

KEY WORDS: SUNSCREEN,
PHOTOCATALYTIC ACTIVITY,
TITANIUM DIOXIDE, ZINC OXIDE

• The authors present a review of studies conducted on titanium dioxide and zinc oxide for their effect on photoreactivity in sunscreens. Organic and inorganic surface treatments are discussed and compared.

• Les auteurs présentent une revue des études sur les dioxydes de titane et leur propriété de type photo réactivité dans les produits solaires. Les traitements de surface organiques et minéraux sont discutés comparativement.

• Die Autoren bieten einen Überblick von Studien, die die Wirkung von Titandioxid und Zinkoxid an der Photoreaktivierungsfähigkeit von Lichtschutzsubstanzen treffen. Sie diskutieren und vergleichen sowohl organische als auch anorganische Mantelstoffe.

• Los autores presentan una revista de los estudios hechos con dióxidos de titanio y sus efectos sobre su fotoreactividad en filtros solares. Se comparan los tratamientos orgánicos e inorgánicos de superficie.



Photocatalytic Activity of Titanium Dioxide and Zinc Oxide

The effect of organic and inorganic surface treatments

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Increased recreational sun exposure, particularly among the younger population, and the rise in UV radiation reaching the biosphere related to ozone layer depletion have prompted concern about radiation damage to human health.⁵ Thanks to state, federal and international regulations that limit the use of chemicals that cause ozone layer depletion, the thinning of the ozone layer is presumed to be slightly decelerated. However, ozone layer depletion is expected to continue for decades due to the existing ozone depleting chemicals, such as chloro-fluoro-carbon-11 (CFC₁₁), CFC₁₂ and CFC₁₃, that are known to remain in the atmosphere for an average of 74 years, 111 years, and 90 years, respectively.²

The use of sunscreen is becoming increasingly more important because of the continuous increase in harmful UV rays filtering through the atmosphere. However, the safety of these widely used products has been questioned. There have been recent concerns about free radicals generation and degradation of other components of the formulation through photocatalytic activity of inorganic ingredients, such as titanium dioxide (TiO₂) and zinc oxide (ZnO).^{1,3,9}

The photocatalytic properties of inorganic sunscreens, TiO₂ and ZnO, are well known. It is for this reason that many manu-

facturers of TiO₂ apply inorganic coatings, such as aluminum oxide (Al₂O₃) and zirconium dioxide (ZrO₂), to lower the photoreactivity of this material, particularly to the ultrafine grades that are more reactive due to their larger surface area.⁴ Perhaps less widely known is that the application of certain organic surface treatments to TiO₂ or ZnO, either with or without inorganic coatings, results in a significant reduction in photocatalytic activity of these materials. It is the purpose of this study to lend further credence that organic surface treatments minimize, if not completely eliminate, the photocatalytic activity of TiO₂ and ZnO.

Materials and Methods

Chemicals: There were 10 samples provided for the study (Table 1-1). Most of the TiO₂ and ZnO samples were obtained from commercial sources. Samples C, D and E contained inorganic and/or organic coatings of Al₂O₃, polyol, or a combination of Al₂O₃, ZrO₂ and methicone, respectively, to increase photostability. Most of the organic surface treatment was completed at US Cosmetics Corp.^a or Miyoshi Kasei Inc.^b The levels and types of surface treatments applied to sample B were 3% polyethylene, 1.5% glyceryl rosi-

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Table 1-1. Physical descriptions of samples. Average particle sizes were obtained from manufacturer specifications

Sample	Crystal form	Grade	Average particle size	Inorg. treatment	Org. treatment
A	Anatase TiO 70% Rutile TiO ₂ 30%	Ultrafine	0.021 μm	None	None
B	Anatase TiO ₂	Pigment	0.41 μm	None	None
C	Rutile TiO ₂	Ultrafine	0.03-0.05 μm	Al ₂ O ₃	None
D	Rutile TiO ₂	Pigment	0.18-0.8 μm	None	Polyol (0.25%)
E	Rutile TiO ₂ 57% ZnO 38%	Ultrafine	(0.01-0.02)x(0.05-0.1) μm	Al ₂ O ₃ , ZrO ₂	Methicone (5%)
F	ZnO	Pigment	0.25 μm	None	None
G	ZnO	Ultrafine	0.015-0.035 μm	None	None
H	ZnO	Ultrafine	0.02 μm	None	None
I	ZnO	Ultrafine	<0.2 μm	None	None
J	ZnO	Pigment	0.78 μm	None	None

nate/octyldodecyl myristate and 1.5% dimethicone, and 2% methicone. On sample C, 1.5% lecithin treatment and 2% dimethicone treatment were applied. Samples G and H were surface treated with 3% and 6% methicone and 6% methicone, respectively.

Experimental protocol: The ability of gaseous acetaldehyde, CH₃CHO, to be oxidized in the presence of photocatalysts such as TiO₂ and ZnO under UV illumination makes it a good indicator to monitor photocatalytic activity of these materials as supplied by the manufacturer, as well as to measure the effect of application of surface treatments in reducing such photocatalytic activity.

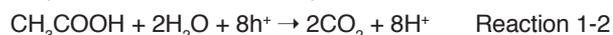
The photocatalytic activity of TiO₂ and ZnO was evaluated in terms of the photodecomposition of gaseous acetal-

dehyde. In an uncovered petri dish, 4 g of dry sample was distributed evenly to minimize the variation of the surface area exposed to UV rays. The petri dish was placed in a 9.2 l glass reaction vessel inside a light-proof cabinet (Figure 1-1). A stirring fan, mounted on the bottom of the reaction vessel, ensured the uniform distribution of gaseous acetaldehyde.

Saturated gaseous acetaldehyde was introduced into the sealed reaction vessel so that the concentration of acetaldehyde in the vessel would be approximately 50 ppm. Temperature within the reaction vessel was at ambient conditions. Concentration of gaseous acetaldehyde was periodically monitored using a gas chromatograph^e equipped with a flame ionization detector and a wide-bore capillary column.^d

After the gaseous and adsorbed acetaldehyde reached equilibrium, indicated by constant gaseous acetaldehyde concentration, irradiation began. Five 10-watt black fluorescent lights^e with peak emissivity at 360 nm served as the UV light source. This light source was placed outside the reaction vessel and parallel to the petri dish so the light intensity at the uncovered petri dish surface was 1.83 mW/cm². The UV light intensity was measured by a radiometer^f equipped with a sensor^g with peak sensitivity at 360 nm.

The photodegradation of gaseous acetaldehyde with a photocatalyst such as TiO₂ and ZnO under UV illumination proceeds as oxidation of acetaldehyde molecules to acetic acid (Reaction 1-1), and subsequent oxidation of acetic acid to carbon dioxide (Reaction 1-2).^{5,6}



The hydroxyl radicals generated by holes are presumed to play a major role in this reaction.⁷ It has also been suggested that other reactive species such as superoxide radicals, adsorbed oxygen and hydrogen peroxide take part in the photodegradation of gaseous acetaldehyde.

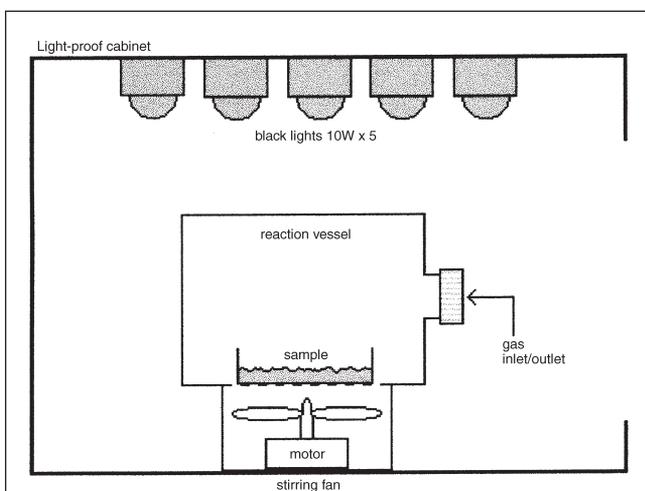


Figure 1-1. Experimental apparatus for photocatalytic activity measurement

Four grams of sample in a petri dish was placed in a 9.2 liter glass reaction vessel. The sealed vessel was filled with gaseous acetaldehyde. The stirring fan was turned on to ensure uniformity of gaseous acetaldehyde. Five black lights were utilized to irradiate the sample and the change in concentration of the gaseous acetaldehyde as a function of irradiation time was measured. A micro sample-injector syringe was used to collect 2 ml of gas from the reaction vessel and to inject into a gas chromatograph.

^eModel GC14-B, Shimadzu, Japan

^dType GS-Q, J&W Scientific, CA

^eModel BL10BL-B, Matsushita Electric, Japan

^fModel UVR-1, Topcon Corp., Japan

^gModel UVR-36, Topcon Corp., Japan

Table 1-2: The first-order reaction rate constants ($\times 10^{-4}$ / sec) of acetaldehyde photodecomposition*

Sample	Untreated	Al ₂ O ₃	Polyol	1.5%LT	3%PT	2%ST	3%ST	6%ST	2%SAT	3%STPM	Inorg & 5% ST
A	3.70										
B	4.76				1.15	<0.01				<0.01	
C	NA	0.13		0.033					<0.01		
D	NA		0.16								
E	NA										<0.01
F	2.56										
G	1.83						<0.01	<0.01			
H	1.94							<0.01			
I	1.85										
J	1.25										

*The percentage indicates the level of treatment. Polyol is a polyhydric alcohol. LT denotes lecithin surface treatment. PT indicates polyethylene surface treatment. ST represents methicone surface treatment. SAT denotes dimethicone surface treatment. The 3 % STPM represents a combination of 1.5 % glyceryl rosinat/octyldodecyl myristate and 1.5 % dimethicone treatments. The inorganic coating agents on sample E are Al₂O₃ and ZrO₂. The samples C, D, and E were supplied with inorganic and/or organic coatings; untreated versions were not available.

The reaction progression was monitored by measuring gaseous acetaldehyde concentration at frequent intervals and subsequently determining the first-order reaction rate constant of gaseous acetaldehyde photodecomposition. A more detailed discussion of the reaction kinetics pertaining to this photodecomposition may be found in the work of Sopyan et al.⁷ This reaction rate constant serves as an indicator of the photocatalytic activity of TiO₂ and ZnO.

Results

Table 1-2 shows the first-order reaction rate constants of gaseous acetaldehyde photodecomposition, calculated from the plot of the acetaldehyde concentration change as a function of irradiation time by means of a linear least-square fit.

For TiO₂ samples B and C and for ZnO samples G and H, these constants show the ability of silicone surface treatment with either methicone, dimethicone or dimethicone in combination with glyceryl rosinat and octyldodecyl myristate to reduce the photocatalytic activity dramatically to almost negligible levels in comparison to the materials with inorganic coating alone or without any organic treatment or inorganic coating.

Sample E, the combined product of ultrafine TiO₂ and ZnO, was also found to have an extremely low reaction rate. However, because this product was not available without the organic surface treatment or inorganic coating, it was not possible to assess the relative contributions of the inorganic coating with Al₂O₃ and ZrO₂ and the organic treatment with methicone in reducing photocatalytic activity.

It is apparent from the data in Table 1-2 that, of the treatments and coatings tested in this study, the silicone treatments most effectively minimize TiO₂ and ZnO photocatalytic activity.

A 3% polyethylene treatment on TiO₂ B resulted in the first-order reaction rate constant of gaseous acetaldehyde photodecomposition of approximately one-fourth of that observed for the untreated TiO₂ B. Similarly, the lecithin treatment at 1.5% reduced the photocatalytic activity of TiO₂ C to about one-fourth of the original value obtained for this material as supplied with Al₂O₃ as an inorganic coating.

Conclusion

Many titanium dioxides, especially the ultrafine grades, are supplied with inorganic coatings, such as Al₂O₃ and/or ZrO₂, to lower the photoreactivity, while zinc oxides do not require inorganic coatings to ensure good light stability. Although such inorganic coatings help reduce the photoactivity to a certain extent, the addition of organic surface treatments, especially silicone-based treatments, serves to reduce the photocatalytic activity of titanium dioxides and zinc oxides to almost negligible levels. Therefore, the importance of organic surface treatments in minimizing the photocatalytic activity and lessening the concern about the use of these pigments under sunlight cannot be overemphasized.

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