

$$\text{II} + R_2CHOH \rightarrow TiO_2 + R_2C{=}O + H_2O_2 \quad (12)$$

Irradiation of titanium and zinc oxide pigments in the 300 to 400 nm range is known to promote chemisorption of oxygen, presumably by electron transfer from the pigment, since the oxygen radical anion (superoxide) has been detected (Equation 6).[24-27] The production of singlet oxygen may occur by reversal of electron transfer (ion-annihilation) with the excess energy stored in the oxygen molecule (Equation 7). This step is preceded by the formation of singlet oxygen on ion-annihilation of superoxide and

ferricenium ions generated electro-chemically.[28] Equations 6 and 7 constitute net electronic energy transfer from the pigment to molecular oxygen. This mode of energy transfer represents a particularly attractive mechanism for photo-sensitization by photo-conductive pigments.

In the presence of water, Complex II may accept a proton (H^+) and an electron to produce perhydroxyl ($HO_2\cdot$) and hydroxyl ($HO\cdot$) radicals, respectively, with the regeneration of TiO_2 (Equation 8). Perhydroxyl radicals are known to disproportionate into hydrogen peroxide and oxygen at diffusional rates (Equation 9).[29] This mode of hydrogen peroxide formation conforms to the known reactivity of superoxide,[30] and is consistent with the finding that both oxygen atoms of hydrogen peroxide are derived from molecular oxygen, as demonstrated with zinc oxide.[23] Analogous schemes for the production of hydrogen peroxide have been suggested.[6,23]

The stationary state plateau of hydrogen peroxide may be attributed to redox decomposition by Ti (III) ions (Equation 10),[19] as well as to direct photolysis to hydroxyl ions, which may be catalyzed by TiO_2 (Equation 11).[18] Thus, the known effect of donor sites, such as Ti (III), in promoting chalking may be attributed, in part, to enhancement of hydroxyl radical formation. Donor sites are also expected to facilitate electron-transfer to molecular oxygen.[3]

Equation 8 depicts the oxidation of water by Complex II. Alternatively, Complex II may participate in the direct oxidation of organic functionality, e. g., alcohols to ketones (Equation 12). Such pigment-catalyzed photo-oxidations have been interpreted in terms of oxidation by pigment holes, represented by $TiO_2^{+\cdot}$.[31] The application of semi-conductor theory to the photo-catalytic activity of pigments is currently receiving considerable attention.[3]

The observed quenching of both singlet oxygen and hydrogen peroxide by low concentrations of *p*-benzoquinone may be attributed to its high electron affinity (approximately 1.40 as compared to 0.87 eV for oxygen).[32,33] Specifically, *p*-benzoquinone is expected to undergo charge-transfer complexation with excited TiO_2 more effectively than oxygen. In fact, the corresponding radical anion of *p*-benzoquinone has been detected on irradiated surfaces of titanium and zinc oxide.[34] In this sense, *p*-benzoquinone may be considered to function as a very effective acceptor site. Such sites, in general, are expected to retard complexation and electron-transfer to oxygen. This concept provides a rationale for improvement of chalk resistance by surface treatment of TiO_2 pigments with potential electron-acceptors, such as Zn (II) and Al (III).[35]

Scheme II is based on a common precursor, the ion-pair complex II, from which are generated the reactive oxidants which initiate chalking. The critical role of this complex is particularly appreciated when one considers that anatase photosorbs oxygen more efficiently than does rutile TiO_2,[25] even though rutile has higher absorptivity in the 300 to 400 nm range.[36] Thus, higher chalking rates with anatase, as well as improvement of chalk resistance by surface treatment with potential electron-acceptors, are explicable within the framework of this scheme. Surface treatment effects on the formation and reactivity of hydroxyl radicals have previously been suggested.[4]

Singlet Oxygen in Chalking

The production of singlet oxygen on irradiation of the pigments raises the question of its role in the chalking process, particularly in view of the correlation of its formation with the inherent chalking tendencies of the pigments. This question relates to the oxidative degradation of the polymeric binder resulting in the physical exposure of pigment at the coating surface, which may be considered as the macroscopic aspect of chalking. In this regard, recent evidence has clearly implicated singlet oxygen as a precursor of hydroperoxides in hydrocarbon polymers[37,38] and fatty acid derivatives.[10] These results are particularly significant since hydroperoxides occupy a key position in autoxidation: increasing in concentration during the induction period, and triggering the accelerated stage, which is self-catalyzing.[39,40] The formation of hydroperoxides is based on the reaction of singlet oxygen with systems containing allylic hydrogens, and occurs concertedly with double-bond migration (Equation 13).[18]

$$RCH_2CH{=}CHR' + {}^1O_2{}^* \rightarrow RCH{=}\underset{\displaystyle OOH}{\underset{|}{C}}HCHR' \qquad (13)$$

In accord with Equation 13, a model system has been studied which demonstrates that singlet oxygen may initiate oxidation at unsaturated polymer ends, terminated by disproportionation.[41] The formation of hydroperoxide has also been reported in the reaction of a saturated hydrocarbon and singlet oxygen.[41] This reaction may involve hydrogen abstraction by the sigma singlet state, which is higher in energy and is predicted to have free-radical reactivity, although its lifetime in solution is exceedingly short (about 10^{-10} sec).[16] However, the hydrocarbons were adsorbed on alumina in these studies, and the lifetime of the sigma state may be extended in a solid matrix due to reduced mobility. Accordingly, sigma singlet oxygen may also be involved in chalking, which occurs in a polymer-pigment matrix.

The production of singlet oxygen provides a new concept to consider with regard to the control of chalking. In addition to the direct degradative effects, the possibility also remains that singlet oxygen may indirectly contribute to chalking. The results, reported herein, of reduced stationary levels of hydrogen peroxide in the presence of triethylamine, an effective singlet oxygen quencher, are suggestive of a possible relationship between singlet oxygen and hydrogen

Dr. S. Peter Pappas, Professor in the Polymers and Coatings Dept. at North Dakota State University, received his A.B. Degree in Chemistry from Dartmouth College in 1958, and his Ph.D. Degree from the University of Wisconsin in 1962. Prior to joining North Dakota State in 1968, he did postdoctoral work at the University of Wisconsin and Brandeis University, and served on the chemistry faculty at Emory University.

Dr. Richard M. Fischer is a Senior Research Chemist in the Research and New Products Group of the 3M Co.'s Adhesives, Coatings and Sealers Div. He received his B.S. Degree in Chemistry and Physics from North Dakota State University, and his Ph.D. Degree in Polymers and Coatings from the same university in 1974.

peroxide formation. Since hydroxyl radicals (HO·), which have been implicated in chalking,[4] are probably formed from hydrogen peroxide, the quenching of singlet oxygen may reduce HO· levels as well. An obvious approach is the incorporation of singlet oxygen quenchers, such as Ni (II) chelates,[42] which have been utilized effectively as stabilizers against photodegradation of polymers.[43]

The generation of singlet oxygen is reasonably attributed to electronic energy transfer from the pigments, via complex II, as shown in Scheme II, Equation 7. While this represents an attractive hypothesis, alternative pathways are conceivable. Two possibilities which we have considered are: (1) formation of oxygen in the excited singlet state in the disproportionation of perhydroxyl radicals (Scheme II, Equation 9); and (2) singlet oxygen production from hydrogen peroxide, by analogy with hypochlorite oxidation.[44] Both of these possibilities may be distinguished from energy transfer by demonstrating hydrogen peroxide quenching with an agent that does not quench the singlet oxygen product. We plan to pursue these and related studies on pigment photo-sensitization.

SUMMARY

Studies on the photo-chemistry of a zinc oxide and three representative TiO_2 pigments are presented. Irradiation of these pigments in the presence of a furan-methanol solution yields 2-methoxy-5-oxo-2, 5-dihydrofuran (1). These findings constitute strong evidence for the intermediacy of singlet oxygen. Further support for singlet oxygen production was obtained by quenching studies. The extent of formation of singlet oxygen product I was found to correlate with known chalking tendencies of the TiO_2 pigments. The formation of hydrogen peroxide on irradiation of the TiO_2 pigments was also investigated and shown to correlate with their chalking tendencies. These results point up basic similarities in the photo-chemical behavior of titanium and zinc oxide pigments. A scheme is presented for the generation of reactive oxidants, which relates the present findings to previous work on chalking. The relative chalking rates of anatase and rutile titanium dioxides, as well as the improvement of chalk resistance by surface treatment, are discussed within the framework of this scheme.

The importance of singlet oxygen as a reactive oxidant, as well as an entity to consider in the control of chalking, is discussed. The production of singlet oxygen is attributed to electronic energy-transfer from excited-state pigments, via electron-transfer and ion-annihilation processes, although alternative hypotheses are also considered.

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