

A uniquely stabilized Zinc Oxide suspension

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Introduction

Over the past several years, and particularly since its acceptance as a Category I sunscreen active by the FDA(1), microfine zinc oxide (ZnO) has become widely recognized as a valuable broad spectrum ultraviolet radiation block. Indeed, with the recognition of UVA as a major health threat(2,3), microfine ZnO could be one of the most important preventative health care advancements in recent years.

Still, with all its attributes, initially ZnO posed some formulating challenges. With particulates such as ZnO, proper, reproducible and sustainable particle size distribution (PSD) is the key to success(4). Success being defined as achieving optimal aesthetics and SPF while using the least amount of pigment. The manufacturing of the particulates, like ZnO, can be properly controlled to produce ultrafine powders with highly consistent PSD(5) and advances in surface modifications have greatly improved the ease of use and the efficacy of both ZnO and TiO₂ as sunblocking agents. The coatings, either hydrophilic or hydrophobic, also allow the powder to be easily suspended into a proper intermediate.

Although it can be a straightforward process to produce well-dispersed high solids suspensions of ZnO and TiO₂ in-house(6), many cosmetic manufacturers prefer to purchase these materials already made. The presuspension products currently available, however, have a tendency to separate out under normal storage conditions. To restore suspension homogeneity it is necessary, indeed imperative, that the pre-dispersed material be rolled or otherwise re-blended before use. While the process of settling is not necessarily an indication of instability it can result in re-agglomeration. Thus, some products may also include a dispersant system to help stabilize the suspension against re-

agglomeration but this, unfortunately, will not stop settling. Also, the dispersant system, often in practice a surfactant or emulsifier, may interfere with the subsequent production of finished formulations. Settling within a finished formulation can also adversely impact the emulsion stability over time.

Penreco[®] has developed patented gelling technology applicable to a wide range of non-polar hydrocarbon systems(7). The proprietary polymer system, used as the gelling agent, utilizes a unique blend of thermoplastic copolymers(8). These gelled systems exhibit outstanding stability, excellent clarity without syneresis, and thermal reversibility(9) and a wide range of rheological properties, from a thickened liquid to a semisolid, can be obtained dependant upon the composition of the hydrocarbon/copolymer blend. They also provide additional moisturization benefits to the skin. This is illustrated in Figure 1.

Here the measured total transepidermal water loss (TEWL) for gelled mineral oil, applied to skin, is compared to that for mineral oil and petrolatum. The latter is considered to be an excellent barrier to water loss.

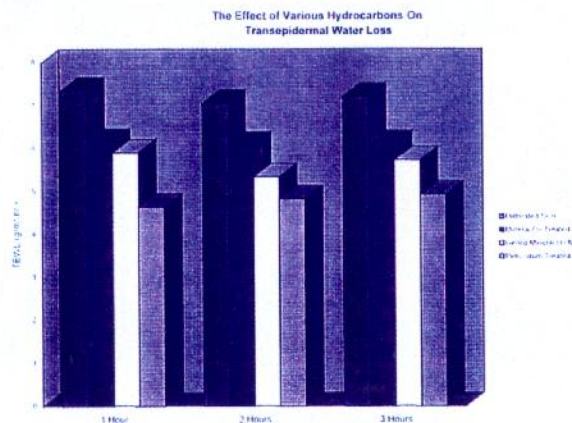


Fig 1.

Table 1.

Material	% Zinc Oxide	Viscosity (cP)
Uncoated ZnO	33%	1480
Dimethicone-Coated ZnO, (ZCoteHP1™)	33%	256

The data in Figure 1 shows that the gelled mineral oil is clearly superior to plain mineral oil and more comparable in performance to petrolatum. In addition, the gelled system provides a more cosmetically acceptable film than either hydrocarbon.

sunSmart™ inc. has developed a proprietary, patented grafting technology(10) to coat the surface of their ZCote® microfine zinc oxide with dimethicone. The purpose of the grafting/coating is to produce a completely hydrophobic, i.e. non-water wetttable, ZnO surface, which is then compatible with non-polar liquids, thus simplifying the dispersion process(11). The coated ZnO, commercially available as ZCoteHP1®, is materially less viscous also aiding in the formulation process. Table 1 compares the viscosities of coated and uncoated zinc oxides at equal concentrations (33%). Since the performance of a given particulate is directly linked to its ease of dispersion/formulation, the product provides superior SPF and aesthetics. Combining the two, Penreco® and sunSmart™, technologies results in a uniquely stabilized ZnO suspension that has performance properties, in particular storage stability, which make it particularly useful, efficient and cost effective to cosmetic formulators. When the copolymer system is dissolved in a hydrocarbon material, the molecular structure of the block copolymers allows them to adopt configurations that result in a three dimensional network. It is this polymer network that gives the solution its gel-like properties. When the dimethicone-coated ZCoteHP1® particles are blended into the system because they are lipophilic they self-disperse and are entrapped within this polymer 3-D network. Suspensions with solid content up to 60% w/w have been successfully made and the suspension products are smooth, consistent, and stable over a broad temperature range.

Suspension Viscosity

The basic gelled hydrocarbon systems, prior to addition of the ZCoteHP1®, have an average viscosity value of approximately 2×10^3 cP at room temperature. With 50%w/w of particulate powders

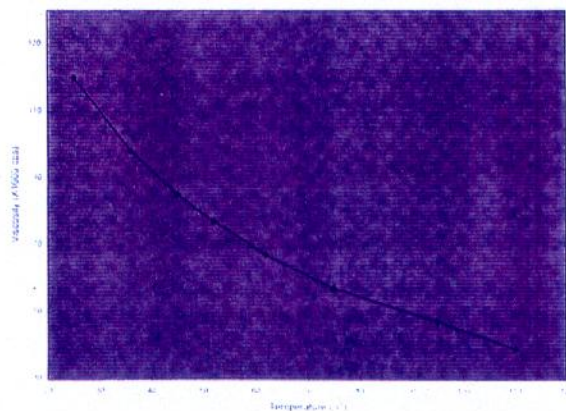
Z-Cote HP1/Gelled Mineral oil (50:50) Suspension
Viscosity vs. Temperature

Fig 2.

suspended into the gel, the suspension viscosity, at ambient temperature, may well reach 140×10^3 cP. However, the viscosity decreases dramatically with increase in temperature, as can be seen from Figure 2. Viscosity measurements were made using a Brookfield DV-2 Viscometer with a T3 Spindle at 5 RPM on a sample of a 50:50 ZCoteHP1®/Gelled Mineral Oil suspension.

At 70°C to 80°C, temperatures typically encountered in the oil phase preparation and emulsification stages of cosmetic formulation, the viscosity of the gelled suspension decreases to about 5×10^3 cP. Although this viscosity range is manageable for most production blending equipment, it is unlikely that a gelled suspension would be ever be used at its maximum concentration of 50%. Typically it would, first, be diluted by about a factor of 5 to 10 with a concomitant reduction suspension viscosity.

This thickening property, however, also serves to drastically reduce the settling rate of the dispersed zinc oxide particles by physically restraining the movement of the particles. In addition, the polymer system, itself, can confer an additional element of steric stabilization to the suspension(12) further enhancing the overall stability of the suspension.

Suspension Stability

Many practical techniques to predict the stability of mixed systems have been developed. Almost all these tests involve some form of "stress" applied to the system, usually in the form of temperature or pressure. Among the most common testing methods for stability are accelerated thermal stress (accelerated ageing) and freeze-thaw(13). Measurements of the PSD of a Z-COTE HP1®/Gelled Mineral Oil (50:50)

suspension were made on a freshly prepared sample and for samples stored in an oven at 52 °C for four months. The measurements were made using X-ray centrifuge sedimentometry(14) using a proprietary analysis algorithm. The technique is highly suited to the analysis of mineral submicronic particles and out performs other techniques on several points such as exceptional resolution and the simplicity of the related physical laws(15). For the size analysis the concentrated suspension was diluted to approximately 2% using straight mineral oil as the diluent. The results in Figure 3 first demonstrate the tightly controlled PSD profile of the initial ZCoteHPI® suspension and then clearly show that there is no change in the PSD profile, within experimental error, following accelerated thermal stress. This confirms that no re-agglomeration has taken place. The four months at 52°C accelerated ageing would suggest a room temperature shelf storage for the product of at least one year. Since PSD clearly affects SPF, this was also measured. A W/O sunscreen emulsion was formulated using the gelled ZCoteHPI® and the sunscreen, containing 10% ZnO, was also subjected to accelerated thermal stress. The before and after in-vitro SPF values (21.5 and 21.3 respectively), measured using an Optometrics SPF-290 Analyzer with Transpore™ tape as the substrate, again were identical within experimental error.

The stability of the suspension product was also studied for possible zinc oxide settling. Three samples that had separately gone through ambient temperature storage (25°C), elevated temperature storage (4 months @ 52 °C) and one freeze/thaw cycle (-20°C to +25 °C for 24 hr) were analyzed for ZnO concentration at different levels inside of the containers: from the top, the middle and the bottom

one-third. The technique used to determine the ZnO concentration was based on Quantitative X-ray Fluorescence. The analytical procedure was adapted from the ASTM standard test method for determining sulfur in petroleum products by X-ray spectrometry(16). The instrument was calibrated for the test specimen. Because of the high concentration of zinc oxide in gelled hydrocarbon systems, direct measurement of the ZnO% through Quantitative X-ray Fluorescence is not possible. Accordingly, samples were diluted with unpigmented gelled mineral oil to approximately 1500 ppm. The final ZnO% results, as presented in Figure 4, are corrected for the dilution ratio. Within the experimental error, no change in ZnO concentration for the top layer, middle layer or bottom layer was seen implying no settling of the dispersed particulate sunscreen. An Ash Test(17) for the aforementioned samples also confirmed the fact that no separations or settling occurred to the suspension product.

Suspension experiments with similar results have also been conducted for high solids ZCoteHPI® in other suitable gelled hydrocarbon systems. (Table 2). Finally, studies are underway on the preparation of high solids gelled suspensions of TCote031®, a dimethicone-coated microfine TiO₂.

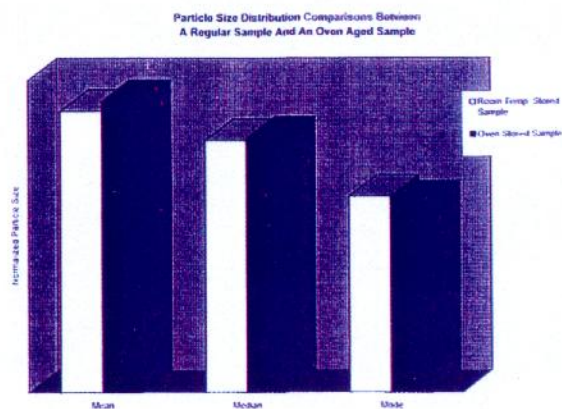


Fig 3.

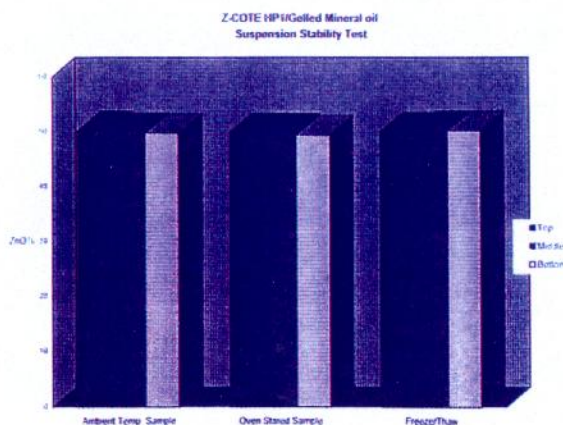


Fig 4.

Hydrogenated Polybutene	C13-14 Isoparaffin
Mineral Oil	C15-16 Isoparaffin
Polyalphaolefin	Polydecene

Conclusion

Penreco's gelled hydrocarbon systems are excellent dispersion vehicles for surface modified fine particle powders such as the sunSmart™ ZCoteHP1™ microfine ZnO. It has been confirmed that the suspension products have desirable rheological characteristics and are very stable under thermal stress. The evaluations conducted, with and without thermal stress, for PSD and ZnO content comparisons have demonstrated both the extraordinary stability and consistency of the suspension product. This gives cosmetic manufacturers the ease-of-handling that is critical for production efficacy allied to cost efficiency. ZnO suspensions can be prepared at up to 60%w/w solids content providing cosmetic manufacturers with the maximum flexibility when incorporating microfine ZnO into formulations. These suspension products are applicable not only to sunscreen products, but also to color cosmetics, baby care products and daily-wear moisturizers.

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