Specialty Silicones for High Performance Skin Lightening Products

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Consumers want smooth, even-toned skin that expresses youth and beauty, despite their age. However, as skin ages, it can become blotchy or develop uneven, dark spots, upsetting its natural uniformity and radiance. As a result, truly effective skin-lightening (also referred to as whitening) formulations continue to be in high demand. As noted by Mintel:

The whitening claim is becoming an increasingly important aspect of South East Asia's beauty launches. The individual markets may appear small when set next to China's vast US$ 2.4 billion whitening market, but the Indian market for example grew 11% to US$ 380 million in 2012 and the Indonesian market grew even more impressively, putting on 27% for a total of US$ 96 million. Skin care unsurprisingly represents three quarters of new whitening launches, with face/neck care unsurprisingly accounting for the lion's share. Other categories to watch are soap & shower products and sun care products, whose share and launch numbers are growing steadily. However, today's consumers are now looking for a more emotional but realistic approach to whitening. The focus is shifting away from a quest for the whitest possible skin to having a pale complexion as an indication that the complexion is perfectly healthy, radiant and hydrated. The words radiant, transparent, translucent and glow are therefore cropping up more and more in on-pack communications (1).

Given the growth of this market and the expectations of consumers, specialty silicone materials hold promise in the development of highly effective skin lightening products.

Silicones Can Provide Solutions
Developing skin lightening products can be a challenge to formulators. Vitamin C is recognized for its antioxidant (2-4) and skin lightening properties (5) in skin care products. From 2009 to 2014, vitamin C and its derivatives have been used in over 27% of new skin care launches that make skin lightening or brightening claims (6).

At the same time, vitamin C is highly susceptible to oxidation (7), especially in water-based systems and when exposed to air. Although vitamin C derivatives have been developed with greater stability, their efficacy and greater formulation cost have led formulators to decrease their use levels (8). In addition, it is difficult to design finished products that remain stable for a long period of time, because most contain a relatively high percentage of water.

Polyols are known to solve the instability issues of vitamin C and other light-sensitive actives in personal care products. However, they also may adversely affect the sensory characteristics of the formulation. When polyols are incorporated into silicone-based formulations, the result can be significantly improved aesthetics.

The first part of this study focused on designing anhydrous silicone formulations containing glycerin, a simple polyol. The objective was to develop an acceptable sensory profile while incorporating and stabilizing a high level of pure vitamin C. In addition, to achieve its pigment reduction activity, the formulation should not hinder release of the vitamin C or its ability to partition into skin. Performance of the anhydrous silicone systems was compared to a pure blend of glycerin and vitamin C as well as to a leading commercial benchmark. Ingredients in the commercial formulation included water, cyclopentasiloxane, glycerin, propylene glycol, ascorbic acid (claimed at 5%), canola oil, sodium citrate, dimethicone copolyol, polymethyl methacrylate, disodium EDTA, citrus amara/citrus aurantium amara flower extract, methylparaben, phenoxyethanol, and propylparaben.

Table 1 shows the basic ingredients used to formulate the anhydrous silicone test formulations.
Table 1. Test Formulation for Anhydrous Silicone Systems with Vitamin C

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-in-silicone emulsifier</td>
<td>0-6</td>
</tr>
<tr>
<td>Dow Corning® ES 5612 Formulation Aid (PEG-10 dimethicone)</td>
<td></td>
</tr>
<tr>
<td>Dow Corning® BY 25-337 (PEG/PPG-19/19 dimethicone)</td>
<td></td>
</tr>
<tr>
<td>Carrier</td>
<td>0-20</td>
</tr>
<tr>
<td>Dow Corning® FZ-3196 (Caprylyl methicone)</td>
<td></td>
</tr>
<tr>
<td>Silicone elastomer powder or blend</td>
<td>4-30</td>
</tr>
<tr>
<td>Dow Corning® 9041 Silicone Elastomer Blend (Dimethicone (and) dimethicone crosspolymer)</td>
<td></td>
</tr>
<tr>
<td>Dow Corning® EL-8040 ID Silicone Organic Blend (Isododecane (and) dimethicone crosspolymer)</td>
<td></td>
</tr>
<tr>
<td>Dow Corning® 9701 Cosmetic Powder (Dimethicone/vinyl dimethicone crosspolymer)</td>
<td></td>
</tr>
<tr>
<td>dl-α-tocopheryl acetate (vitamin E)</td>
<td>0-1</td>
</tr>
<tr>
<td>L-ascorbic acid (vitamin C)</td>
<td>1-10</td>
</tr>
<tr>
<td>Polyol (e.g., glycerin, propylene glycol, ethylene glycol)</td>
<td>40-75</td>
</tr>
</tbody>
</table>

The commercial benchmark contained 5 wt% pure vitamin C. Its aluminum tubes were designed to prevent contact with air.

Formulations were observed visually. Figure 1 indicates the commercial formulation containing 5% vitamin C showed distinct visual signs of instability by the third day. In contrast, the anhydrous silicone system showed no indication of visual instability for as long as 28 days. Using ultra performance liquid chromatography (UPLC), it was further demonstrated that less than 1% of the light-sensitive active initially present in the formulation is degraded following prolonged storage (22 days) at 50°C.

Evaluations of Aesthetics and Efficacy
The next phase of the study focused on understanding formulation parameters that have the most significant impact on percutaneous penetration of vitamin C. These would allow formulations to be optimized for stability, sensory properties and vitamin C release.

Formulation aesthetics were evaluated using multiple paired comparisons on 18 panelists under controlled humidity (50 +/- 5%) and temperature (22 +/- 3°C). Statistical analysis of data was performed via an ANOVA one-way test for parametric data and the Mann-Whitney test for non-parametric data. Based on panel results, some generalizations about sensory characteristics can be made:
- In formulations containing silicone elastomer gels, faster absorption is observed, while the gloss and greasiness of glycerin-rich formulations are decreased.
- Silicone emulsifiers impact formulation texture and spreading, and in some cases they can increase formulation viscosity by a factor of ten.

![Figure 1. Visual stability of vitamin C after storage.](image-url)
- Oil phase volatility impacts sensory characteristics after absorption by decreasing gloss, film residue and greasiness.
- Polyol type affects tackiness after absorption. For example, using propylene glycol versus glycerin would tend to decrease tackiness.
- Water, if included in the formulation, gives a lighter sensory perception, but at the expense of vitamin C stability.

Overall, it was possible to produce highly stable vitamin C incorporated into glycerin-in-silicone formulations with improved sensory characteristics compared to pure glycerin systems. Panelists noted the perception of significantly faster skin absorption, less gloss and a more powdery feel with levels of vitamin C as high as 10%.

The percutaneous/absorption profiles of vitamin C from three different systems (glycerin-in-silicone, pure glycerin blend, and commercial benchmark) were assessed using an automatic Franz-type diffusion cell-based device and full-thickness skin tissues at 32°C. The receptor medium was made of 0.5% acetic acid in ultrapure water. Experiments were done over a six-hour period, and diffusion cells were sampled every hour. At the end of the diffusion period, the different layers (stratum corneum, epidermis, and dermis) of the full-thickness skin tissues were separated for recovery analysis. Permeated samples were directly analyzed by UPLC to limit vitamin C oxidation.

Although similar skin penetration profiles of vitamin C were obtained for the three formulations evaluated (about 10% of the applied quantity), the absorption of vitamin C in the different skin compartments was formulation-dependent (Figure 2).

With the pure blend of vitamin C and glycerin, a significant amount of the released vitamin C was found in the dermal compartment and the receptor chamber of the Franz-type diffusion cells after six hours of diffusion. This might indicate that in vivo vitamin C is being rapidly absorbed by the systemic circulation. If this were the case, it might not be readily available in the lower layers of the epidermis to accomplish its biological activity.

In comparison, with both the anhydrous glycerin-in-silicone system and the commercial benchmark, the vitamin C was concentrated in the uppermost layers, which may act as a reservoir that progressively feeds the lower layers of the epidermis, sites of action for vitamin C. It is interesting to note that in the case of the anhydrous silicone system, most of the vitamin C remaining in the donor compartment was still biologically active, while for the pure blend of glycerin and vitamin C and to a greater extent for the commercial benchmark, a significant proportion of the vitamin

Figure 2. Skin absorption profiles of vitamin C (represented by %) following its diffusion through full-thickness skin tissues.
C present in the donor chamber was degraded and could no longer be detected by UPLC. This observation strongly indicates that the entrapment of vitamin C in a silicone elastomer matrix is a way of ensuring long-term stability of this light-sensitive active, without compromising its delivery to the skin layers and its biological activities while it is available on the skin surface.

Finally, a skin model based on melanocyte-containing pigmented reconstituted human epidermis was used to assess the effect of vitamin C on reducing skin pigment. Test formulations were applied at days 7 and 12, using 5 mg of treatment per square centimeter of tissue. A commercial pigment removal serum (9) was used as a positive control, and melanin was extracted from the tissue samples at day 16. Results showed that an anhydrous silicone system containing 5% vitamin C induced a 34% inhibition of melanin synthesis compared to the control, an untreated skin model.

The anhydrous silicone system displayed statistically similar performance to the blend of vitamin C and glycerin and outperformed the commercial benchmark containing 5% vitamin C. The presence of water in the benchmark formulation likely inhibits the long-term efficacy of vitamin C.

Conclusions
Study results showed that specialty silicone technologies can be used to formulate anhydrous silicone systems that stabilize vitamin C levels as high as 10% for a much longer period of time compared to a water-based commercial benchmark. In addition, the anhydrous silicone systems significantly improve sensory characteristics compared to systems formulated with a pure glycerin blend with vitamin C.

This work also demonstrated that the strong stabilization of vitamin C inside a silicone elastomeric matrix does not affect its release from the formulation, diffusion through skin models or its skin lightening efficacy. These findings suggest that silicone-based anhydrous formulations should be considered as suitable delivery carrier systems to maximize the efficacy of actives such as vitamin C that are sensitive to oxidation.

References
1. Personal communication, Vivienne Rudd, Director of Global Innovation and Insight, Beauty & Personal Care, Mintel, August 29, 2014.
9. Iklen® Rucinol Serum (Merck).
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