

Physicochemical Characterization of Nanosize Zinc Oxide and Titanium Dioxide used as UVR Sunscreen Agents in Cosmetic Formulations

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ABSTRACT

The physical (particulate) sunscreen agents ZnO and TiO₂, are increasingly used to provide UV protection in a wide variety of cosmetic and personal care products. The particle size distribution (PSD) of each oxide directly impacts product performance in two critical ways. First is the UV attenuation efficiency. Second, cosmetically acceptable and aesthetically pleasing products must also be transparent (non-whitening) when applied to the skin. The actual PSD in the final sunscreen formulation is very dependent upon the method of preparation and especially the quality of the oxide dispersion in the particular cosmetic vehicle. ZnO and TiO₂ have their own chemical compatibility that must be recognized to obtain maximum performance. This requires a detailed knowledge of the particulate surface chemistry and how that relates to the other (chemical) components in the product. For example, the majority of titanias currently used in cosmetic applications have been surface modified. This results in a very wide, variation of surface chemistry that critically affects dispersibility, especially when formulating mixed oxide systems. All these factors will be reviewed and illustrated.

Keywords: particle size, zeta potential, sunscreens, UV radiation, cosmetic formulations

1 INTRODUCTION

Particulate (physical) sunscreens have begun to gain acceptance over the past decade. They can be conveniently divided into two groups: organic and inorganic. The organic particulates include natural materials such as melanin and encapsulated versions of traditional organic (soluble) actives; these have, to date, found only limited application. The inorganic particulates include a variety of metal oxides, kaolin, mica and barium sulphate to name but a few. Of this latter group only zinc oxide (ZnO) and titanium dioxide (TiO₂) are currently globally allowable as sunscreen active ingredients. As insoluble particulates they lay on top of the skin and are not absorbed systemically. For this reason they are perceived as safer than traditional organic "chemical" sunscreen actives. However, there still remains a great deal of misunderstanding about these two materials, especially as

it pertains to their formulation, and this has limited their universal acceptance. The following paper presents an overview of the physicochemical characteristics of these oxides and their role as physical sunscreen actives, as well as an attempt to explain their benefits in comparison with the traditional organic sunscreens.

1.1 Solar Radiation and Sunscreens

Ultraviolet radiation (UVR) exposure, from sun or artificial sources, is a well-documented health hazard causing serious adverse effects in skin. The UVR spectrum comprises two distinct regions: UVB (290-320nm) and UVA (320-400nm). The UVA region is, itself, divided into two: short UVA (320-340nm) and long UVA (340-400nm). Both UVB and UVA cause catastrophic and carcinogenic events in the skin but they do so in very different ways. What is not always totally appreciated is the danger from increased UVA exposure. Recent advances in the understanding of photoaging and aggressive skin cancers highlight the need for sunscreen agents that not only prevent erythema (sunburn) but also block UVA radiation. There has been an average annual increase of over 6% in UVB radiation since the early 1980's. But, although UVB radiation is 100 times more efficient in producing erythema than UVA radiation, about 20 to 30 times more UVA reaches the earth's surface per day. Additionally, it now appears likely that it is the long UVA that is the causative factor in the photoaging process. Also, UVA radiation is a relatively constant, year-round phenomenon. Thus, maximum protection can be afforded only by the use of sunscreen formulations that contain actives capable of blocking both UVA and UVB radiation (i.e. so-called "broad spectrum" coverage) and, in addition, formulating to achieve an SPF value of at least 15. The clinical need for full spectrum UV protection is also increasing. A recent study from Australia emphasizes the serious problem of skin cancer in transplant patients, patients whose immune systems are suppressed.

To satisfy both the above criteria with current organic sunscreens necessitates the use of combinations of two, or more, active ingredients with overlapping or complementary absorbance spectra, because typical organic sunscreens individually block only a portion of the total UVR spectrum. In practice this can prove difficult since the total amount of an individual organic sunscreen that can be used may be limited; in Japan, for example, it is 10%. There are potential

difficulties associated with long-term use of organic sunscreens; issues of photo-induced and nonphoto-induced toxicity and allergy are becoming increasingly important. Organic sunscreen actives have been the mainstay of photoprotection for decades, mostly used in beach products. Today, however, virtually all types of topical products, from moisturizers to shampoos, include organic sunscreens. Increased daily exposure to these chemicals will likely result in the incidence of adverse reactions. However, inorganic sunscreens such as ZnO and TiO₂ are non-toxic, non-irritating and physiologically inert; there is little chance of any adverse reactions. This can be especially important in children's products and those topicals aimed at individuals with sensitive skin. Additionally, ZnO is recognized, by the US FDA, as a Category I skin protectant.

2 GENERAL BACKGROUND

ZnO and TiO₂ are physical sunscreen actives. They thus exist, and participate, as a discrete particular entity i.e. they have a particle size distribution (PSD) when suspended in either an oil or water-based vehicle. This is in contrast to the organic sunscreen actives that are only soluble in the typical oil vehicles used in cosmetic formulations. Thus, unlike the organic actives there is little chance of absorption through the skin; application of a 40% zinc oxide ointment has not been found to raise the serum zinc level. An important consequence of this is the lack of opportunity for these oxides to directly contact any meaningful cellular structures.

Both oxides are generally available as "pigment grade" or "micro fine grade." This refers only to the particle size (PS); there is no chemical difference. The pigment grade has a larger average PS and usually a broader PSD. For example pigmentary USP grade ZnO and TiO₂ are approximately 0.7 micron and 0.25 micron respectively. In comparison, the micro fine grades of each are typically 120 nm and 70 nm respectively. Thus, in absolute terms, there is less than an order of magnitude difference in size between the two grades and even within the pigmentary grade there is always a micro fine fraction, often referred to as the "fines". In other words, "micro fine" is really only a refinement in PS and not an entirely new class of sizes. With the advent of "nanotechnology" and all the associated buzz and marketing hype, the micro fine grades are now often sold as "nanosize" materials.

3 OPTICAL PROPERTIES

3.1 Visible Spectrum

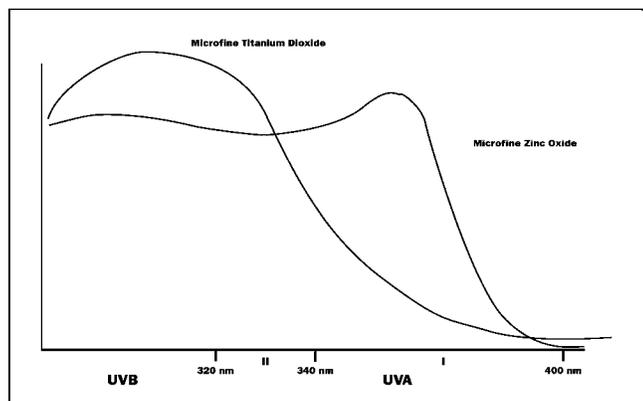
All particles both absorb and scatter a given wavelength. For white light (i.e. the visible spectrum), the dominant process for both ZnO and TiO₂ is that of scattering. They are white pigments, with a refractive index (R.I.) of ca 2.0 and 2.6 respectively; as such they are very efficient scatterers of

visible light. Until the introduction of TiO₂, ZnO had the second largest sales volume, after white lead (basic lead carbonate), of the primary opacifying pigments used in paints. The scattering efficiency is a sensitive function of the particle size and can be calculated using Lorenz-Mie theory. The theoretical calculations demonstrate quite clearly that, for virtually all particle sizes of interest, i.e. at the micro fine or nanosize level, size-for-size TiO₂ scatters visible light more efficiently than ZnO. TiO₂ with a much larger R.I. provides superior hiding power and tinting strength. Hence, the almost universal use of pigmentary grade TiO₂ in foundation and make-up. Herein lies one of the major advantages of ZnO: it is inherently easier to camouflage it in a cosmetic vehicle (which typically will have an R.I. of around 1.5). The importance of this cannot be understated. No one will use a sunscreen formulation - no matter how effective - if it is not cosmetically acceptable and this includes "transparency". The degree of perceived transparency is also a function of the film thickness, i.e. how much is applied to the skin. Most sunscreen formulations are emulsions (O/W and W/O) that appear white. However, on "rub-out" the "whiteness" disappears. At a given film thickness it is easy to demonstrate (either *in-vitro* or *in-vivo*) that micro fine TiO₂ is almost twice as whitening as ZnO. This tends to limit the amount of TiO₂ that can be used in sunscreen formulations. It should be noted that the FDA mandated application rate of sunscreen used to determine the Sun Protection Factor (SPF) is 2mg/cm² and this would represent a film thickness of approximately 20 microns. All powders, however, consist of a range of particle sizes, i.e. they have a PSD that dramatically affects the total practical scattering efficiency.

3.2 Ultraviolet Spectrum

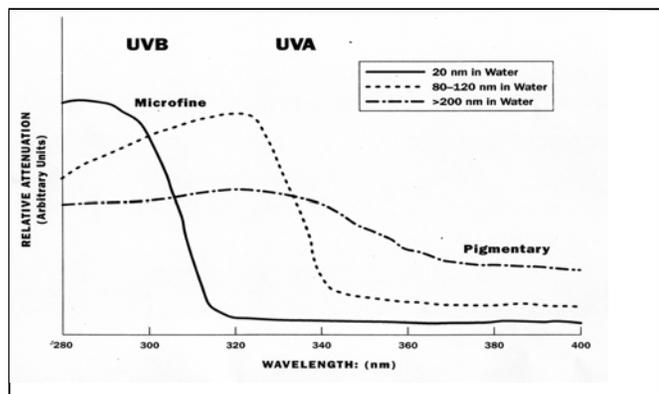
The UV absorption and scattering properties of oxides like zincite and titania have been utilized in cosmetic applications for over 50 years. In ultraviolet light, zinc oxide is an absorber - in effect a "black" pigment. It cuts off the UV more sharply than any other white pigment and is used to improve the weather resistance of resins and plastics. Since the real portion of the refractive index of ZnO is smaller than that for TiO₂, absorption plays a more important role in the attenuation of UV radiation than does scattering. Effectively, ZnO is primarily an absorber over the complete spectrum from about 380nm down to 200nm. The PS dictates only the amplitude of UV attenuation. The smaller the PS the more material per unit weight and the larger the surface area coverage and this translates into an increase in measured SPF. In contrast, it has long been recognized that the response of TiO₂ to UV radiation is more complex; it is predominately a scatterer in the UVA (from 400nm down to 320nm) and an absorber in the UVB (290 to 320nm). Figure 1 indicates the complimentary attenuation of UVA and UVB obtained from the use of a combination of TiO₂ and ZnO.

Figure 1: Attenuation of Light Spectra using TiO₂ and ZnO



Consequently, the particles size (PS) of TiO₂ critically affects the UV absorption characteristics leading to a marked difference in behavior between the pigmentary and micro fine grades of TiO₂. Figure 2 indicates the change in absorption and scattering properties for TiO₂ with particle size.

Figure 2: Particle Size dependence of TiO₂ on UVA and UVB Properties



However, size-for-size and weight-for-weight TiO₂ is a more efficient attenuator of UVB radiation and hence provides a higher SPF. On the other hand, micro fine ZnO provides more photoprotection in the UVA. Thus, the two oxides are not interchangeable; they have complimentary UV attenuation properties and, ideally should be used in combination.

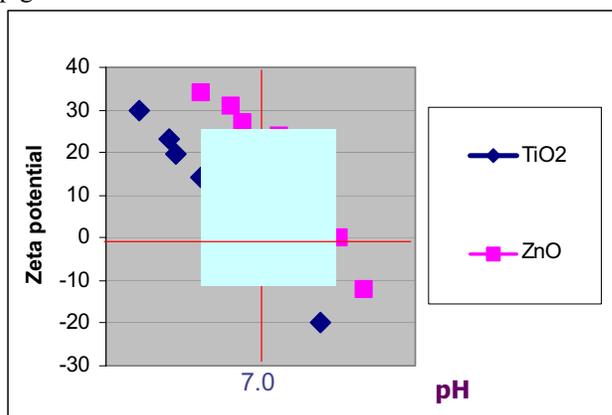
3.3 Formulation parameters

The key to success with the particulates is to achieve a stable (non-agglomerating) reproducible PSD. Success is defined as achieving optimal aesthetics (minimum whitening) and performance (SPF and UVA attenuation), while using the least amount of material. Both are uniquely related to the surface charge of the material(s). To take maximum advantage of the properties inferred by the small PS of both micro fine ZnO and TiO₂ requires that the material be evenly distributed within the suspension vehicle and be kept so. However, no matter what the so-called primary size of

the particles, it is the state of dispersion of the final product that determines the effectiveness. And this is especially critical when formulating with a mixture of particulates.

Both ZnO and TiO₂ have their own interfacial chemistry that must be recognized in order to obtain the best performance. There is a tendency to treat both particulates as the same. The assumption that simply mixing them together will result in a well-dispersed system is rarely the case in practice. To address the stability problem that exists between these two compounds requires knowledge of their surface chemistries. All materials placed in a fluid acquire a charge; the presence of charged surface groups/sites directly affects their performance and processability. In water, the magnitude of the surface charge is affected by the solution conditions such as pH and electrolyte concentration. Measurement of the zeta potential is a simple but useful indicator of the surface charge. Oxides like ZnO and TiO₂ are both sensitive to pH. However, zeta potential measurements reveal that ZnO is alkaline while TiO₂ is weakly acidic. Figure 3 indicates the zeta potential vs. pH results of each oxide, TiO₂ and ZnO.

Figure 3: Zeta potential vs. pH of uncoated TiO₂ and ZnO pigments.



Thus, when suspended in neutral water the ZnO particles are positively charged while the TiO₂ is slightly negatively charged. Mixing them together under these conditions will result in heterocoagulation, i.e. the formation of aggregates between particles of different materials. This can be readily monitored by measuring the change in PS with time. If this process were to occur in a real formulation it would result in increased whitening and decreased SPF. In theory it is possible to prepare a stable, mixed suspension of ZnO and TiO₂ at solution pH values below pH5 or above pH10. At these pH regimes both oxides would carry the same sign of surface charge. However, in practice this is neither clinically nor cosmetically acceptable for sunscreen formulations.

When preparing O/W or W/O sunscreen formulations that need to contain mixtures of ZnO and TiO₂ it is usual practice

to separately disperse the ZnO in the oil phase and the TiO₂ initially in the water phase in an attempt to eliminate, or at least minimize heteroaggregation. This is not only time consuming but overly complicates the formulation since two distinct dispersing processes are required. In addition, during the emulsification it is possible for transfer of either oxide from one phase to the other, resulting, again, in aggregation. A further point to consider is that the vast majority of titanias currently used in cosmetic applications have been surface modified. Typical coatings include hydrated alumina, silica and zirconia, silicones and fatty acids. Although originally adopted to improve durability and weather resistance of paint films and plastics, subsequently it was found that surface treatments could also be used to improve dispersibility of the titania in both aqueous and non-aqueous media. The advantage of such surface modification is that it alters only the dispersion characteristics while leaving the bulk properties, such as hiding power, essentially unaffected. In contrast to TiO₂, apart from fatty acid coatings for specialized use in the rubber industry, virtually all ZnO presently sold is used in its uncoated form. Therefore it is the treated surface and not a pure TiO₂ surface that must be contended with. The isoelectric point (IEP) of these coated titanias varies dramatically with the different amounts of silica and alumina. This is because it is the chemical composition of the particle surface, not of the bulk material, that determines the zeta potential. The bulk percentages of each component, determined from elemental analysis, and usually reported, but not always, on the MSDS, are not a reliable indicator of how the surface of the particle will behave in a fluid. The actual zeta potential must be determined lot-to-lot for each oxide to accurately monitor the surface properties. One solution to preparing suspensions of mixed oxides is to utilize dispersing aids. These are always beneficial. The “dispersant” is a form of *in-situ* surface coating produced by the process of physical adsorption. Of course, the shortcoming of this type of coating is that it can be displaced during subsequent formulation processing by a moiety with an even stronger affinity for the particle surface, or because of the severe thermal and mechanical agitation employed. Chemical grafting can produce a more viable, and permanent coating. While clearly more durable and efficient this adds considerably to the material cost.

4 CONCLUSIONS

Finally, second-generation “nanosize” materials are currently superseding the first-generation micro fine grades of ZnO and TiO₂. These oxides have a PS as small as 20nm and have exceptional low polydispersity. They are thermodynamically more stable, certainly far more “transparent” and provide superior SPF values. They are also considerably more expensive and they still need to be formulated with the same surface chemistry concerns that plagued previous generations of products. In addition, a

product prepared with smaller PS components has raised safety concerns by both the FDA and EPA. The concerns include the possibility of oral and cutaneous penetration, problems associated with dry powder handling and environmental contamination.