RHEOLOGY - ITS EFFECT ON physical SPF

The efficacy of physical sunscreen actives is influenced by the rheological properties of the vehicle, typically an emulsion, by which the active is delivered onto the skin. Julian Hewitt of Tioxide Specialties Ltd and G H Dahms of IFAC GmbH report their investigations of this influence.

Physical sunscreens, primarily titanium dioxide and zinc oxide, have been commercially available for several years. Initially, use of these materials was limited by difficulties encountered in achieving stable, effective and elegant formulations. However, as formulation technology for physical sunscreens has advanced, they have gained in importance, in both the sun care and skin care fields.

The most commonly used physical, or inorganic, sunscreen is titanium dioxide. To achieve optimum effectiveness from TiO₂ as a sunscreen, the formulator must select material with the correct crystal size and ensure that the particles remain well dispersed in the formulation and that they are evenly distributed on the skin surface. Some guidelines to formulating with TiO₂, and maintaining a good dispersion in the formulation, have been described previously. This paper is concerned with the third stage of the process, namely achieving an even product distribution on skin.

Figure 1 shows schematic diagrams of good and poor product distribution. For high SPF, we require a coherent protective film covering the skin surface with the sunscreen active evenly distributed within this film. Formation of such an even film is critically influenced by the rheology of the formulation. In particular, we must consider the rheological behaviour at high shear rates, typical of those involved in spreading a cosmetic product on skin. The relationship between efficacy of physical sunscreens (as measured by in vitro SPF values) and three rheological parameters was studied:

- thixotropy
- high-shear viscosity
- recovery time, ie the time taken for a product to recover its structure after spreading under high shear

The physical sunscreens used in these studies were Tioveil dispersions (Tioxide). These are dispersions of fine particle titanium dioxide in various carrier media, and contain 40% w/w TiO₂ solids.

Rheological measurements were carried out using a Carri-Med CSL100 rheometer, with a cone and plate measuring geometry. All measurements were carried out at 25°C.

Thixotropy and high shear viscosity were taken from flow curves measured in shear rate controlled experiments, at shear rates of up to 1000 s⁻¹.

Recovery time was measured by an indirect method. The emulsion was initially subjected to a mean shear rate of 1000 s⁻¹, similar to the shear forces on application of a cream or lotion to the skin. Subsequently, the structure build up was followed by means of oscillation measurements performed in the viscoelastic region. During this measurement, the structure is no longer broken down. It is subjected to only a small stress which oscillates in a sinusoidal fashion. From the response of the system to this oscillation, we can derive the storage modulus G' (which describes the elastic forces) and the loss modulus G″ (viscous forces). The ratio of dispersed energy to stored energy is given by the angle of loss δ in the relationship tan δ = G″/G'.

If the viscous forces (G″) dominate, tan δ is greater than 1 and the system flows. As soon as tan δ becomes <1, a strong flow resistance builds up and the system stops flowing. By measuring tan δ at a certain time after the high shear force has been removed it is possible to assess the extent of structure build up. The lower that tan δ is at this point, the more the structure has been rebuilt, indicating a shorter recovery time. In these experiments, tan δ was taken 120 seconds after shearing.

SPF values were measured by the in vitro technique of Diffey and Robson using an instrument developed by Optometrics Inc.

Effect of thixotropy on SPF - This was studied initially via an oil-in-water formulation, containing both oil-based and aqueous dispersions of TiO₂ and with a total active concentration of 4%. By varying the manufacturing conditions for the formulation, products with a range of rheological properties were produced from exactly the same formulation. When the in vitro SPF values for these different samples are plotted against thixotropy, it can be seen that SPF tends to increase with decreasing values of thixotropy.

However, data obtained from a set of w/o emulsions, which exhibited much lower thixotropy values, show the opposite trend. These emulsions also contained 4% active TiO₂, with different carrier oils used in order to vary the rheological properties. Here the SPF increases with increasing thixotropy. It seems that there is an optimum value for thixotropy in order to achieve the highest possible SPF. Below this value, there is insufficient spreadability to permit good distribution of the sunscreen. Above the optimum thixotropy, there is insufficient recovery of structure to give an even product film.

Effect of high shear viscosity on SPF - These measurements were carried out on the same products from the o/w formulation, as discussed in the previous section. Figure 2 shows the in vitro SPF data for these products, plotted against high shear viscosity. It is apparent from the results that SPF increases with
Cosmetic test formulation

**Phase A**
- *% w/w*
  - Abil EM90: 2.0
  - Isohexadecane: 8.0
  - Octyl palmitate: 6.0
  - Wheatgerm oil: 4.0
  - Dimethicone 10Ks: 2.0

**Phase B**
- Sodium chloride: 0.5
- Demineralised water: to 100%

**Phase C**
- Tioell FIN: 20.0

**Phase D**
- Preservative: qs


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**Table 1**

<table>
<thead>
<tr>
<th>Rheological additive</th>
<th>Concentration</th>
<th>In vitro SPF</th>
<th>UVA/UVB Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-</td>
<td>13.1</td>
<td>0.57</td>
</tr>
<tr>
<td>Gilugel MIN</td>
<td>5.0*</td>
<td>14.6</td>
<td>0.61</td>
</tr>
<tr>
<td>Gilugel MIN</td>
<td>10.0*</td>
<td>18.4</td>
<td>0.60</td>
</tr>
<tr>
<td>Candellilla wax</td>
<td>1.0</td>
<td>28.7</td>
<td>0.59</td>
</tr>
<tr>
<td>Candellilla wax</td>
<td>2.0</td>
<td>30.8</td>
<td>0.62</td>
</tr>
</tbody>
</table>

*Gilugel MIN is a lipogel, composed of 20% aluminium/magnesium hydroxystearate and 80% mineral oil. Therefore 10% Gilugel corresponds to 2% of the hydroxystearate.

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**Table 2 - In vivo results**

<table>
<thead>
<tr>
<th>Rheological additives</th>
<th>FDA</th>
<th>COLIPA</th>
<th>SPF (1)</th>
<th>SPF (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.88</td>
<td></td>
<td>27.04</td>
<td>25.5</td>
</tr>
<tr>
<td>10% Gilugel SILS + 1% Candellilla wax</td>
<td>27.04</td>
<td>25.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) AMA Laboratories, New York, US (2) Laboratoire Durmcan, Villeurbanne, France
All tests were carried out on five volunteers.

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The lower the viscosity, the higher the spreadability. Therefore it is not surprising that low values of high shear viscosity lead to high sun protection factors.

**Effect of recovery time on SPF** - The influence of recovery time was assessed by study of a series of w/o emulsions, similar to those described in the thixotropic section, in which different waxes were incorporated. Once again, the active level was 4% TiO₂. For each product, in vitro SPF and tan δ∞ were measured using the techniques described earlier. The results are plotted in Figure 3.

It is apparent that a short recovery time, i.e. low tan δ∞∞, leads to a high SPF. In these model systems, SPF values of >20 were achieved in some cases, from only 4% TiO₂. These results show that while a low viscosity is required during spreading to ensure a good coverage of the skin, it is also desirable that the product should rapidly recover its structure so that it maintains an even film and does not continue to flow into the wrinkles of the skin. From a formulator's point of view, what this means is that SPF values of w/o emulsions containing TiO₂ can be increased by incorporation of waxes or other rheological additives. This is illustrated in Figures 4 and 5 which show the effect of various waxes on the SPF of formulations based on two different emulsifiers.

These findings were tested in a more realistic cosmetic emulsion by incorporating candellila wax and aluminium/magnesium hydroxystearate (Gilugel MIN) into Formulation 1. In vitro SPF values are shown in Table 1.

The UVA/UVB absorbance ratios are significant because if agglomeration of TiO₂ occurs, not only is the SPF decreased but the UVA/UVB ratio increases due to increased UVA extinction. The fact that there is no significant change in the ratio indicates that TiO₂ agglomeration is not the cause of the lower SPF values when there is no rheological additive present. We can therefore conclude that the improvement in SPF arises from modified rheology rather than any improvement in the dispersion of the TiO₂.

**In vivo SPP tests** have also been carried out on two versions of this formulation, confirming the positive effect of the rheological additives (Table 2).

The results presented in this paper demonstrate the importance of rheological properties in determining the effectiveness of sun protection products based on physical sunscreens. Based on this data, we can describe in qualitative terms the ideal rheological behaviour for such products:

- A low viscosity in the shear rate range above 800 s⁻¹
- A low thixotropy, such that the product can be spread easily over the skin but then recovers its viscosity to form an even protective film
- Rapid recovery of structure and viscosity after spreading has stopped.

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**References**

1. Dahms S H, Cosmetics & Toiletries, 107, 87-92 (October 1992)
4. Tapley C, SOPF, 120, 518 (September 1994)
5. Tioxide Specialties Limited, Formulation of Sunscreen Cosmetics Incorporating Tiowet Physical Sunscreens (product information release)