Photocatalytic Activity of Inorganic Sunscreens

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ABSTRACT

Some inorganic pigments are used as ingredients for sunscreens as they can absorb, reflect or scatter UV radiation. Titanium dioxide and zinc oxide, which are used for this purpose, are semiconductor oxides and show photocatalytic activity. As a consequence, they can promote transformation of organic molecules upon absorption of radiation. This work studies the activity of some of these pigments, provided by cosmetic producers, towards phenol, chosen as a model aromatic molecule. An attempt is made to explain the different activity of the various pigments, coated or uncoated, towards phenol.

INTRODUCTION

The harmful effects of sunlight, and in particular of its ultraviolet radiation component, on human skin are well known. Light-induced formation in the skin of activated singlet oxygen ($^1O_2$) and oxygen-containing radicals (superoxide radical anion, $O_2^{\bullet-}$, and hydroxyl radical, $^{\bullet}OH$) is thought to be the primary cause of actinic skin damage. This damage is due to the alteration of cell membrane lipids and to the formation of peroxides promoting dermal inflammation (1).

Topically applied sunscreens absorb, reflect or scatter UV radiation and reduce the amount reaching the dermal layers beneath the *stratum corneum*. An ideal sunscreen absorbs UV energy, which is dissipated with conversion to lower energy radiation, relatively less dangerous. However, several undesirable photo-oxidative pathways for energy dissipation are also possible. The magnitude of this undesirable reactivity is largely dependent on the intrinsic properties of the individual sunscreen chromophore in its photoexcited states (1).

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Some sunscreens can photo-degrade after UVA/UVB irradiation. Moreover, they can act as photosensitizers and can initiate harmful reactions for the skin, especially photo-induced mutagenicity. Acute UV exposure of the skin promotes an immediate inflammatory response, the visible effect of which is sunburn erythema. On the contrary, repeated and chronic UV exposure can lead to the photo-aging of the skin (actinic elastosis) and to initiation of skin cancer. Moreover, the high activity of uncoated physical sunscreens, such as TiO_2 and ZnO, on the photo-oxidation of uric acid (1) and the photo-catalytic activity of coated TiO_2 under irradiation (2) have been demonstrated.

These inorganic sunscreens are largely used for the preparation of high-SPF solar emulsions. In the present work the photo-catalytic activity of some microfine inorganic pigments, coated or uncoated, was evaluated.

EXPERIMENTAL

The pigments used as sunscreens, listed in Table 1, were provided by cosmetic producers (3). Degussa P25 was also used as reference material. The particle diameters were measured with a Coulter® Model N4 MD laser-based sub-micron particle analyser. To measure the diameters, 0.050 g/l stock dispersions were prepared by 30-minute sonication. The sonication time was chosen to make sure that the pigments were homogeneously dispersed in the flasks. Aliquots of the stock dispersions were taken and diluted to 0.010 and 0.005 g/l. The diluted dispersions were then sonicated for 5 minutes and immediately analysed. The values of the diameters thus obtained, averaged over the two series of analyses (0.010 and 0.005 g/l), are reported in Table 1. In two cases (ZnO no. 6 and TiO_2 no. 8) the particles have a bimodal distribution, the two groups having comparable weight.

Laser analyses were also carried out on samples left still for 10 min. after sonication. In this case, a certain degree of aggregation of the particles with time could be observed, together with a decrease in the reproducibility of the measurements. Interestingly, it was not possible to homogeneously disperse the pigments TiO_2 no. 1 and no. 4, for which no value of the diameter is given in Table 1. These results have some consequences on the interpretation of the photocatalytic activity of such pigments.

Phenol has been chosen as a model for an oxidizable substrate in order to evaluate the photocatalytic activity of the pigments. The TiO_2 Degussa P25 was used as a reference for phenol degradation, because its photocatalytic behaviour is well known (4,5). In a similar way, as many cosmetic pigments are based on the rutile form of titanium dioxide, while the Degussa P25 is mainly anatase, TiO_2 no. 8 has been used as a reference for rutile.

The pigments were dispersed in water (0.50 g/l) by five-minute sonication and irradiated in the presence of phenol in closed Pyrex glass cells (diameter 4.0 cm, height 2.5 cm). The irradiation was carried out in a

Table 1. *Pigments Used for the Experiments*

Name	Firm	Features	Diameter (nm)
TiO_2 (P25)	Degussa	Uncoated TiO_2 80% Anatase 20% Rutile	300
Micro Titanium dioxide MT-100TV (1)	Tayca Corporation	TiO_2 Rutile, coated with Alumina and Stearic Acid	–
Oxide de titane standard (2)	Wackherr	TiO_2 Anatase, uncoated	290
UV Titan M262 (3)	Variati & Co	TiO_2 Rutile, coated with Alumina and Dimethicone	200
Kemira UV Titan M160 (4)	Variati & Co	TiO_2 Rutile, coated with Alumina and Stearic Acid	–
Suns mart inc., Z-cote (5)	L.Crosetto & Co	ZnO, coated with Dimethicone	370
ZnO (6)	Haarmann & Reimer GmH	ZnO, uncoated, neutral	210 2500
UV Sperse (7)	Biogenikko	TiO_2 Rutile, coated with 1,3-Butanediol, Benzoic Acid, Alumina	285
Titanium(IV) oxide (8)	Aldrich Chemical Company	TiO_2 Rutile, uncoated	285 1400

Solarbox® (CO.FO.ME.GRA., Milano, Italia) equipped with a 1500 Watt Xenon lamp, a 340 nm cut-off filter and Kartell TKS® magnetic stirrers. Irradiation time has been chosen on the basis of the pigment photocatalytic activity. Irradiation time scales varied from 2 to 18 hours.
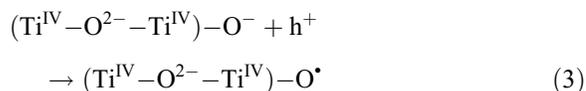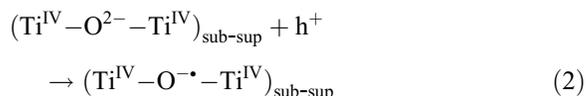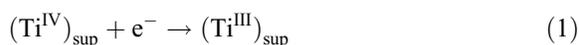
The intensity of incident radiation in the solution, actinometrically measured using $K_3Fe(C_2O_4)_3$ (6), was 0.03 W/cm^2 for wavelengths below 510 nm, where the actinometer absorbs. The value has been calculated taking into account the spectral distributions of lamp emission, actinometer absorption and quantum yield for the formation of Fe(II).

The decrease with time of the phenol concentration and the formation of two degradation intermediates, catechol and hydroquinone, has been followed by HPLC analysis. A Merck-Hitachi® cromatograph was used, equipped with a reverse-phase column RP-C18 LiChroCART® (Merck, 12.5×0.4 cm), packed with LiChrospher® 100 RP-18 (particle diameter 5 μm), eluting with a mixture of acetonitrile/NaH$_2$PO$_4$ 0.02 M 30/70. The compounds were detected at 210 nm. In these conditions, retention times are: phenol 3.75 min, catechol 2.15 min, hydroquinone 1.60 min.

Concentration values have been corrected for the adsorption of these compounds on the pigment. To evaluate the adsorption, solutions of catechol and of hydroquinone were prepared, at equal concentration in the presence and in the absence of the pigments. The concentration values were of the same order of magnitude as the concentrations of catechol and hydroquinone formed upon phenol degradation. Pigment suspensions were filtered and both homogeneous solutions and filtered suspensions were analysed. The difference in concentration between a homogeneous solution and a filtered suspension is due to the loss, during filtration, of the organic compound that is adsorbed on the pigment. As a consequence, from these data it is possible to correct the concentration values of catechol and hydroquinone found in filtered phenol samples after irradiation.

RESULTS AND DISCUSSION

The absorption of radiation by semiconductor oxides leads to the formation of e^-/h^+ couples (electron–hole pairs) (7). These couples can undergo thermal recombination or migrate to the surface, where they can be trapped by surface or sub-surface species, the thermal recombination of which is very slow:

$$(Ti^{IV})_{sup} + e^- \rightarrow (Ti^{III})_{sup} \qquad (1)$$

$$(Ti^{IV}-O^{2-}-Ti^{IV})_{sub\text{-}sup} + h^+$$
$$\rightarrow (Ti^{IV}-O^{-\bullet}-Ti^{IV})_{sub\text{-}sup} \qquad (2)$$

$$(Ti^{IV}-O^{2-}-Ti^{IV})-O^- + h^+$$
$$\rightarrow (Ti^{IV}-O^{2-}-Ti^{IV})-O^\bullet \qquad (3)$$

These species can interact with dissolved molecules in solution. For example, degradation of phenol by the groups $Ti^{IV}-O^{2-}-Ti^{IV}-O^\bullet$ (commonly defined $^\bullet OH_{ads}$) mainly leads to formation of catechol and hydroquinone. On the contrary, the contribution given by the groups $Ti^{IV\bullet}-O^{-\bullet}-Ti^{IV}$ (usually indicated as h$^+$) leads to the formation of the radical cation PhOH$^{+\bullet}$, which may then react with $O_2^{\bullet-}$, producing other degradation intermediates (8). Consequently, the determination of the percentage of phenol that degrades giving catechol and hydroquinone may allow estimating the relative role of h$^+$ and $^\bullet OH_{ads}$ on the photocatalytic process.

Figure 1 shows, as an example, the degradation of phenol and the formation of catechol and hydroquinone in the presence of 0.50 g/l TiO$_2$ n°2 (A) and 0.50 g/l TiO$_2$ n°3 (B). The different irradiation time scales reflect the different photocatalytic activities of the pigments.

Figure 2A shows phenol degradation and catechol and hydroquinone formation in the presence of 0.50 g/l TiO$_2$ n°1. Figure 2B shows the adsorption of catechol on TiO$_2$ n°1. From this curve it was possible to correct the concentration of catechol found in the analyses of irradiated phenol samples, and Figure 2A reports the concentration of catechol, corrected for adsorption. Negligible adsorption of hydroquinone could be detected on TiO$_2$ n°1.

In Figure 3 the pseudo-first order degradation constants of 1.1×10^{-3} M phenol in the presence of the different pigments (0.50 g/l) are shown. We can observe that the uncoated anatase forms of TiO$_2$ (P25 and n°2), and the two zinc oxides (n°5, coated, and n°6, uncoated), are the most active pigments.

Rutile forms of TiO$_2$ have a lower activity. This is not surprising, since the lower activity of TiO$_2^-$ rutile with respect to anatase has long been observed (9).

In particular, the activities of the uncoated reference rutile (n°8) and of those treated with alumina and stearic acid (n°1 and n°4) are similar. As already mentioned in the experimental part, the pigments TiO$_2$ n°1 and n°4 are very difficult to disperse. This means that the reactivity of these pigments towards phenol is depleted by the system being not finely dispersed, and that the photocatalytic activity of TiO$_2$ n°1 and n°4 has probably been underestimated.
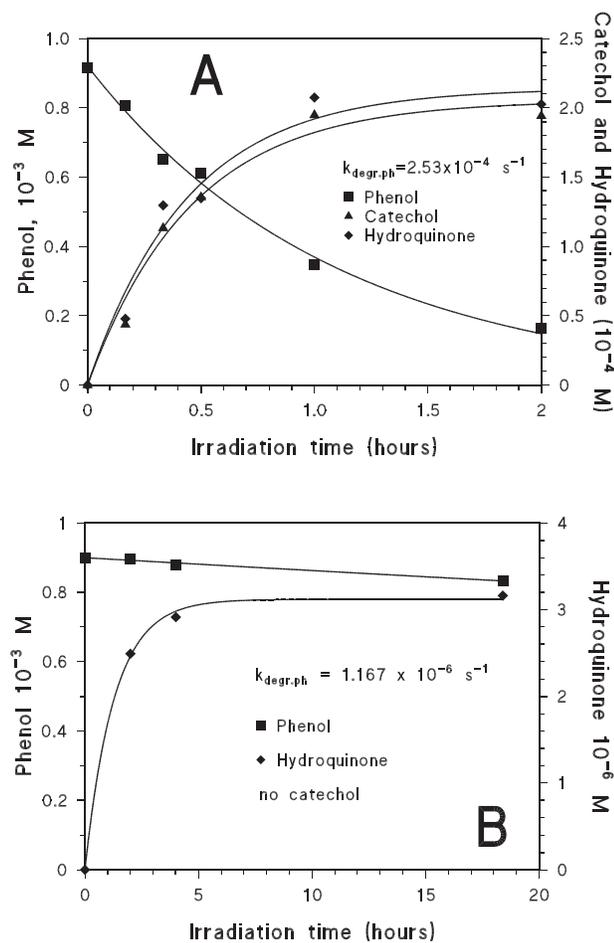
Figure 1. Degradation of phenol 1.1×10^{-3} M in the presence of: (A) 0.50 g/l TiO$_2$ n°2 (B) 0.50 g/l TiO$_2$ n°3.
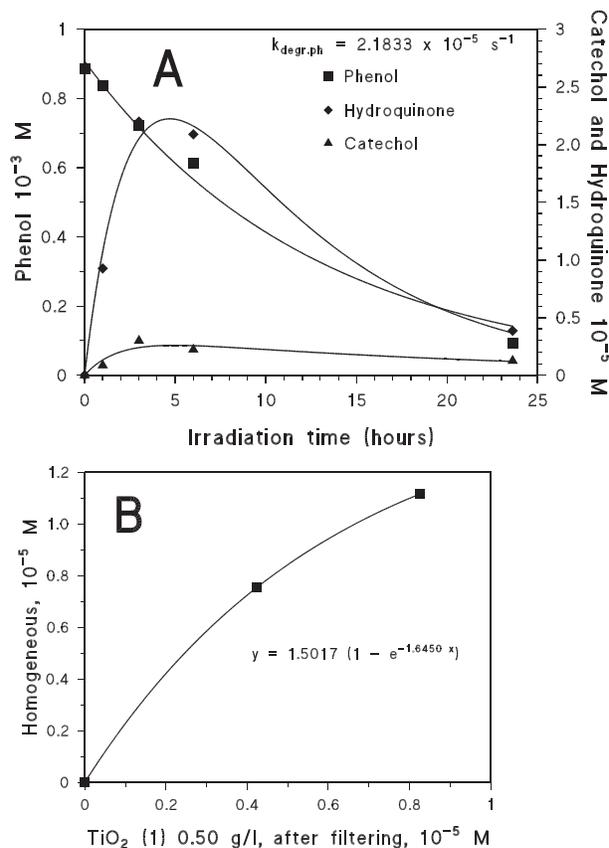

Figure 2. (A): Degradation of phenol 1.1×10^{-3} M in the presence of 0.50 g/l TiO$_2$ n°1. (B): Adsorption of catechol on 0.50 g/l TiO$_2$ n°1.

The pigments TiO$_2$ n°1, n°4 and n°8 are more active than those based on rutile treated with alumina and dimethicone or 1,3-butanediol (n°3 and n°7). These last two sunscreens have almost no activity.

Figure 4 shows the percentages of different degradation intermediates (subdivided as catechol, hydroquinone and others) that form upon irradiation of phenol in the presence of the different pigments. These percentages have been calculated for each pigment by dividing the initial formation rates of the intermediates by the initial degradation rate of phenol.

In the case of the TiO$_2$ P25 and n°3 and of ZnO n°5 and n°6, about half of the amount of the degradation intermediates is constituted by catechol and/or hydroquinone. This percentage rises to 87% for TiO$_2$ n°8 and to 100% for TiO$_2$ n°2, while it is only about 20% for TiO$_2$ n°1 and n°4. These latter, for which it is possible to
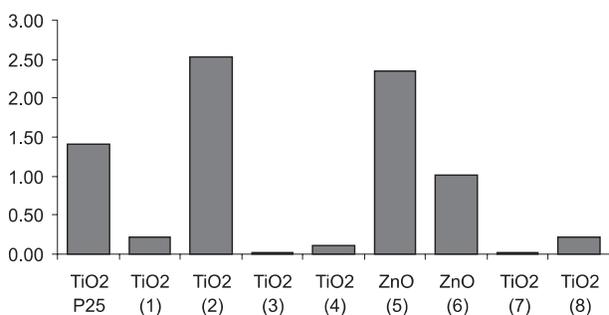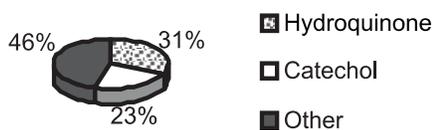

Figure 3. Pseudo-first order degradation constants (10^{-4} s^{-1}) for phenol 1.1×10^{-3} M in the presence of the different pigments.

suppose a reduced activity of $^{\bullet}$OH$_{ads}$ groups compared with h$^+$ species, have some features in common. They both consist of TiO$_2$ in the rutile form, have been treated
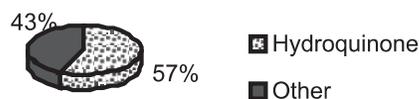
TiO$_2$ P25
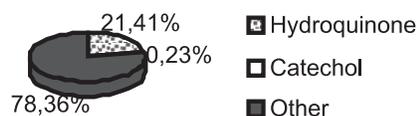
46%   31%
23%

- Hydroquinone
- Catechol
- Other

TiO$_2$ (1)

19%
2%
79%

- Hydroquinone
- Catechol
- Other

TiO$_2$ (2)

48%
52%

- Hydroquinone
- Catechol

TiO$_2$ (3)

43%
57%

- Hydroquinone
- Other

TiO$_2$ (4)

21,41%
0,23%
78,36%

- Hydroquinone
- Catechol
- Other

ZnO (5)

32%   40%
28%

- Hydroquinone
- Catechol
- Other

ZnO (6)

52%   40%
8%

- Hydroquinone
- Catechol
- Other

TiO$_2$ (8)

13%
21%   66%

- Hydroquinone
- Catechol
- Other
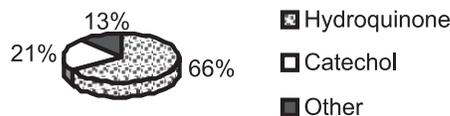
with alumina and stearic acid and, maybe most important of all, they are both very difficult to disperse. Indeed, the low percentage of catechol and hydroquinone is not a feature of rutile. In fact, the uncoated rutile TiO$_2$ n°8 gives rise to the production of catechol and hydroquinone in an amount equal to 87% of transformed phenol.

Moreover, in the case of the pigments TiO$_2$ n°3, n°1 and n°4, hydroquinone is almost the only hydroxylated phenol derivative. On the contrary, phenol hydroxylation by the most active pigments (P25 and n°2, anatase in both cases, and n°5 and n°6, zinc oxides) leads to the formation of both catechol and hydroquinone. The greater prevalence of hydroquinone over catechol also occurs for uncoated rutile (TiO$_2$ n°8), thus it could not be

a feature induced by superficial treatment. In the case of pigment TiO$_2$ n°7 it has not been possible to detect catechol and hydroquinone formation because their concentration was below the detection limit.

CONCLUSIONS

In this work we have demonstrated that some pigments used as sunscreens show photocatalytic activity on organic molecules, for which phenol was employed as a model. The wavelength range having the highest importance for human health is the UVA/UVB region, as stated in the introduction. In our experiments, UVB radiation (280–320 nm) was

Table 2. *Half-Life Times for Phenol in the Presence of the Different Pigments*

Pigment	$t_{1/2}$ (h)
TiO$_2$ (P25)	1.37
Micro Titanium dioxide MT-100TV (1)	8.83
Oxide de titane standard (2)	0.76
UV Titan M262 (3)	160
Kemira UV Titan M160 (4)	17.8
Suns mart inc., Z-cote (5)	0.82
ZnO (6)	1.89
UV Sperse (7)	128
Titanium(IV) oxide (8)	9.18

Values are derived from the pseudo-first order degradation constants reported in Figure 3.

absorbed by the 340-nm cut-off filter and did not reach the solution, thus the range of interest is 340–400 nm, included in the UVA region. The radiation intensity reaching the solution in this wavelength interval is about 0.01 W/cm^2, to be compared with the flux of solar energy at the ground in the UVA region under standard conditions (0.012 W/cm^2 (10)).

This similarity in the flux values means that the irradiation time under the lamp in our experiments is directly comparable with sunbathing times and that the photocatalytic activity of the most active tested pigments occurs on time scales that are comparable with common sunbathing times. To ease the comparison, half-life times of 1.1×10^{-3} M phenol in the presence of 0.50 g/l of the different pigments are reported in Table 2.

The photocatalytic activity of the pigments, as a consequence of sunlight absorption, can lead to the degradation of organic additives of protective creams and to the generation of active species inducing the transformation of biological molecules present on the skin (11). Different pigment treatments, in particular for TiO$_2$ rutile, have different effects on phenol degradation rate. The experimental data show that probably stearic acid is less effective than 1,3-butanediol and dimethicone to prevent phenol photodegradation.

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