Improved Oxidative Stability in Lipstick Systems

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Lipsticks are complex systems formulated through a combination of "art" and "science." A molded, semi-solid base, consisting of a mixture of crystalline and amorphous waxes, oils, esters and fatty alcohols, forms a microstructure in which several colorants are dispersed and suspended to yield the desired shade of a high fashion lipstick. Simply put, a lipstick is a composition of emollients (62-75%), waxes (12-20%) and "dries" (3-15%). The emollients are often castor oil and man-made esters, and the "dries" are primarily the coloring agents, made up of organic pigments, inorganic pigments, and/or nacreous pigments. Due to its stability and consistency, castor oil has been the primary emollient used in lipsticks in the U.S. for over 40 years. The reputation of castor oil's purgative effect has, over the past decade, caused lipstick formulators to look for alternatives. There has been a tendency to replace castor with other ingredients, including natural esters and oils, as the emollients of choice in these lipstick systems.

The selection of emollients for use in lipstick systems should take into account the oxidative stability of the emollients and its effect on the long-term shelf life of the product. If not chosen judiciously, unstable emollients can deteriorate rapidly causing rancidity and off odors in lipstick. Examples of oxidatively stable emollients with superior cosmetic properties in lipsticks are macadamia oil, high oleic sunflower oil, and jojoba esters.

**RANCIDITY**
Rancidity is generally recognized by a rotten or spoiled odor usually associated with old vegetable oils. Rancidity is caused by the action of oxygen on these materials, attacking points of unsaturation within the fatty acid portion of the vegetable oil triglyceride molecule. As the oxidation process continues, shorter chain acids, aldehydes, and ketones are created, altering the original texture and consistency of the lipstick, releasing peroxides and free radicals that can affect the original color and odor of the lipstick. Inexpensive vegetable oils such as almond, apricot kernel, safflower, grapeseed, wheat germ, etc. are expensive for a reason; they do very little to contribute to the long term shelf life of any lipstick or high color cosmetic.

**CAUSES OF RANCIDITY**
In order for a lipstick to be commercially viable it must be able to resist oxidative attack. Lipsticks are compounded and molded at relatively high temperatures (>75°C) under vigorous agitation, and then they are distributed through commercial warehouses and retail establishments, often for months, under less than optimum conditions. A combination of these events, plus use of unstable emollients in the formula, leads to rancidity and poor shelf life.

The primary causes of rancidity are oxidation. In order for a material to oxidize it must have sites for oxygen to attack. Generally these sites are unsaturated portions in the carbon chain, or double bonds, that can produce free radicals when in contact with oxygen. These free radicals are further degraded to short chain compounds such as acids and aldehydes that are odoriferous. The more double bonds present, the more likely a material will succumb to oxidation and become rancid.

Some examples of emollients with high levels of unsaturation (oxidatively unstable) are kiwi, rose hip, borage, and evening primrose oils. Although these are expensive oils, they are much more prone to rancidity than the inexpensive and unstable oil examples previously given. Other compounds enhance oxidation and are labeled pro-oxidants. In lipstick systems these are usually iron oxides, which are used as colorants.

The desire to use non-purging (non-castor), natural lipid and ester emollients in lipstick and other high cost systems needs to result in any sacrifice of shelf life, oxidative stability, or emollient effect. Macadamia oil, hybrid sunflower oil, and jojoba esters are all excellent emollients that deliver different degrees of gloss, payout and moisture retention, and at the same time are oxidatively stable. Lipstick formulas containing these emollients exhibit long shelf lives and resist rancidity.

**MEASUREMENT OF RANCIDITY OR OXIDATIVE STABILITY**
There are many methods of chemically evaluating the oxidative stability of materials or individual compounds. These methods involve monitoring the formation of short chain compounds by chromatographic, spectrophotometric, or electronic methods, measuring the uptake of oxygen, or monitoring the formation of oxygenated compounds such as peroxides. The time-honored method for determining oxidative stability of lipid materials is the Active Oxygen Method (AOM) (AOCS Official Method Cd 12-5793). This method entails the heating and holding of an oil at 97.8°C and determining periodic peroxide values until the peroxide value reaches 30. The time taken for the value to reach 100 is the AOM value. This method requires the determination of many peroxide values, which is very time consuming. The method of choice is now the Oxidative Stability Index (OSI) (AOS Official Method Cd 12b-92). This superior, automated method has had a long history of development. This method has been shown to produce more reliable and reproducible results than testing by the AOM method.

The OSI instrument, with its associated computer system, determines the oxidative stability index value. This is accomplished by passing a stream of air through an oil sample held at a constant temperature. As the test proceeds the effluent air from the sample then passes through a vessel containing deionized water, where conductivity of the water is continuously monitored. The effluent air, forced through the oil sample, contains volatile organic acids, swept by the oxidizing oil, thereby increasing the conductivity of the water. The length of time required for the conductivity rate of change to exceed a calculated value is the oxidative stability index value, expressed in OSI hours.

Figure 1 depicts the increased oxidative stability of various cosmetic oils according to Oxidative Stability Index values. All oils test-
ed in this study were purchased from cosmetic ingredient suppliers and were analyzed in duplicate for oxidative stability as soon after purchase as possible. Test results showed high oleic (>85% oleic) sunflower and macadamia oils to be among the most stable of non-purgetive oils. These oils show excellent oxidative stability even when compared to non-renewable materials such as mineral oil and saturated emollients such as squalane.

WAYS TO AVOID RANCIDITY AND IMPROVE SHELF LIFE

Castor oil has very good oxidative stability (OSI of 65-70 hours) and has been utilized extensively in lipsticks sold in the U.S. Apart from its well-known purgative effect, castor oil has also the disadvantage of causing a “dragging” sensation when applied to the lips. Much effort has been directed toward development of oils that are superior to castor oil for compounding lipsticks. Desirable improvements include: greater solvent power for staining dyes, lower viscosity or viscosity-temperature coefficient, less odor and greater stability, and a dependable supply. A more favorable consumer perception is also desired.

We have evaluated the stability of high-oleic sunflower oil and macadamia oil, alone and with iron based pigments used in lipstick formulations. In Table 1 we have compared the OSI stability of castor, macadamia, high-oleic sunflower, high-oleic safflower, almond, palm, and sesame oils, both neat and in the presence of iron oxides.

While it is obvious that the iron-based pigments reduced the oxidative stability of all oils tested, high-oleic sunflower, macadamia and castor oils lost relatively less than the other oils. All three of these oils have high levels of monoenoic fatty acids and very low levels of polyunsaturation. Both high-oleic sunflower and macadamia oils can be produced with low color and odor, and have relatively low viscosities.

In oxidative stability tests with actual lipstick formulations, a high-oleic sunflower formulation was tested against the same formula with sesami oil used in the place of high oleic sunflower. The stability of the high-oleic sunflower formulation far exceeded that of the sesame oil formulation. The lipstick made with the sesame became rancid in about six months when stored at ambient temperatures. The degradation of the sesame formulation can be predicted from the OSI data found in Figure 3.

The incorporation of antioxidants such as natural tocopherols is generally thought to prevent oxidation in all oils. However, those oils that are inherently unstable (high in polyunsaturates) will only be marginally improved by tocopherol addition. Those emollients with inherently stable compositions (low polyunsaturates) will be significantly improved through the addition of tocopherols. Macadamia and hybrid sunflower oils benefit significantly by the addition of tocopherols. Both of these oils are naturally stable due to their low levels of polyunsaturates. The addition of as little as 500ppm natural tocopherols to these oils boosts their oxidative stability significantly. Conversely, the addition of as much as 5000ppm (0.5%) tocopherols has been shown to have very little affect on oils that are inherently unstable. Figure 4 illustrates this point with a number of oils used in cosmetic formulations.

CONCLUSION

Natural emollients can be used effectively in cosmetic formulations. The use of emollients with high levels of polyunsaturates in lipsticks and other cosmetic systems will lead to rancidity and limited shelf life. Hybrid sunflower (Helianthus annuus) oil and Hawaiian macadamia oil (Macadamia integrifolia) contribute to long shelf life and have excellent emollient properties, particularly in highly pigmented cosmetic systems.

Table 1. OSI values (hours) of lipstick emollients.

<table>
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<tr>
<th>Emollient (*)</th>
<th>No Pigment</th>
<th>Iron Oxide</th>
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<tbody>
<tr>
<td>High-Oleic Sunflower (4.4%)</td>
<td>56.8</td>
<td>36.5</td>
</tr>
<tr>
<td>Macadamia Oil (3.1%)</td>
<td>53.3</td>
<td>41.9</td>
</tr>
<tr>
<td>Castor Oil (7.9%)</td>
<td>37.2</td>
<td>28.9</td>
</tr>
<tr>
<td>Palm Oil (8.0%)</td>
<td>17.0</td>
<td>8.5</td>
</tr>
<tr>
<td>High-Oleic Safflower (13.7%)</td>
<td>11.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Almond Oil (24.8%)</td>
<td>9.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Sesame Oil (43.8%)</td>
<td>9.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Traditional Sunflower (66.9%)</td>
<td>4.3</td>
<td>1.2</td>
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* Percent Polyunsaturates in the Named Emollient

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