

## Determination of the Photocatalytic Activities of Titanium Dioxides and Other White Pigments

GETHER IRICK, JR., *Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662*

### Synopsis

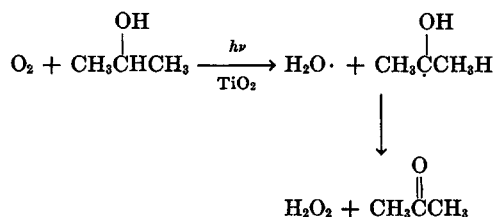
Titanium dioxide, zinc oxide, and other white pigments are widely used in protective coatings and textile applications. An undesirable property of such pigments is their behavior as photo-oxidation catalysts. As a measure of the activities of various pigments, quantum yields were determined for the photo-oxidation of isopropyl alcohol to acetone in a system where the pigment was the only absorbing species. An absolute quantum yield of 0.5 was found for reagent-grade anatase; relative quantum yields were determined for various commercial anatase and rutile titanium dioxides, zinc oxide, barium sulfate, and barium tungstate. A good correlation was found between the photodegradation rates of pigmented polypropylenes, the photodegradation rates of the dyes in pigmented cellulose acetate butyrate, and the activities of the pigments determined by the isopropyl alcohol oxidation method.

### INTRODUCTION

White pigments (e.g., titanium dioxide and zinc oxide) are widely used in protective coatings, textiles, and other applications where a white product and/or a controlled luster are required. Although the pigments may, in certain instances, provide protection from photodegradation to the material in which they are incorporated,<sup>1-4</sup> a more common effect is decreased resistance to photodegradation (or weathering)<sup>5-9</sup>; this is particularly true for thin films and for polymers containing low concentrations or pigments.

The mechanism of action of metal oxides as heterogeneous photo-oxidation catalysts has been the subject of numerous publications.<sup>10-18</sup> It is generally agreed that their activities are related to semiconductor properties. The absorption of light of wavelengths less than 390 nm by titanium dioxide promotes electrons into a conduction band; transfer of these electrons to adsorbed oxygen generates strong oxidizing sites on the titanium dioxide surface and leaves a positive hole in the crystal lattice. An additional photolysis effect is the ejection of oxygen from the crystal lattice, leaving  $Ti^{3+}$  defects; reoxidation to  $Ti^{4+}$  by molecular oxygen occurs readily.<sup>11,12</sup> It appears that the photoactivity of titanium dioxide can usually be attributed to the adsorbed oxygen radical anion ( $O_2^-$ ); however, evidence has been obtained for the formation of metal peroxides,<sup>18</sup> atomic

oxygen,<sup>11</sup> and other radical,<sup>19-21</sup> nonradical, and ionic oxygen species on metal oxide surfaces by both thermal and photolytic paths.<sup>19-21</sup> The activities of the pigment surfaces are highly influenced by the thermal histories of the pigments, impurities, and availability of oxygen and water. Because of the variety of oxidation paths available, complete mechanisms for heterogeneous metal oxide-catalyzed photo-oxidations are not generally available. Although the exact oxidation kinetics are complicated and are dependent on a number of variables, it is qualitatively adequate to consider that the oxidation of a species, such as isopropyl alcohol, occurs by the following overall process:



Unlike zinc oxide,<sup>10</sup> titanium dioxide does not form hydrogen peroxide when photolyzed in the absence of an oxidizable substrate.

The abstraction of hydrogen by ultraviolet-irradiated titanium dioxide/oxygen has been used to initiate crosslinking of polypropylene and polymerization of vinyl monomers.<sup>22</sup> Photodegradation of unpigmented polypropylene has been attributed to light absorption by polymerization catalyst residues (mainly titanium and aluminum oxides)<sup>23,24</sup>; the degradation processes were dependent on the availability of oxygen and the concentration of the metallic residues.

Although schemes, such as the bleaching of dyes, have been proposed as means of determining the photoactivities of titanium dioxides,<sup>25</sup> the published literature indicates that only polymer degradation processes are widely used for such purposes. In view of the large extent to which inorganic anions and trace metals (e.g., those encountered in commercial polymers) can influence pigment activities,<sup>8,11,18,25-27</sup> schemes involving polymeric systems can be misleading. The purpose of this paper is to describe a quantitative method for the determination of pigment activities and to report certain results obtained by the use of this method.

## EXPERIMENTAL

Reagent-grade anatase samples were obtained from J. T. Baker Chemical Co. and Fisher Scientific Co.; unless otherwise noted in this paper, reagent-grade anatase refers to the J. T. Baker product. The commercial zinc oxide and titanium dioxide pigments were obtained from manufacturers (St. Joseph Lead Co.; E. I. du Pont de Nemours and Co., Inc.; Titanium Pigment Corp.; and American Cyanamid Co.). The pigments were selected in a random fashion; no attempt was made to evaluate pigments from all manufacturers or all pigments offered by a single manufacturer.

Barium sulfate, barium tungstate, and isopropyl alcohol were obtained from sources within Eastman Kodak Company; the isopropyl alcohol was redistilled before use and contained no detectable acetone (less than 0.01%). All pigments were allowed to equilibrate in air at 60% relative humidity for 24 hr before use. Serum caps were boiled in isopropyl alcohol and dried at 60°C prior to use. The polypropylene was an unstabilized, crystalline, commercial product which had been extracted to remove amorphous polymer (inherent viscosity in Tetralin at 145°C was 1.75). The cellulose acetate butyrate (CAB) was a commercial molding plastic which contained 7.7% (w/w) dibutyl azelate plasticizer and no weathering stabilizers (inherent viscosity in acetone at 25°C was 1.48).

### Light Sources for Photolyses

All liquid photolyses were performed with a 100-W mercury lamp (George W. Gates and Co., Model GBL-100C). The lamp used in the photolyses by procedure A consisted of a 100-W mercury arc (General Electric Co., Model H100PS44-4) fitted with an ultraviolet-transmitting filter; greater than 99% of its output was the pair of mercury lines in the 366-nm region. The emission of the lamp was constant ( $2.9 \times 10^{-5}$  Einstein/min by ferrioxalate actinometry) during the photolyses. The same lamp was used in the photolyses by procedure B, but the filter was removed. Emission consisted of the mercury lines from 360 to 579 nm; there was very little pressure broadening. Polymer photolyses were run with an unfiltered 1000-W mercury lamp (General Electric Co., Model H1000RDXFL 36-15) whose emission consisted of the mercury lines  $>280$  nm. Air temperature was 32°C, black panel temperature was 50°C, and relative humidity was 49%.

### Photolysis Procedure A (Stirred)

A mixture of pigment (3.0 g) and freshly distilled isopropyl alcohol (300 ml), in a 1000-ml tall-form Pyrex beaker covered with a Pyrex petri dish, was stirred with a magnetic stirrer at a rate sufficient to produce a  $1/4$ - to  $1/2$ -in. deep vortex, during irradiation through the cover, perpendicular to the surface of the suspension at  $34^\circ \pm 2^\circ\text{C}$ . Aliquots of the mixture were centrifuged to remove the pigment, and the acetone content of the supernatant liquid was determined by gas chromatography at 80°C, using a two-section column which consisted of 12 ft of 20% Ucon oil on Chromosorb P and  $1\frac{1}{2}$  ft of 30% Carbowax 400 on Chromosorb P. Relative quantum yields were obtained by dividing the per cent acetone produced with a given pigment by the per cent acetone produced with the reagent-grade anatase titanium dioxide (Table I). No changes were noted in the acetone contents of the photolyzed isopropyl alcohol/pigment/acetone systems after 24 hr in the dark. No hydrogen peroxide was detected after the photolyses of titanium dioxides in aqueous media, but peroxides were detected after the photolyses in isopropyl alcohol.

TABLE I  
Relative Quantum Yields for Acetone Formation After Photolysis  
of Pigments in Isopropyl Alcohol (Procedure A)

Pigment	$\Phi_{rel}$
Titanium dioxide, reagent-grade anatase <sup>a</sup>	1.0
Titanium dioxide, reagent-grade anatase <sup>b</sup>	1.0
Titanium dioxide, Titanox AMP <sup>c</sup> (anatase)	0.4
Zinc oxide, St. Joe 922 <sup>d</sup>	0.4
Titanium dioxide, Ti-Pure 33 <sup>e</sup> (anatase)	0.4
Titanium dioxide, Ti-Pure R-100 <sup>e</sup> (rutile)	0.3
Titanium dioxide, Ti-Pure R-110 <sup>e</sup> (rutile)	0.3
Titanium dioxide, Ti-Pure R-990 <sup>e</sup> (rutile)	0.2
Titanium dioxide, Unitane OR-450 <sup>f</sup> (rutile)	0.2
Titanium dioxide, Ti-Pure R-992 <sup>e</sup> (rutile)	0.2
Barium sulfate, commercial grade	0.09
Titanium dioxide, Titanox RANC-Improved <sup>e</sup> (rutile)	0.09
Titanium dioxide, Ti-Pure R-610 <sup>e</sup> (rutile)	0.03
Barium tungstate	<0.03

<sup>a</sup> J. T. Baker Chemical Co.

<sup>b</sup> Fisher Scientific Co.

<sup>c</sup> Titanium Pigment Corp.

<sup>d</sup> St. Joseph Lead Co.

<sup>e</sup> E. I. du Pont de Nemours and Co., Inc.

<sup>f</sup> American Cyanamid Co.

### Photolysis Procedure B (Rotated Radially)

A mixture of pigment (2.0 g) and freshly distilled isopropyl alcohol (8.0 ml) in a 16-mm o.d.  $\times$  150-mm Pyrex test tube, having a serum-cap stopper wired in place, was purged with oxygen and placed under 4 to 7 psi oxygen pressure. The tube was then placed radially on a ferris-wheel rotation assembly (Cole-Parmer Multi-Purpose Rotator, Model 7621-2) and rotated at 6 rpm during irradiation, at 28°C, from a direction perpendicular to the plane of rotation. Rotation is this manner inverted the tube once with each revolution and provided a freshly washed surface for each photolysis interval. The samples were centrifuged and the supernatant liquid was analyzed for acetone as in procedure A. Quantum yields were calculated relative to reagent-grade anatase. Because of the limited oxygen contents of the tubes, the conversions to acetone were kept below 1%. The formation of peroxides, presumably hydrogen peroxide, during the photolyses was demonstrated by the potassium iodide/acetone test. No attempt was made to determine the peroxides quantitatively.

### Determination of Absolute Quantum Yield for Acetone Formation by Reagent-Grade Anatase Titanium Dioxide

A mixture of 3.0 g reagent-grade anatase (0.03% water-soluble salts, 0.001% As, 0.002% Fe, 0.006% Pb, and 0.002% Zn) and 300 ml isopropyl alcohol was stirred in a one-necked, 1000-ml, round-bottomed Pyrex flask

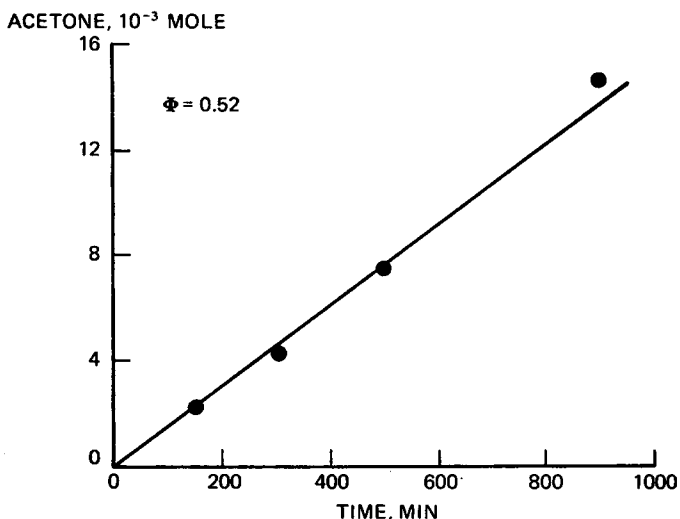


Fig. 1. Rate of formation of acetone during 366-nm photolysis of reagent-grade anatase titanium dioxide.

(silvered on the exterior surface) during irradiation with the 366-nm mercury arc are described previously. Aliquots were removed periodically for acetone analyses. The rate of acetone formation was obtained from a plot of acetone formed (mole) versus time (min) (Fig. 1). The absolute quantum yield was calculated as follows:

$$\Phi = \frac{\text{mole acetone/min}}{\text{Einstein/min}} = \frac{1.5 \times 10^{-5}}{2.9 \times 10^{-5}} = 0.52.$$

#### Determination of the Effects of Oxygen and Water on Pigment Activity

Samples of reagent-grade anatase were dried at  $200^{\circ}\text{C}$  ( $10^{-4}$  mm). Isopropyl alcohol was added, and one sample was degassed by three freeze-pump-thaw cycles. The degassed sample was sealed under vacuum and photolyzed by procedure B; the dried, but not degassed, sample was photolyzed in air by a similar procedure. Relative quantum yields for acetone formation are shown in Table II.

TABLE II  
Effect of Oxygen and Water on Quantum Yields for Acetone Formation  
with Reagent-Grade Anatase (Procedure B)

Sample treatment	Atmosphere during photolysis	$\Phi_{\text{rel}}$
None	air	1.0
Dried at $200^{\circ}\text{C}$ ( $10^{-4}$ mm)	none	0.07
Dried at $200^{\circ}\text{C}$ ( $10^{-4}$ mm)	air	1.5

### Dark Reactions

Samples of reagent-grade anatase and a commercial zinc oxide (St. Joseph Lead Co., St. Joe 922) were prepared for photolysis by procedure B. After the samples were rotated in the dark for 120 hr, no acetone was detected. Three additional samples of reagent-grade anatase were photolyzed for 16 hr by procedure B. A sample which was centrifuged and analyzed immediately had an acetone content of 0.46%; one which was centrifuged and held 48 hr prior to analysis had an acetone content of 0.46%; and a sample which was held 48 hr prior to centrifugation had an acetone content of 0.48%.

### Preparation of Polymeric Samples

Polypropylene powder and additives were mixed dry for 6 hr; then they were extruded through a  $1/16$ -in. die and pelletized. Films (10 mil) were then pressed from the pellets. Cellulose acetate butyrate powder, pigment, and an azo dye (0.1% w/w, C. I. Disperse Orange 25) were ground together in a mortar, mixed dry for 6 hr, and pressed into 10-mil films.

## RESULTS AND DISCUSSION

### Photolysis of Isopropyl Alcohol Suspensions

Photolysis of a suspension of reagent-grade anatase in isopropyl alcohol in air with 366-nm light (a wavelength near the 340-nm absorption maximum of the pigment) resulted in the oxidation of the isopropyl alcohol to acetone at a rate linear with time (Fig. 1); the absolute quantum yield of 0.52 for the process is similar to values reported for the formation of hydrogen peroxide after photolysis of aqueous suspensions of zinc oxide (0.25 to 0.5). Quantum yields for all of the other pigment photolyses in this paper are relative to this sample.

Photolysis of a series of pigments by procedure A (stirred) resulted in relative quantum yields of <0.03 to 1.0 for acetone formation (Table 1). As was expected, the anatase titanium dioxides (reagent grades, Ti-Pure 33 and Titanox AMP) and zinc oxides were more reactive than the rutile titanium dioxides.

The use of procedure B permitted a large number of samples to be photolyzed simultaneously. Rotation of the samples with inversion, under oxygen, provided a freshly coated glass surface for photolysis and eliminated the possibility that oxygen diffusion would be a limiting variable. One possible drawback to this method is the fact that the light must pass through the Pyrex glass in contact with the solvent/pigment mixture; even fused quartz is not totally inert to visible and near-ultraviolet light. To decrease the photolysis times, the fully mercury arc output above 350 nm was used; thus, the results are due to a combination of ultraviolet and visible light photochemistry of the pigments. This procedure was used for the remainder of the experiments discussed here.

### Effects of Oxygen, Water, and Other Additives

Samples of zinc oxide and rutile and anatase titanium dioxides which were dried at 150°C (100 mm) had activities nearly identical to those of the samples which had been equilibrated in air at 60% relative humidity. Drying reagent-grade anatase under more rigorous conditions [200°C (10<sup>-4</sup> mm)] significantly increased its photocatalytic activity (Table II). It is interesting that a sample which was dried and photolyzed in thoroughly degassed isopropyl alcohol resulted in significant acetone formation. This result is consistent with the observation of gas-phase oxidation of isopropyl alcohol by illuminated titanium dioxide in the absence of oxygen<sup>12</sup> and may be due to tenaciously adsorbed oxygen or to the removal of oxygen from the crystal lattice of the titanium dioxide. The sample which was photolyzed under degassed conditions developed the blue-gray coloration characteristic of Ti<sup>3+</sup> defects in titanium dioxide; oxidation to the colorless Ti<sup>4+</sup> state occurred over a period of about 4 hr upon admission of air to the sample.

Both water and acetic acid, when present in the isopropyl alcohol, decreased the activity of reagent-grade anatase; hexamethylphosphoric triamide (HPT) did not have a detectable effect (Table III). It is probable that the protic compounds (water and acetic acid) are more strongly adsorbed on the pigment surface than is HPT, and thus they compete with isopropyl alcohol for the reactive sites.

TABLE III  
Effect of Additives on Quantum Yields for Acetone Formation (Procedure B)

Pigment/additive <sup>a</sup>	$\Phi_{rel}$
Reagent-grade anatase	1.0
Reagent-grade anatase/water	0.8
Reagent-grade anatase/acetic acid	0.4
Reagent-grade anatase/hexamethylphosphoric triamide	1.0
Reagent-grade anatase/30% hydrogen peroxide <sup>b</sup>	2.8

<sup>a</sup> 1.0 ml Additive/8 ml isopropyl alcohol.

<sup>b</sup> Pressure increased during the photolysis and was relieved intermittently by insertion of a hypodermic needle into the serum cap. A quantity of acetone sufficient to account for 0.8 of the observed 2.8 quantum yield was formed in an identical sample held in the dark.

Hydrogen peroxide nearly tripled the quantum yield for acetone formation with reagent-grade anatase (Table III). Since 0.8 of the observed 2.8 quantum yield could be attributed to a dark reaction, it is apparent that titanium dioxide decomposes hydrogen peroxide by a radical mechanism at an appreciable rate.

### Photolysis of Polymeric Samples

Pigmented polypropylene samples along with pigmented cellulose acetate butyrate samples containing an orange azo dye were photolyzed to deter-

TABLE IV  
Comparison of Pigment Photoactivities in Isopropyl Alcohol and Polymeric Media

Pigment	$\Phi_{rel}$ in isopropyl alcohol	Time to 10% dye loss in CAB, hr <sup>a</sup>	I.V. loss of Polypropylene after 30-hr exposure, %
Titanium dioxide, reagent-grade anatase	1.0	10	44
Titanium dioxide, Ti-Pure 33 (anatase)	0.4	32	36
Titanium dioxide, Ti-Pure R-100 (rutile)	0.3	92	27
Titanium dioxide, Unitane OR-450 (rutile)	0.2	80	20
Titanium dioxide, Titanox RANC (rutile)	0.09	100	16
Titanium dioxide, Ti-Pure R-610 (rutile)	0.03	130	14

<sup>a</sup> Determined by reflectance measurements at 470 nm.

mine the reliability of the isopropyl alcohol test method for predicting pigment behavior in polymeric media. A good correlation was found between the activities of the pigments in these three systems (Table IV).

## CONCLUSIONS

The pigment-sensitized photo-oxidation of isopropyl alcohol can be used to determine the photochemical activities of titanium dioxide and zinc oxide pigments and to predict the behavior of these pigments in polymeric media. Because of possible effects of polymer structure, additives, and impurities in the polymers, care should be taken in extrapolation of the activity data.

The author thanks C. Dingus and C. L. Harrison for the numerous gas-chromatographic analyses performed during this project.

## References

1. R. D. Deanin, S. A. Orroth, R. W. Eliassen, and T. N. Greer, *Polym. Eng. Sci.*, **10** (4), 228 (1970).
2. W. L. Dills and T. B. Reeve, *Plast. Technol.*, **16** (6), 50 (1970).
3. E. T. Ruehl (to E. I. du Pont de Nemours and Co.), U.S. Pat. 3,175,990 (1965); H. C. Arvidson, Jr., and N. Blake (to E. I. du Pont de Nemours and Co.), U.S. Pat. 2,999,839 (1961).
4. D. S. Carr, B. Baum, A. Margosiak, and A. Llompарт, *Mod. Plast.*, **47** (5), 114 (1970).
5. F. J. Golemba and J. E. Guillet, *J. Paint. Technol.*, **41**, 315 (1969).
6. G. S. Egerton and K. M. Shah, *Nature*, **202**, 81 (1964).
7. A. Agster, *Melliand Textilber.*, **35**, 1209 (1954).
8. H. A. Taylor, W. C. Tincher, and W. F. Hamner, *J. Appl. Polym. Sci.*, **14**, 141 (1970).
9. G. S. Egerton and K. M. Shah, *Text. Res. J.*, **38**, 130 (1968).
10. M. C. Markham and J. Laidler, *J. Phys. Chem.*, **57**, 363 (1953).
11. W. A. Weyl and T. Förland, *Ind. Eng. Chem.*, **42**, 257 (1950).
12. V. N. Filimonov, *Dokl. Akad. Nauk SSSR*, **154** (4), 922 (1964).
13. H. D. Müller and F. Steinbach, *Nature*, **225**, 728 (1970).
14. A. Bernas, *J. Phys. Chem.*, **68**, 2047 (1964).



15. J. C. Kuriacose and M. C. Markham, *J. Phys. Chem.*, **65**, 2232 (1961).
16. M. Yamamoto and G. Oster, *J. Polym. Sci. A-1*, **4**, 1683 (1966).
17. G. Oster and M. Yamamoto, *J. Phys. Chem.*, **70**, 3033 (1966).
18. H. Knoll and U. Kühnhold, *Angew. Chem., Int. Ed.*, **6**, 978 (1967).
19. P. F. Cornaz, J. H. C. van Hooff, F. J. Pluijm, and G. C. A. Schuit, *Discuss. Faraday Soc.*, **41**, 290 (1966); and discussions thereof by D. Iyengar, M. Codell, J. Karra, and J. Turkevich, *ibid.*, pp. 323-327.
20. A. J. Tench and T. Lawson, *Chem. Phys. Lett.*, **7**, 459 (1970).
21. A. J. Tench and T. Lawson, *Chem. Phys. Lett.*, **8**, 177 (1971).
22. J. F. Rabek, *Photochem. Photobiol.*, **7**, 5 (1968).
23. C. Kujirai, S. Hashiya, H. Furuno, and N. Terada, *J. Polym. Sci. A-1*, **6**, 589 (1968).
24. C. Kujirai, S. Hashiya, K. Shibuya, and K. Nishio, *Kobunshi Kagaku*, **25**, 193 (1968); *C. A.*, **69**, 59768j (1968).
25. W. Costain, H. J. Palmer, and T. R. White (to Imperial Chemicals Ltd.), U.S. Pat. 3,352,821 (1967).
26. W. M. Corbett, J. F. L. Roberts, and J. M. Yates (to Imperial Chemicals Ltd.), U.S. Pat. 3,547,882 (1970).
27. A. T. Betts and N. Uri (to National Research and Development Corp.), Brit. Pat. 1,212,181 (1970); *Plast. Abstr.*, **12** (46), 6988 (1970).

Received September 22, 1971

Revised April 17, 1972