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Skin Inc.
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SUSPENSION OF PHYSICAL SUNSCREENS

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Biography

Ms. Lin Lu is currently a Research Associate of the Industrial Specialties Department at Penreco. Ms. Lu received her MS in Chemistry from Sam Houston State University in Texas and BS in Polymer Science from BITC in the People’s Republic of China. Ms. Lu has been involved in research and development work in a variety of personal care product categories. Ms. Lu is an active member in SCC.

BACKGROUND

Penreco has developed a series of patented or patent-pending anhydrous gelled systems. These systems include polar and non-polar intermediates such as mineral oil, isohexadecane, isopropyl myristate, etc. (Table I). They exhibit outstanding stability, excellent clarity without syneresis, and thermal reversibility. The gelled systems provide additional moisturization benefits to the skin when compared to non-gel intermediates (Figure 1). These gelled systems can be customized in a wide range of rheological properties, from a thickened liquid to a semisolid. Because of their versatility, the gelled systems have been found in some unique applications such as controlled-release base for fragrances, gel candles, etc.

Recent studies have demonstrated that some gels (Table I) are also superior suspension vehicles for fine particles. For hydrophobic-treated ZnO, suspensions with solid content up to 60 wt% have been successfully made with the gels. These suspension products appear to be smooth, consistent, and stable over a broad temperature range. 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. Accelerated thermal stress (accelerated aging) and freeze-thaw are the most common testing methods for stability. The zinc oxide and gelled system suspension were tested under thermal stress and the results are illustrated as follows.

<table>
<thead>
<tr>
<th>Table I. Suitable Gelled Systems For Fine Particle Suspension</th>
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<tr>
<td>Gelled Hydrogenated Polybutene</td>
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<tr>
<td>Gelled Mineral Oil</td>
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<tr>
<td>Gelled Isopropyl Myristate</td>
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<td>Gelled C_{12-15} Alkyl Benzoate</td>
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MATERIAL

Zinc oxide and titanium dioxide are the most frequently used particulates for absorbing and/or scattering UV rays when applied to the skin either in dry powder state or incorporated into other suitable vehicles. The primary diameters of these particulates are the most critical factors for their light scattering efficacy. It is generally recognized that an opaque powdered material maximizes the scattering at a given wavelength of light when the particle diameters are equal to half of that wavelength. When the maximum
protection against UVA (320-400 nm) and UVB (290-320 nm) is required for sunscreen product formulations, a consistent primary particle size of the particulate below 0.2 micron becomes essential.

Recent advances in the powder industry, such as micronizing processes and surface modifications, have greatly improved the ease of use and the efficacy of zinc oxide and titanium dioxide as sunblocking agents. The manufacturing of the particulates can be properly controlled to have ultrafine powders produced with highly consistent particle size distributions. The coatings, either hydrophilic or hydrophobic, also allow the powder to be easily suspended into a proper intermediate.

Although both ZnO and TiO₂ are micronized as well as treated with a hydrophilic or a hydrophobic coating, the producers for finished commercial products may still struggle to achieve a target SPF and simultaneously minimize the amount of powder used. While the micronizing process allows proper particle sizes to be obtained, acceptable suspension characteristics are not guaranteed. Agglomeration of the primary particles and their aggregates are the principal contributors to this problem.

In conjunction with surface modification, pre-suspension has been considered as a solution to the problem. The pre-suspension products currently available, however, have a tendency to separate under normal storage conditions. Some products may also include a dispersant system to help stabilize the suspension against settling and agglomeration. This dispersant system may interfere with finished formulations. Until now, stability issues surrounding the settling and agglomeration of fine particle suspension products have not been satisfactorily resolved.

TESTING METHODS

QUANTITATIVE X-RAY FLUORESCENCE

This type of analysis utilizes a band of continuous radiation produced by an X-ray tube. It is used to determine the elements present in a sample by studying the secondary “fluorescence” X-ray spectrum produced by the irradiated sample. The instrument should be calibrated for the test specimen. All test samples should be stabilized at ambient temperature before testing.

ASH TEST – ASTM D482-95

A diluted sample contained in a suitable vessel is ignited and allowed to burn until only ash and carbon remain. The carbonaceous residue is reduced to an ash via heating in a muffle furnace at 775 °C, and then cooled and weighed. The specific gelled system used for dispersion and the surface modified pigments should be tested for ash as well. The final ash content of the dispersion product is the sum of the component weights. The pure pigment content can be calculated.

SPECIMEN

Because of the high concentration of zinc oxide in gelled systems, direct measurement of the ZnO% through Quantitative X-ray Fluorescence and Ash Testing is not possible. Samples that undergo tests should be diluted with unpigmented gel to approximately 1500 ppm and the dilution should be made in the same gelled system as the suspended pigment. For all stability tests, the top-layer sample is referred to as the top 1/3 of the product in the container, the middle-layer sample is referred to as the next 1/3 of the product, and the bottom-layer is referred to as the last 1/3 of the product from the same container. The final ZnO% results are then calculated based on dilution ratio.

RESULTS

SUSPENSION

The solid, hydrophobic-treated zinc oxide or titanium dioxide is suspended in a gelled hydrocarbon system at 100 ± 10 °C. Gelled systems have a typical viscosity value of 10,000 cps at the aforementioned mixing temperature. With 50 wt% of powders suspended into the gel, the viscosity may well reach 40,000 cps. This viscosity range is manageable for most production blending equipment, but the response of the viscosity to decreasing temperature remains in question.

To answer this question, a study was performed for a 50:50 (wt) Z-COTE HPÖ/Gelled Mineral Oil suspension in which the variation of the suspension viscosity with temperature was investigated (Figure 2). The results indicate that the viscosity of the completed suspension will increase drastically when temperature
decreases; it may well reach $140 \times 10^3$ cps at $25^\circ C$. This thickening property physically stabilizes the suspended powder in a gelled system. Suspension experiments with similar results were also conducted for other suitable gelled systems.

**Stability**

Surface modified powders are less prone to agglomeration when compared to untreated powders. The agglomeration and reagglomeration, however, still appear to be problematic for many manufacturers. The most direct outcome of the agglomeration is losing SPF and transparency on the skin. Subsequently, the emulsion stability will be adversely affected.

Studies have been conducted on the particle size distribution of a Z-COTE® HP1/Gelled Mineral Oil (50:50) suspension. The results show that the suspension has particle sizes close to the primary sizes of the zinc oxide, with little or no agglomeration. Particle sizes were also tested for samples stored in an oven at $52^\circ C$ for four months. The comparison results in Figure 3 demonstrate no change in particle sizes for the suspension product at elevated temperatures.

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. Accelerated thermal stress (accelerated aging) and freeze-thaw are the most common testing methods for stability. The zinc oxide and gelled system suspension were tested under thermal stress and the results are illustrated as follows.

The stability of the suspension product was studied for possible zinc oxide settling. Three samples that had separately gone through ambient temperature storage ($25^\circ C$), elevated temperature storage (4 months @ $52^\circ C$) and one freeze/thaw cycle (-20°C to $25^\circ C$ for 24 hr) were tested for ZnO concentration at different sites inside of the containers by using Quantitative X-ray Fluorescence. Within the experimental errors, no change in ZnO concentration for the top layer, middle layer or bottom layer was seen (Figure 4). An Ash Test for the aforementioned samples also confirmed the fact that no separations or settling occurred to the suspension product.

**Discussion**

Gelled systems have relatively low viscosity when the temperature reaches a certain level, usually around 85 to 95°C. At this temperature, the powders are suspended with moderate to high agitation. As the finished suspension product reaches ambient temperature, the viscosity increases drastically and physically stabilizes the suspended particles.

The proprietary polymers used in Penreco’s Versage® are a blend of copolymers. When the polymers are blended into a suitable intermediate, they form a three dimensional network which consists of many submicroscopic particles. The intermediate oil is trapped inside. Dimethicone coated particles, such as Z-COTE® HP1, are lipophilic and are attracted to the oil that is trapped in the polymer network. On a microscopic scale, the polymer network may also restrain the movement of the solid particles once enclosed in the network. Positive results of further stability study of the suspensions under extreme thermal stress, at a temperature 100°C, has validated the above theory (Figure 5).

Experience has demonstrated that it is easier to achieve a high quality 50 wt% or 60 wt% suspension than a 15 wt% dispersion. In the pigment industry, it is also a well known fact that a high solids suspension is critical in order to reduce particle agglomerations due to collisions between particles during milling and grinding. Neither milling nor grinding is required for our suspension product, and it is believed that the collision between particles in this high solids suspension during agitation also helps minimize agglomeration. In order to establish the quality of the suspension at different solids content, further studies need to be conducted.

**Conclusion**

Gelled systems are excellent vehicles for surface modified fine particle suspensions. Possible fine particles include, but are not limited to, zinc oxide and titanium dioxide. It has been confirmed that these suspension products have unique rheological properties and are very stable under thermal stress. The evaluations conducted for particle size distribution comparisons with and without thermal stress have also
demonstrated the extraordinary consistency of the suspension product. This suspension will also allow finished product manufacturers the easy handling that is critical for production efficacy. They are offered at 50 wt% or 60 wt% solids content. This provides formulators with the maximum flexibility to incorporate the suspension product into formulations. These suspension products are applicable not only to sunscreen products, but also to color cosmetics, baby care products, daily moisturizers, etc.

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![Graph showing the effect of various hydrocarbons on transepidermal water loss](image)

**Figure 1**
Z-Cote HP1/Gelled Mineral oil (50:50) Suspension
Viscosity vs. Temperature

Figure 2

Particle Size Distribution Comparisons Between
A Regular Sample And An Oven Aged Sample

Figure 3
Figure 4.

ZnO Suspensions Stability Test @100°C

Figure 5