Oxidative Stability of Botanical Oils in Color Cosmetics

James H. Brown, Robert Kleiman and Melanie Cummings

International Flora Technologies, Ltd., Gilbert, Arizona USA

Key words

botanicals, emollients, lipstick, testing, measuring oxidative stability

Abstract

Some cosmetic emollients are particularly susceptible to oxidative degradation when used in the presence of metal oxides. This study examines the results of studies to identify emollients that are less susceptible.

Although consumers prefer labels that communicate "natural" or "botanical" themes (see sidebar), there are often both real and perceived risks associated with the use of natural- or botanical-based ingredients, particularly if the ingredients are unknown to the formulator or if they are being used in a cosmetic system for the first time.

In our lab, we have evaluated botanical and chemical emollients in lipstick systems containing high levels of pigment that challenge the oxidative stability of the formulation. A new device for measuring oxidative stability and a procedure for using it have allowed us to compare the oxidative stability of some botanical-based oils versus standard "chemical emollients" broadly used in cosmetics.

In the present study, we have identified both botanical and chemical emollients that help ensure extended product shelf life in the presence of high pigment loading. We have also identified other emollients that the formulator should minimize or avoid altogether in formulations in order to reduce the risk of oxidative degradation that decreases the shelf life of cosmetic products.

Some Botanicals Bring Risks

Mother Nature often proves to be a difficult partner in commercial ventures. Crop failures in remote parts of the world, inconsistency in quality and uncontrollable events sometimes interrupt the supply chain of botanicals. This supply uncertainty may discourage the use or even trial of natural or botanical ingredients. The increasing cost of toxicological research and efficacy testing is also a barrier to the proliferation of new botanical ingredients.

Our research has focused on comparing the oxidative stability of some old and new botanical emollients as compared to well-known chemical (synthetic) emollients. We have shown that some broadly used botanical emollients bring risks of degradation due to oxidative instability. We have identified some botanical emollients that are as stable as chemical emollients commonly used in the industry. We have also identified some chemical emollients that are not stable in the highly pigmented system that we used to evaluate the emollients.

The Botanical Bias

Consumer awareness of cosmetic ingredients has increased worldwide over the past quarter century as full disclosure labeling has been implemented in the USA (March 1974), Europe (January 1997) and Japan (April 2001). In more recent years, botanical ingredients (as well as other natural ingredients) have increasingly been chosen for their label appeal. Often, ingredient choices are made in response to real or perceived dangers, such as the infamous Mad Cow Disease (BSE) scare that brought sweeping changes to the cosmetic and other industries in 1996-1997.

The focus on "botanicals" brings new marketing opportunities but, at the same time, some challenges to formulators.

Measuring the OSI of Emollients

With the new technology we selected – the Omnion Oxidative Stability Instrument (OSI) and the AOCS method – we are able to predict the oxidative stability of commonly used emollients and therefore identify their likely contribution to either a long or short shelf life of cosmetic products in which they may be used.

In our study we focus on comparing the oxidative stability of commercially available botanical emollients to a group of chemical emollients commonly used in lipsticks. We chose the lipstick system for this evaluation because of the challenging environment created by high levels of pro-oxidant pigments (iron oxides) typically used in lipsticks. Although it is impossible to translate oxidative stability in lipsticks to oxidative stability across all cosmetic systems, it is probable that principles we discovered in our study can serve as guidelines when considering use of these emollients in other formula systems.

Determining oxidative stability: The Omnion OSI instrument[a] and corresponding American Oil Chemists' Society (AOCS) method Cd 12b-92 is rapidly becoming the method of choice for determining the oxidative stability of lipid materials in the cosmetics industry. This instrument and method is the latest technology, replacing the previously used

Active Oxygen Method (AOM) for determining oxidative stability.

The instrument is quite simple to use, requires very little manpower and is an accurate and reproducible indicator of the oxidative stability of lipid materials. The operation of the instrument is presented in Figure 1 and involves a measured amount of ambient air (as an oxygen source) being forced through a 5-gram sample of the test material held at a constant temperature. As oxidative degradation (onset of rancidity) of the lipid material begins, short-chain fractions of the lipid break away from the lipid molecule and are swept with the air stream into a conductivity cell. This cell detects minute increases in conductivity created by the presence of the short-chain fractions that have been swept into the distilled water. A computer examines the signal from the detector and plots the endpoint of the reaction, which is recorded as an inflection point measured in OSI hours. A typical collection of OSI data plotting the oxidative stability of different emollients is presented in Figure 2.

Emollients selected for study: We purchased a number of commercially available lipsticks and, from ingredient statements on those labels, we selected a group of botanical and chemical emollients for our study. Samples of each emollient were obtained from suppliers and the emollients were tested as received. Table 1 lists the botanical and chemical emollients that we tested. The solid bars in Figure 3 shows the OSI (in hours) of each as it was received from the supplier.

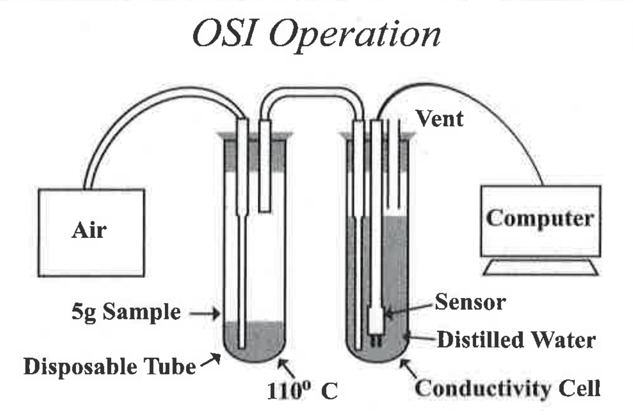

Figure 1. OSI Operation

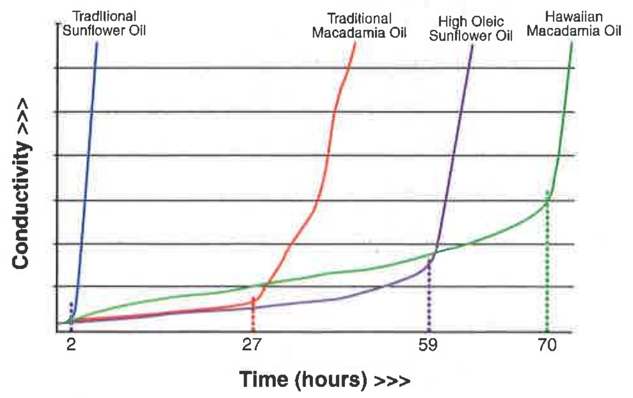

Figure 2. Typical OSI graph

Results of OSI Studies

Inherent oxidative stability: As expected, Mother Nature does not introduce equivalent oxidative stability in all botanical emollients. The oxidative stability of chemical emollients also varies considerably, as can be seen in Figure 3. We did find, however, that as a rule of thumb, botanical oils containing less than 5% polyunsaturated fatty acids or fatty alcohols exhibited inherent oxidative stability while those with greater than 5% polyunsaturates were inherently unstable.

To demonstrate this finding, we plotted the OSI of various botanical oils against the percentage of polyunsaturates found in the oil. A tremendous improvement in oxidative stability can be seen in Figure 4 when the polyunsaturate level of the botanical oil is less than 5%.

Adding tocopherols: Antioxidants can be used to extend the oxidative stability of emollients, both botanical and chemical. In the next phase of our testing we added 1000-ppm mixed natural tocopherols to each of the selected emollients and repeated the OSI testing. The results are presented in the hatched bars of Figure 3 and are quite dramatic for some of the emollients, particularly those in the chemical group.

Improvements in OSI results were noted as tocopherols were added to the inherently stable botanical emollients, however, adding tocopherols to inherently unstable botanical emollients (such as safflower oil, almond and sesame oil) did not significantly improve the oxidative stability of those oils. To demonstrate this principle further, we added increasing amounts of tocopherols (up to 5,000 ppm) to both inherently stable and inherently unstable botanical emollients and plotted their resulting OSI's vs. the amount of tocopherol added. Figure 5 clearly demonstrates the improvement in oxidative stability of the inherently stable emollients upon addition of tocopherols and the futility of adding higher levels of this antioxidant to inherently unstable emollients.

Table 1. Botanical and synthetic materials tested

Botanical	Synthetic
High Oleic Sunflower Oil (Florasun 90)	Caprylic/Capric Triglyceride
Hawaiian Macadamia Nut Oil	Octyl Dodecanol
Jojoba Esters (60)	Isopropyl Isostearate
Sesame Oil	Cetyl Alcohol
Hybrid Safflower Oil	Octyl Palmitate
Almond Oil	Oleyl Erucate
Lanolin Oil[1]	Triolein
Castor Oil	

[1] Natural product but not botanical based.

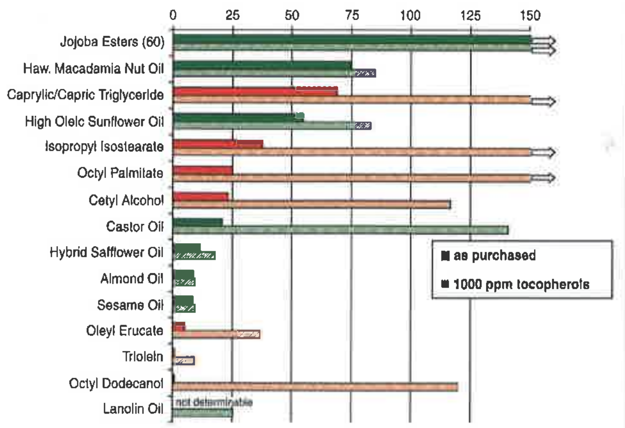

Figure 3. OSI comparison of "As Purchased" plus addition of 1000 ppm tocopherols

Adding tocopherols and pigments: In the next phase of our testing we added 10% titanium dioxide (TiO$_2$) to each of the emollients containing tocopherols and determined the OSI of the emollient in the presence of the TiO$_2$. We had previously considered titanium dioxide as a pro-oxidant in lipsticks and were surprised to find (Figure 6) that the combination of TiO$_2$ with tocopherols actually extended the oxidative stability of several of the emollients, in particular Hawaiian macadamia nut oil, high oleic safflower oil and octyl dodecanol. TiO$_2$ had marginal effect on the other emollients tested and, with the exception of almond oil, did not decrease the OSI of any emollient.

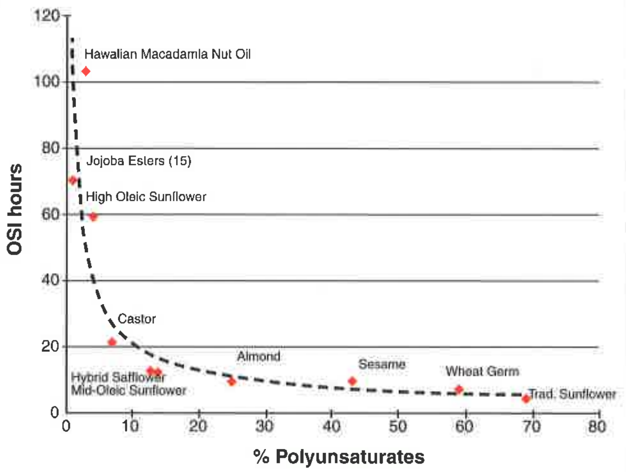

Figure 4. OSI vs. level of polyunsaturates

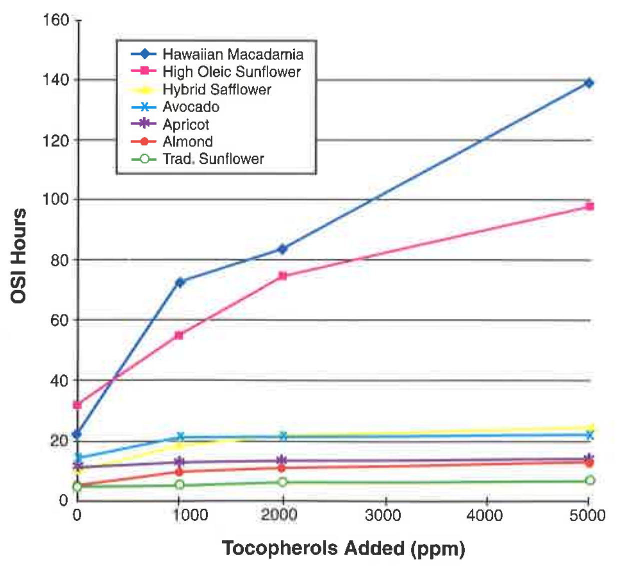

Figure 5. More antioxidants are not the answer!

We next added 10% iron oxide pigment to each of the emollients containing tocopherols and determined the OSI of the mixture. The addition of 10% iron oxide to the emollients reduced the OSI of each emollient with the exception of cetyl alcohol. Other than this noted exception, both botanical and synthetic emollients were affected by the presence of the iron oxide. Some of the most dramatic reductions in stability can be seen (Figure 7) with caprylic/capric triglyceride, isopropyl isosterate, castor oil and octyl dodecanol. Jojoba esters 60, octyl palmitate and cetyl alcohol remained relatively stable in the presence of iron oxide.

Oxidative stability of commercial lipsticks: Without revealing brand names, Table 2 illustrates a typical range of OSI values obtained when testing a variety of off-the-shelf lipstick products. A "mocha brown" shade of six commercial brands was purchased and tested to determine the OSI value of each lipstick. Table 3 illustrates shade-to-shade variation in oxidative stability that we found within one popular brand of moisturizing lipstick purchased in Phoenix, Arizona.

The 5% limit on polyunsaturates: As a practical demonstration, we prepared a Moisturizing Lipstick containing 3% polyunsaturates as exhibited in Formula 1 of Table 4. The OSI of this formulation was determined to be 36 hours. We then substituted 5% sesame oil and 5% wheat germ oil for an equivalent amount of high oleic (>85%) sunflower oil and macadamia nut oil to achieve a polyunsaturate level of 7% in the formula. The presence of this 7% polyunsaturate level in the formula caused the OSI of Formula 2 to be reduced to 17 hours. Small differences in polyunsaturate levels cause exponential differences in the oxidative stability of lipid-based products.

Acceptable OSI values: In general, we would expect an OSI result of 20 hours to equate to one year of commercial shelf life, although this guide is difficult to offer as a rule of thumb due to the many different factors that come into play as manufactured products enter the distribution chain. Cosmetic manufacturers should insist that emollient suppliers deliver products of known oxidative stability and with a shelf life guaranteed from the date of delivery.

Summary

Selected botanical emollients can be used in highly pigmented color cosmetics without sacrifice of oxidative stability. Examples of

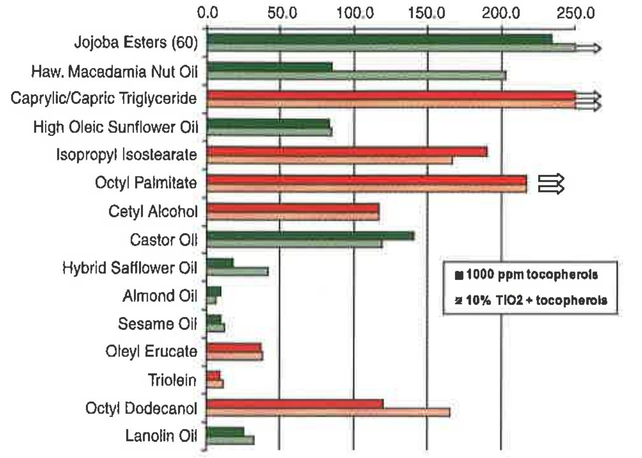

Figure 6. OSI comparison of emollients with 1000 ppm tocopherols plus 10% TiO$_2$

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[a] *The Omnion OSI 8 is manufactured by Omnion, Inc., Rockland, MA USA*

botanical emollients that performed well in oxidative stability testing are jojoba esters 60, Hawaiian macadamia nut oil and high oleic (>85%) sunflower oil. Octyl palmitate, caprylic/capric triglycerides and isopropyl isostearate were chemical emollients that also performed well in our tests.

Formulators who wish to maximize the shelf life of their products should minimize the use of emollients containing in excess of 5% polyunsaturates. The list of those botanical emollients that should be used sparingly or not at all due to their high level of polyunsaturates includes the following oils: sesame, almond, wheat germ, hybrid safflower and traditional sunflower. Lanolin oil, octyl dodecanol, oleyl erucate and triolein are also high in polyunsaturates.

Octyl dodecanol, oleyl erucate and triolein are synthetics that performed poorly in our testing. Titanium dioxide, in the presence of tocopherols, was found to improve the oxidative stability of most emollients and marginally reduced the stability of almond oil, a typically unstable emollient. Iron oxide causes a reduction in oxidative stability in both botanical and chemical emollients and effects some emollients more than others.

Oxidative stability testing is an inexpensive routine, which can be employed to help formulators predict the ultimate shelf life of products containing botanical or chemical emollients.

Table 2. Brand-to-brand lipstick stability comparison (red/brown tone)

Brand	Shade	OSI Hours
A	Toffee	67
B	Silver Plum	65
C	Mochaccino	35
C	Hazelnut	86
D	Autumn Leaves	28
E	Mochaccino	46
F	Megaccino	10

Table 3. Shade-to-shade lipstick stability comparison (within one brand)

Shade	OSI Hours
Iced Pink	48
Sunset Frost	22
Chocolate Mousse	>150
Mulberry	107
Really Pink	59

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References

Address correspondence to James H. Brown, c/o Editor, *Cosmetics & Toiletries* magazine, 362 South Schmale Road, Carol Stream, IL 60188-2787 USA.

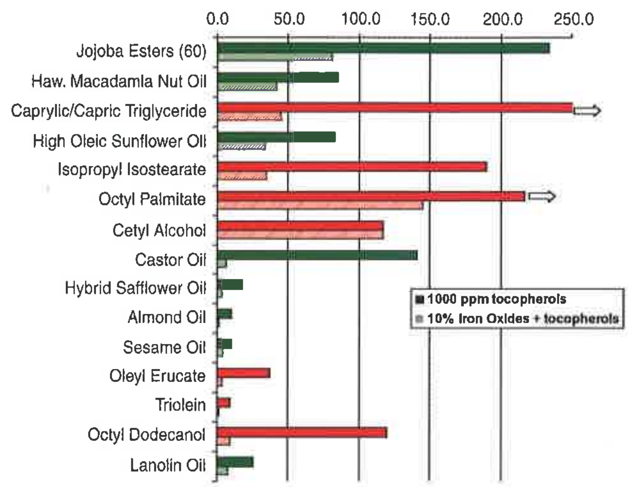

Figure 7. OSI comparison of emollients with 1000 ppm tocopherols plus 10% iron oxide

Table 4. Lipstick formula comparison

		#1	#2
A.	Hybrid sunflower (*Helianthus annuus*) oil (Florasun 90, Floratech)	11.4	6.4
	Macadamia integrifolia seed oil (Floramac Hawaiian Macadamia Nut Oil, Floratech)	22.0	17.0
	Jojoba esters (Floraesters 30, Floratech)	17.0	17.0
	Sesame (*Sesamum indicum*) seed oil (Sesame Oil, Arista)	0	5.0
	Wheat (*Triticum Vulgare*) germ oil (Wheat Germ Oil, Croda)	0	5.0
	Jojoba esters (Floraesters 70, Floratech)	1.0	1.0
	Carnauba (*Copernica cerifera*) wax (Carnauba Wax #1 Yellow SP 63, Strahl & Pitsch)	4.0	4.0
	Candelilla (*Euphorbia cerifera*) wax (Candelilla Wax SP 75, Strahl & Pitsch)	5.0	5.0
	Beeswax (*Cera alba*) (Yellow Beeswax SP 6P, Strahl & Pitsch)	3.5	3.5
	Microcrystalline wax (Microcrystalline Wax SP 18, Strahl & Pitsch)	4.0	4.0
	Polybutene (Indopol H-100, Amoco)	5.0	5.0
	Propylparaben	Q.S.	Q.S.
	Silica (CAB-O-SIL M 5, Cabot)	0.5	0.5
B.	Castor (*Ricinus communis*) seed oil (Crystal "O", CasChem)	13.0	13.0
	Polyhydroxystearic acid (Arlacel P-100, ICI)	0.5	0.5
	Titanium dioxide (Titanium Dioxide 10-34-PC-0748, Noveon)	5.5	5.5
	Iron Oxides (red) (Pur Oxy Red BC 34-3511, Noveon)	4.5	4.5
	FD&C Red 30 Talc Lake (FD&C Red 30 Talc Lake 10-31-DA-3130, Noveon)	2.0	2.0
	FD&C Blue 1 Al. Lake (FD&C Blue 1 Al. Lake 09903, Warner-Jenkinson)	0.1	0.1
	Iron oxides (black) (Pur Oxy Black BC 34-3068, Noveon)	0.5	0.5
C.	Tocopherol (Covi-Ox T-70, Cognis)	0.1	0.1
	Fragrance (*parfum*), optional	Q.S.	Q.S.
		100.0	**100.0**

Figure 1 was revised by Flora Technologies, Ltd. after issue date of material with permission of the publisher.
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