Oxidative Stability of Botanical Emollients

Testing new combinations of botanicals and actives to ensure more stable products

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One of the basic criteria for cosmetic and personal-care formulations is for them to have a shelf life sufficient enough to ensure product quality when purchased within a reasonable period of time. The ability of a product to resist oxidation is an important component of customer satisfaction; a stable formula will help ensure that the desired functionality and appearance of the product will not be significantly altered over time because of exposure to air. The product will remain fresh and deliver the selected fragrance, or lack thereof, when the consumer inevitably lifts the container for the first sniff.

Animal-based ingredients: Knowledge of the real or perceived danger from animal-based ingredients has pushed marketers toward the use of botanical ingredients. Recent events have strengthened the aversion to animal ingredients at the consumer level. The most dramatic has been the Mad Cow Disease (BSE) crisis, which resulted in European legislation banning the use of most cow-, goat- and sheep-derived cosmetic ingredients. The advent of full disclosure labeling in Europe (January 1, 1997) will add strength to the movement toward use of botanicals. Ingredients of botanical origin are preferred by consumers over ingredients that are of animal origin or that have chemically-sounding names.

The global trend toward botanically derived emollients, as well as other ingredients, has created new challenges for formulating scientists. This movement toward animal-free formulations has prompted new studies to determine the safest and most effective methods of use for botanical ingredients. In our study, we have focused on the use of botanically derived emollients and their stability when combined with a variety of "active" or "functional" ingredients.

Emollients

Emollients constitute a high percentage of most cosmetic formulations and are among the ingredients in cosmetics that feed the oxidative process. There is little more than intuitive knowledge of oxidative stability when the emollient is used in combination with new actives such as chemical exfoliatives (α- and β-hydroxy acids), skin whiteners (arbutin, kojic acid, magnesium ascorbyl phosphate) and metal oxides (titanium dioxide, zinc oxide, iron oxides). The results obtained in our testing program confirm that intuition does not always provide the correct answer.

Oxidative stability: In our study, we determined the inherent oxidative stability of a group of botanically derived emollients selected for their popularity in contemporary formulations (Table 1-1). The emollients were first examined neat and then with added antioxidants. Emollients containing antioxidants were then examined for oxidative stability after being combined with functional levels of actives (Table 1-2).

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**Table 1-1. Botanical emollients**

<table>
<thead>
<tr>
<th><strong>Oils</strong></th>
<th><strong>Esters</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Almond</td>
<td>Jojoba esters 15</td>
</tr>
<tr>
<td>Traditional sunflower</td>
<td>Jojoba esters 60</td>
</tr>
<tr>
<td>Hybrid sunflower</td>
<td></td>
</tr>
<tr>
<td>Macadamia</td>
<td></td>
</tr>
<tr>
<td>Palm</td>
<td></td>
</tr>
<tr>
<td>Sesame</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1-2. Cosmetic actives tested**

<table>
<thead>
<tr>
<th><strong>Metal oxides</strong></th>
<th><strong>Chemical exfoliatives</strong></th>
<th><strong>Skin whiteners</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>10% - Titanium dioxide (TiO₂)</td>
<td>5% - Malic acid</td>
<td>1% - Kojic acid</td>
</tr>
<tr>
<td>10% - Zinc oxide (ZnO)</td>
<td>2% - Salicylic acid</td>
<td>3% - Magnesium ascorbyl phosphate</td>
</tr>
<tr>
<td>10% - Iron oxides</td>
<td></td>
<td>7% - Arbutin</td>
</tr>
</tbody>
</table>

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An oxidative stability index (OSI), as determined by an oxidative stability instrument, was used to quantify the stability of the selected emollients in the presence of the actives. This recently developed method (AOCS Cd 12b-82) has been shown to provide reliable and reproducible results. The results will be referred to as "OSI stability" throughout this paper. Of course, other factors, such as processing parameters, packaging materials and storage conditions, must be taken into consideration when determining the shelf life of products.

Selection of Stable Emollients

The term emollient implies an ingredient that helps lubricate the skin and gives cosmetics a soft, silky-smooth feeling. Generally, formulators use emollients that have a pleasant skin-feel and remain non-tacky on the surface of the skin, impeding water loss. The oxidative stability of a lipid material can generally be predicted by the amount of polyunsaturated fatty acids present. The fatty acid composition of a lipid material can be predicted by the amount of polyunsaturated fatty acids present. The fatty acid composition of the selected emollients is detailed in Table 1-3 and Table 1-4. The high levels of diene content and is oxidatively stable. As the level of polyunsaturates in the massage oil formulas decreased from 22% to 5%, the OSI stability of the massage oil formulas increased by 375% (Figure 1-1). Increasing levels of high oleic hybrid sunflower oil and decreasing levels of other oils high in polyunsaturates (Table 1-5).

Hydro sunflower oil is defined as having in excess of 85% oleic acid (monoene) content and is oxidatively stable. As the level of polyunsaturates in the massage oil formulas decreased from 22% to 5%, the OSI stability of the massage oil formulas increased by 375% (Figure 1-1). Increasing levels of high oleic hybrid sunflower oil and decreasing levels of other oils high in polyunsaturates (Table 1-5).

To illustrate the oxidation potential of formulations containing high levels of polyunsaturates, we prepared and tested massage oil formulations containing increasing levels of high oleic hybrid sunflower oil and decreasing levels of other oils high in polyunsaturates (Table 1-5).

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Botanical Emollients and Antioxidants

Stable emollients: In recent years, formulators have tended to decrease the use of synthetic antioxidants (BHA-BHT, propyl, etc.) and instead have adopted the use of natural antioxidants, such as mixed natural tocopherols isolated from soybean Glycine soja oil. We determined the OSI stability of the selected group of emollients first without antioxidants and then with the emollients stabilized by adding 1,000 ppm mixed natural tocopherols (Figure 1-2). The OSI stability of the emollients was improved by adding tocopherols. However, the more pertinent observation is that the efficacy of tocopherol stabilization is augmented by, and positively correlated with, the inherent natural stability of the emollient oil. The more intrinsic oxidative stability exhibited by the emollient, the more the absolute improvement in OSI stability was achieved by the addition of tocopherols.

Unstable emollients: It is a common misconception that an antioxidant can be used to stabilize an inherently unstable emollient. To debunk this, we studied the effect of adding increasing levels of mixed natural tocopherols to traditional sunflower oil and to hybrid sunflower oil. Traditional sunflower oil is high in linoleic acid (diene) content and typically susceptible to oxidation. We added up to 5,000 ppm tocopherols to both oils and determined the OSI stability of each oil at each level of tocopherol addition (Figure 1-3). The addition of tocopherols at all levels only slightly improved the OSI stability of traditional sunflower oil, whereas the OSI stability of the inherently more stable high oleic type was significantly improved, even at lower levels of added tocopherols.
The first generation of skin-care products containing AHA's caused a slight increase in the consumer's sensitivity to sunlight. The Cosmetic Ingredient Review (CIR) panel has recommended using sunscreen in products containing hydroxy acids.1 For this reason, we also tested the oxidative stability of the selected emollients containing 10% micronized titanium dioxide in combination with either 5% malic acid or 2% salicylic acid.

The combination of TiO2 and salicylic acid increased the OSI stability of hybrid sunflower oil, macadamia oil, and palm oil. Jojoba esters were slightly reduced in stability but were still stable in the presence of these two actives. The emollients providing the best OSI results in the presence of salicylic acid and TiO2 were jojoba esters 60, macadamia oil, and hybrid sunflower oil (Figure 1-9).

When we tested with both TiO2 and malic acid, we found that hybrid sunflower oil, palm oil, and jojoba esters 15 increased their OSI stability. Surprisingly, in the presence of these two actives, jojoba esters 60 decreased in OSI stability by 90%. Jojoba esters 15 and hybrid sunflower oil provided the best OSI results in the presence of malic acid and TiO2 (Figure 1-10).

Skin Whiteners and Botanical Emollients

Skin whiteners are not new, although in recent years new actives have been developed to achieve the desired effect. We examined the oxidative stability of the selected botanical emollients containing 1000 ppm tocopherols in combination with arbutin, kojic acid, and magnesium ascorbyl phosphate. Arbutin (7%) caused a decrease in the OSI stability of jojoba esters, traditional sunflower oil and almond oil. There was very little effect on the stability of hybrid sunflower oil or palm oil. The stability of both jojoba esters was significantly reduced in the presence of 1% ZnO, although jojoba esters 60 provided the best OSI results of all emollients tested with this active (Figure 1-5). Hybrid sunflower oil also performed well in the presence of ZnO.

**Titanium dioxide:** We found that by adding 10% micronized TiO2 we could extend the OSI stability of all emollients in the study except almond oil. The extended oxidative stability was most dramatic with macadamia oil, jojoba esters and hybrid sunflower oil. We expect the extended stability found in the presence of titanium dioxide may be due to regeneration of the tocopherols, a phenomenon observed with ascorbyl palmitate. An explanation of this counter-intuitive result is beyond the scope of this study. Jojoba esters 60 and macadamia oil gave the best OSI results of all emollients tested in the presence of titanium dioxide (Figure 1-6).

**Chemical Exfoliatives and Botanical Emollients**

The success of skin treatment products containing α- and β-hydroxy acids prompted us to examine the oxidative stability of the selected group of botanical emollients containing 1000 ppm tocopherols in combination with malic or salicylic acids. Malic acid is generally considered to be an AHA, although structurally it is both an AHA and a β-hydroxy acid (BHA). Salicylic acid is a BHA. We attempted to test lactic and glycolic acids (AHAs) as well, but they were volatile under test conditions and the results obtained were inconclusive.

Malic acid (5%) materially improved the OSI stability of jojoba esters 15 (melting point about 15°C), palm oil, macadamia oil and hybrid sunflower oil. The stability of jojoba esters 60 was significantly reduced in the presence of malic acid. Traditional sunflower oil and almond oil also lost OSI stability in the presence of malic acid. Macadamia oil and jojoba esters 15 provided the best OSI results of all emollients tested in the presence of this active (Figure 1-7).

Salicylic acid (2%) caused slight improvements in the OSI stability of sesame oil, palm oil, macadamia oil and hybrid sunflower oil. The stability of jojoba esters, traditional sunflower oil and almond oil was reduced. Macadamia oil and hybrid sunflower oil gave the best OSI results of the emollients tested in the presence of salicylic acid (Figure 1-8).

**Chemical Exfoliatives and Titanium Dioxide With Botanical Emollients**

The first generation of skin-care products containing AHA's caused a slight increase in the consumer's sensitivity to sunlight. The Cosmetic Ingredient Review (CIR) panel has recommended using sunscreen in products containing hydroxy acids.1 For this reason, we also tested the oxidative stability of the selected emollients containing 10% micronized titanium dioxide in combination with either 5% malic acid or 2% salicylic acid.

The combination of TiO2 and salicylic acid increased the OSI stability of hybrid sunflower oil, macadamia oil, and palm oil. Jojoba esters were slightly reduced in stability but were still stable in the presence of these two actives. The emollients providing the best OSI results in the presence of salicylic acid and TiO2 were jojoba esters 60, macadamia oil, and hybrid sunflower oil (Figure 1-9).

When we tested with both TiO2 and malic acid, we found that hybrid sunflower oil, palm oil, and jojoba esters 15 increased their OSI stability. Surprisingly, in the presence of these two actives, jojoba esters 60 decreased in OSI stability by 90%. Jojoba esters 15 and hybrid sunflower oil provided the best OSI results in the presence of malic acid and TiO2 (Figure 1-10).
macadamia oil, hybrid sunflower oil or sesame oil. The oxidative stability of palm oil was improved slightly in the presence of arbutin. Jojoba esters 60 and macadamia oil provided the best OSI results of all emollients tested in the presence of this active (Figure 1-11).

Kojic acid (1%) had very little effect on the OSI stability of sesame oil but caused an improvement in the OSI stability of jojoba esters, palm oil, macadamia oil, and hybrid sunflower oil. The stability of traditional sunflower oil and almond oil decreased in the presence of this active. The two jojoba esters tested and macadamia oil provided the best OSI results of the emollients tested in the presence of kojic acid (Figure 1-12).

The oxidase enzymes in the presence of this active. Macadamia oil and jojoba esters 15 also performed well in the presence of magnesium ascorbyl phosphate.

Summary
Formulations containing emollients with high levels of polyunsaturates tend to oxidize rapidly. The oxidative stability of these formulations can be significantly improved by substituting increasing levels of emollients high in monounsaturates such as hybrid sunflower oil, macadamia oil or jojoba esters 15. Substitution of these botanically derived emollients does not reduce lubricity or emolliency and results in a pleasant skin feel. One practical aspect of improving the oxidative stability of massage oil formulas is reducing the "rancid oil" odor typical in many massage facilities. This odor is especially difficult to mask with fragrance.

Emollients used in these studies improved the oxidative stability of the inherently unstable emollients tested but had very little effect on inherently unstable emollients. The addition of up to 5000 ppm of mixed natural tocopherols to traditional sunflower oil (an oil with relatively low stability) did not significantly improve its oxidative stability. Conversely, the addition of even low levels of tocopherols to a high oleic hybrid sunflower oil (an oil with good inherent stability) significantly improved oxidative stability. Within the group of botanical emollients tested, we found that the efficacy of tocopherol stabilization was augmented by, and positively correlated with, the inherent natural stability of the emollient.

Macadamia oil, hybrid sunflower oil or sesame oil. The oxidative stability of palm oil was improved slightly in the presence of arbutin. Jojoba esters 60 and macadamia oil provided the best OSI results of all emollients tested with this active. Macadamia oil and hybrid sunflower oil also provided good OSI results in the presence of iron oxides. The combination of 1000 ppm tocopherols and 10% titanium dioxide materially improved the OSI stability of both jojoba esters, yet when macic acid (5%) was added to this combination in jojoba esters 60, the emollient lost 95% of its OSI stability. Jojoba esters 15 was not similarly affected. With the noted exceptions, hybrid sunflower oil, macadamia oil, and the two jojoba esters performed well in our testing. In some cases the OSI result for one of these emollients was significantly diminished in the presence of an active, yet the emollient still exhibited more OSI stability than others in the tests. As an example, zinc oxide, iron oxides and arbutin reduced the stability of jojoba esters 60 by more than 50%, yet this emollient had the best OSI stability of all emollients tested in the presence of these actives. The OSI results in tabular form are presented in Table 1-6.

Conclusions
Formulations are recommended when BHAs or BHAs are incorporated in cosmetics. The combination of 10% titanium dioxide and salicylic acid (2%) improved the OSI stability of hybrid sunflower oil, macadamia oil, and palm oil. The stability of sesame oil, palm oil, macadamia oil and hybrid sunflower oil were slightly improved in the presence of salicylic acid. Macadamia oil and hybrid sunflower oil provided the best OSI results of all emollients tested in the presence of this active. The best OSI results of all emollients tested in the presence of TiO2 and salicylic acid were provided by jojoba esters 60, macadamia oil and hybrid sunflower oil.

The combination of 1000 ppm tocopherols and 10% titanium dioxide materially improved the OSI stability of both jojoba esters, yet when malic acid (5%) was added to this combination in jojoba esters 60, the emollient lost 95% of its OSI stability. Jojoba esters 15 was not similarly affected. With the noted exceptions, hybrid sunflower oil, macadamia oil, and the two jojoba esters performed well in our testing. In some cases the OSI result for one of these emollients was significantly diminished in the presence of an active, yet the emollient still exhibited more OSI stability than others in the tests. As an example, zinc oxide, iron oxides and arbutin reduced the stability of jojoba esters 60 by more than 50%, yet this emollient had the best OSI stability of all emollients tested in the presence of these actives. The OSI results in tabular form are presented in Table 1-6.

The non-animal ingredient bias on the part of consumers has been uncovered as a result of the BSE (bovine spongiform encephalopathy) crisis in Europe. Consequently, marketers are specifying that botanical ingredients be used in formulations. This trend will increase with the advent of full disclosure labeling in Europe. Marketers will use the label statement as a billboard to highlight botanical ingredients which are perceived by consumers as more beneficial than chemical or animal ingredients.
Conclusion

The oxidative stability of cosmetic formulations is one of the most significant factors influencing the first impression of a consumer when they open and examine a container of a cosmetic product. Minimizing oxidative degradation in a formula will help ensure that the first impression will fit the target profile for the product. While the oxidative process is not well understood, there are empirical means available to rapidly and reliably evaluate the stability of components of a formula. The cost of this insurance is formulating with stable emollients and expending laboratory testing time; it is a small price to pay in return for underwriting a successful consumer trial.

References

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5. Regulations, Happi 34(3) 40 (1997)

Recommendations to Formulators and Marketers

- Avoid the use of high levels of almond oil, traditional sunflower oil and sesame oil in cosmetic formulations in order to achieve maximum oxidative stability.
- Minimize the use of other emollients containing high levels of polyunsaturates when an extended shelf life is required.
- Use hybrid sunflower oil, macadamia oil or jojoba esters containing tocopherols to provide emolliency as well as superior resistance to oxidative breakdown.
- Test all emollients individually for oxidative stability and in combination with any “active” ingredients to be incorporated in a formula. Do not assume that an emollient exhibiting oxidative stability in one system will perform the same in a different system.
- Test the combined oil phase of your formulation together with functional levels of any actives to be used in the formula.
- Know the shelf life of purchased emollients. Rotate raw material stocks frequently.

Table 1-6. Oxidative stability of botanical emollients in the presence of cosmetic “actives”

Example: To find the OSI stability (in hours) for 7% arbutin in combination with macadamia oil, find arbutin under “Additives”; follow the row across to the check mark, then down the column to the row containing OSI Hours for macadamia (100.5).

<table>
<thead>
<tr>
<th>Additives</th>
<th>1000 ppm Tocopherols</th>
<th>10% TiO₂</th>
<th>10% ZnO</th>
<th>10% Iron oxides</th>
<th>1% Kojic acid</th>
<th>7% Arbutin</th>
<th>2% Salicylic acid</th>
<th>5% Malic acid</th>
<th>3% Magnesium ascorbyl phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emollients (Neat)</td>
<td>OSI Hours</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Almond oil</td>
<td>5.2</td>
<td>9.6</td>
<td>6.5</td>
<td>4.4</td>
<td>0.9</td>
<td>4.8</td>
<td>5.5</td>
<td>2.3</td>
<td>4.8</td>
</tr>
<tr>
<td>Traditional sunflower oil</td>
<td>2.7</td>
<td>4.1</td>
<td>4.3</td>
<td>5.4</td>
<td>1.2</td>
<td>2.0</td>
<td>1.8</td>
<td>1.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Hybrid sunflower oil</td>
<td>31.7</td>
<td>59.2</td>
<td>84.5</td>
<td>53.7</td>
<td>34.2</td>
<td>66.0</td>
<td>56.5</td>
<td>70.7</td>
<td>97.1</td>
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<tr>
<td>Macadamia oil</td>
<td>21.0</td>
<td>103.6</td>
<td>203.1</td>
<td>36.5</td>
<td>41.9</td>
<td>114.2</td>
<td>100.5</td>
<td>120.2</td>
<td>148.6</td>
</tr>
<tr>
<td>Palm oil</td>
<td>21.3</td>
<td>30.6</td>
<td>42.0</td>
<td>27.0</td>
<td>17.0</td>
<td>47.7</td>
<td>40.3</td>
<td>42.7</td>
<td>69.0</td>
</tr>
<tr>
<td>Sesame seed oil</td>
<td>8.6</td>
<td>9.6</td>
<td>12.2</td>
<td>11.6</td>
<td>3.9</td>
<td>9.5</td>
<td>9.7</td>
<td>13.7</td>
<td>11.3</td>
</tr>
<tr>
<td>Jojoba esters 15</td>
<td>34.3</td>
<td>79.0</td>
<td>134.3</td>
<td>15.1</td>
<td>9.8</td>
<td>99.2</td>
<td>49.6</td>
<td>24.5</td>
<td>106.3</td>
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<tr>
<td>Jojoba esters 60</td>
<td>175.0</td>
<td>225.1</td>
<td>300.0</td>
<td>87.3</td>
<td>80.8</td>
<td>250.0</td>
<td>94.5</td>
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