Orange Peel Wax

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The cosmetic industry changes at such a rapid rate that many times, it is difficult to keep up, especially with raw materials. Demands from cosmetic manufacturers considering a new raw material include: active chemical functionality, quality, environmentally friendly technology and cost-effectiveness.

As disposal costs rise and outlets for by-products dwindle, by-products of industrial processes are becoming of greater interest. One such by-product is orange peels from the food industry. From these, essential oils can be derived for the personal care industry. The impurities in the oils are then refined, without solvents, to produce the orange peel wax.

Citrus peel products have long been used for grease removing, moisturizing, emollient, and refreshing and toning effects on the skin. The orange cuticle and surface waxes are most important in regulating the fruit's water loss; uptake and loss of chemicals; resisting and reducing bacterial invasion; and resisting freezing. Skin lipids have similar attributes and functions.

In this paper, we will establish the chemistry of orange wax[a] and to substantiate its multi-functional properties, which make it suitable for cosmetic applications.

Chemistry and Physical Attributes

Orange wax is light reddish-brown to orange in color, depending on the level of refinement. A semi-solid, it has a mild to very low characteristic odor, which is also refinement dependent. These basic physical properties are attributed to a wide array of chemical functionality. Some of the typical physical properties are shown in Table I. A comparison of these values with those of lanolin (Reference 1) shows remarkable similarities. The melting point of orange peel wax is slightly higher than that of lanolin, but the acid, saponification and hydroxyl values, and the appearance, are all basically the same. Many one-to-one substitutions of orange wax for lanolin, using published formulas, have resulted in products with no observable differences in feel or stability. In some cases, an off-color and slight, characteristic odor were detected, due to high usage levels. Sample formulas, giving suggested uses in various color cosmetic and skin care products, accompany this article.

Table I. Physical properties of orange peel wax

	Refined	*Deodorized*
Melting point	45 to 57°C	35 to 50°C
Congealing point	45 to 55°C	30 to 45°C
Acid value	8 to 20	10 to 20
Saponification value	70 to 110	70 to 110
Hydroxy value	20 to 50	10 to 40
Appearance	Semi-solid	Semi-solid

One of the attractions of using a naturally derived product is its inherent chemical diversity. Orange wax is no exception. Table II illustrates the global chemical composition.

Approximately 50% of the orange peel wax consists of unsaturated monoesters (neutral lipids) of unsaturated fatty acids and long-chain alcohols. The fatty acid portion has been determined, through separation of the saponifiable and unsaponifiable fractions of the wax followed by gas chromatographic analysis, to consist of linoleic, oleic, linolenic, arachidic and erucic acids. The fatty alcohol portion of the ester is predominantly dotriacontanol (C-32) and tetratriacontanol (C-34). Esters of this type are typically used for their moisturizing and emollient properties. Other sources of unsaturated fatty acids in orange wax are the glycolipids and phospholipids, which average approximately 75% unsaturated fatty acid, the remainder being saturated and hydroxy fatty acids.

Nature has provided the plant kingdom with a host of biologically active compounds. Orange wax contains: carotenoids

[a] Patent pending, Koster Keunen

Table II. Primary chemical composition of orange wax by percent

Unsaturated-monoesters, hydroxy-monoesters and monoesters	50 to 65%
Free fatty acids; C-12 to C-26	6 to 15
Hydrocarbons; C-21 to C-33	8 to 15
Sterol esters	5 to 18
Free sterols	4 to 8
Free alcohols	2 to 7
Carotenoids	0.5 to 2
Glycolipids	0.5 to 2
Phospholipids	0.5 to 2
Flavonoids	0.2 to 1
Fragrance compounds (natural)	0.2 to 0.8

Eye Shadow Stick

Orange wax[a]	10.00%
Light mineral oil	41.00
#1 Yellow carnauba[a]	3.00
Candelilla wax[a]	7.00
Cetyl stearyl alcohol	4.00
Isopropyl palmitate	10.00
Hexanediol behenyl beeswax[a]	6.00
Ozokerite 170[a]	4.00
Titanium dioxide[b]	14.00
Purified navy blue[b]	1.00
	100.00

[a]Koster Keunen
[b]Whittaker, Clark & Daniels

Procedure: Disperse pigments in orange wax over low heat in a beaker with a glass stirring rod. Once dispersed, add remainder of components, mix and melt. Continue mixing; pour into molds at approximately 60°C.

Table III. Components of orange peel wax with color or aroma characteristics

Color compounds		Aroma compounds
Carotenoids	*Comments*	*Alcohols, aldehydes, ketones, esters and hydrocarbons*
phytoene		octan-1-ol
phytofluene		nonanal
α-carotene	vitamin A precursor	linalool
β-carotene	vitamin A precursor	*p*-mentha-2,8-dien-1-ol
γ-carotene	provitamin A	sabinol
δ-carotene	vitamin A precursor	isopulegol
lycopene		4-methylacetophenone
cryptoxanthin	similar to vitamin A	α-terpineol
hydroxy-α-carotene		ethyl-octanoate
cyroflavin		decanal
rubiflavin		carveol
rubixanthin	similar to vitamin A	neral
lutein		carvone
canthaxanthin	oral suntanning agent	piperitone
zeaxanthin		geranial
antheraxanthin		perillyl alcohol
violaxanthin		α-cubebene
luteoxanthin		hexyl hexanoate
auroxanthin		β-elemene
β-citraurin		β-farnesene
flavoxanthin		caryophyllene
sintaxanthin		γ-selinene
xanthophylls		β-copaene
		δ-cadinene
		bisabolene
		valencene

(anti-oxidants, vitamin precursors and natural pigmentation), essential oils (aromatherapy), sterols (anti-inflammatory activity) and flavonoids (anti-microbial, anti-oxidant and sunscreen-enhancing properties).

The chemical compounds associated with color and aroma have been characterized in the literature (References 2 and 3). Their importance has spurred research in natural food coloring and antioxidants. Orange essential oils have long been sources of aroma and flavor. Table III gives a general summary of the compounds associated with these sensory properties.

With citrus products, a major concern is the presence of certain types of terpenes (for example, 5-methyl-psoralen), which are phototoxic. However, when we analyzed orange wax by using gas chromatography/mass spectrometry (GC/MS), we found no phototoxic compounds and only low concentrations of assorted terpenes.

Sterols were identified through method of addition, the incorporation of a pure compound into the overall mixture at a predetermined concentration. Orange wax had a few percent of stigmasterol and sitosterol added to the composition. Their excess recovery by GC analysis provided a general concentration of these compounds in our wax. Sitosterol and esters of sterol glycosides make up the bulk of this fraction. Our research into this fraction is still under investigation. Also worth mentioning are the phospholipids, with the predominant type being phosphatidylcholines, and lesser amounts of phosphatidylglycerols, phosphatidylserines and phosphatidylinositols (Reference 2).

Orange wax flavonoids may be the most important of the biologically active compounds in this product. Their activity and presence in natural products in general has been the subject of research in many laboratories. The predominant flavonoids of orange wax are: hesperidin (trihydroxy-methoxy-flavanone) and naringin (trihydroxy-flavanone) (References 4 and 5). Also isolated with the flavonoids, from the same reference source, were the phenolic acid compounds ferrulic acid and caffeic acid, which are known anti-oxidants and anti-microbial agents.

Chemistry and Effective Activity

Chemists designing cosmetics must consider the functional effects products will have on the skin. Cosmetic preparations that are applied to the skin generally consist of few types of ingredients: lipids, inorganics and surfactants, which may alter the epidermis. Finished products containing lipids emulsified with surfactants may penetrate into the stratum corneum more rapidly then individual lipids. Once the applied lipids absorb and mix with the naturally present lipids, the mixture may undergo chemical changes due to the skin environment. These chemical changes can alter the permeability of the lipid layer, in turn affecting the true physiology of the skin. Basic skin physiology functions to protect the body from toxic agents and damage from ultraviolet radiation.

In general, skin lipids comprise polar lipids, neutral lipids and sphingolipids. All of these general chemical groups are represented in orange peel wax. (For a detailed comparison, refer to Table IV.)

Table IV. Skin lipid composition compared to orange wax chemistry

Lipid type	*Human skin (various sites)*	*Orange wax*
Wax esters	15 to 25%	50 to 65%
Sterol esters	2 to 6	5 to 18
Triglycerides and complex esters	12 to 25	
Free sterols	2 to 10	4 to 8
Free fatty acids	2 to 20	6 to 15
Hydrocarbons/alkanes	3 to 6	8 to 15
Squalene	3 to 10	
Glycosphingolipids I and II	2 to 7	0.5 to 2
Ceramides	10 to 22	
Phospholipids	3 to 6	0.5 to 2
Cholesterol sulfates	1 to 6	

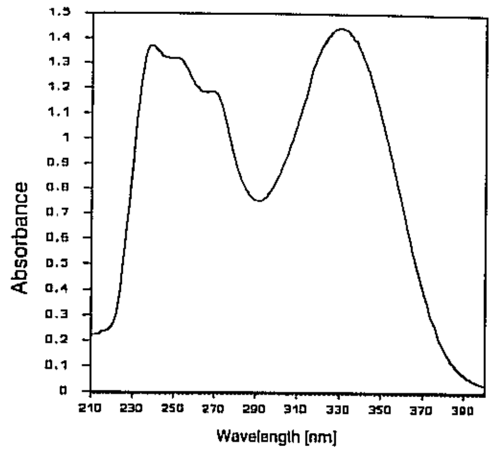

Figure 1. UV/VIS absorption spectrum of orange wax in butanol; 1.028 x 10^{-4} g/ml

There are striking similarities in the chemical compositions of orange wax and skin lipids. In both, chemical functionality and component weight percent distribution are alike.

Sunscreen-Enhancing Properties

Flavonoids, carotenoids and unsaturated monoesters all have strong UV-absorptive properties. Figure 1 is the absorption spectrum of orange wax in butanol, which was chosen for its solubility properties and low absorption in the far-UV range (210 to 240 nm).

The extinction coefficient (EC or ε) for orange wax is ε = 7793 at 330 nm and ε = 6770 at 270 nm, if we approximate the molecular weight of the wax as 580 g/m. An EC this high will produce UVA and UVB sunscreen properties. Becau orange wax is not a category I sunscreen under the FDA monograph, formulators can only use orange wax to enhance a product's UV-absorbing properties. However, reducing the concentrations of synthetic sunscreens by use of UV enhancers produces finished products of high efficacy and lower irritation potential.

Anti-Oxidant Properties

Many of the cosmetic ingredients used today are prone to oxidation, causing the onset of product rancidity. The components in orange wax responsible for its sunscreen-enhancing properties also show remarkable anti-oxidant properties. This was easily demonstrated by an auto-oxidation experiment. Oxidation by-products alter the physical and chemical properties, and can be easily measured.

We auto-oxidized orange wax to first see if the product forms oxidation by-products. Oxidation was carried out at 100°C, with an air flow of ≈100 cc/minute through a sparger bubbling through the molten wax. To create an environme. which promotes oxidation, a free radical initiator (benzoyl peroxide) was added to the molten wax.

Peroxide values were determined to detect the chemical functionality which is first produced in an auto-oxidation experiment. Benzoyl peroxide forms free radicals during thermal degradation; subsequent abstraction of hydrogen ions from a lipid forms radicals with which oxygen reacts, creating peroxides. It is clear from Table V that orange wax does not auto-oxidize, even under conditions designed to promote oxidation.

Another important criterion is how effective the anti-oxidant properties are when it is incorporated into an oil that is highly susceptible to oxidation. For the test, linoleic acid was chosen for its poor thermal stability and ease of oxidation.

Figure 2 illustrates the anti-oxidant properties of orange wax compared to two common anti-oxidants. Adding orange wax to linoleic acid at a 5% concentration provides stronger anti-oxidant properties than 0.5% BHT. Orange wax is also a better inhibitor of peroxide formation in linoleic acid than is vitamin E.

Table V. Orange wax auto-oxidation

Time (hr)	*Peroxide value (ppm)*	*Temperature (°C ± 5°C)*	*Benzoyl peroxide concentration (ppm)*
0	1.5	100	0
2	1.5	100	0
4	1.5	100	25
8	1.5	100	-
10	1.5	100	75
12	1.5	100	-
14	1.5	100	-
18	1.5	100	-
24	1.5	100	-

Antimicrobial Properties

A simple microbial challenge test was performed on the orange wax after it was incorporated into a water dispersion at 10% concentration.[b] Varying bacteria, yeast and mold were used at an initial concentration of 100,000 organisms per ml. Though the sample of the 10% orange wax dispersion did not retard microbial growth of all organisms for the 28-day test period, it did show mild antimicrobial activity against mold and *S. aureus*. This function is attributed to some of the same compounds which are responsible for the UV-absorbing and anti-oxidant properties.

[b] By Collaborative Laboratories, East Setauket, NY

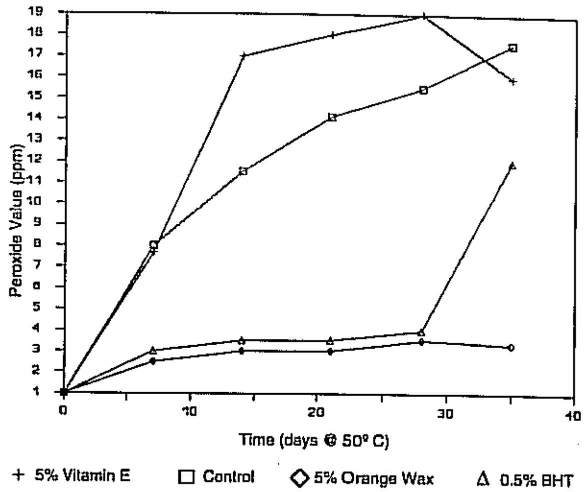

Figure 2. Oxidation inhibition in linoleic acid; orange wax vs commercial antioxidants

Sunscreen Cream with Orange Wax

Orange wax should enhance expected SPF of 4 - 6.

A.	Orange wax[a]	4.00%
	Stearic acid[a]	2.00
	Ceresine 130/135[a]	0.50
	Emulsifying wax NF[a]	1.00
	Light mineral oil	3.00
	Beeswax NF white[a]	1.00
	Cetyl stearyl alcohol	2.00
	Octyl methoxycinnamate (Parsol MCX)[b]	5.00
B.	Propylene glycol	5.00
	Water	75.50
	Triethanolamine	0.20
	Carbomer 940	0.30
C.	Vitamin E	0.50
		100.00

[a]Koster Keunen
[b]Givaudan-Roure

Procedure: Mix and melt A at 80°C. Mix B to dissolve; heat to 80°C. Add A to B under agitation; mix and cool to 50°C. Add C; mix until homogeneous. Pour into container.

Pesticides

We live in a world where a common belief is "better living through chemistry." Producers/refiners of natural products must deal with the habitual use of chemical pesticides in agriculture.

We spent much of our initial research time determining technology which would render orange wax pesticide-free. After three years and dozens of batches, we have produced a short, historical database on this newly developed raw material. This database contains the basic chemistry and, more importantly, pesticide data. Each batch of orange wax was analyzed at two certified laboratories on two continents in New York and Germany. The two classes of pesticides most often used in agriculture, based on our sources, are organohalogen and organophosphorus compounds. Analysis for these classes is done by GC/MS, which actually compares spectra of compounds too numerous to list in the above-mentioned pesticide categories. We are safe in saying that orange wax contains not more than 50 ppb of any individual pesticide. The U.S. Pharmacopeia allows one

Lipstick

	Pink	Neutral
Orange wax[a]	12.00%	12.00%
Hexenediol behenyl beeswax[a]	15.00	15.00
Candelilla wax[a]	3.00	3.00
#1 Yellow carnauba[a]	3.00	3.00
Ozokerite 170[a]	3.00	3.00
Apricot kernel oil	10.00	10.00
Sweet almond oil	30.00	27.50
Phenyl trimethicone (Silicone 556)[b]	15.00	15.00
Light mineral oil	5.00	5.00
Titanium dioxide[c]	3.00	3.00
D&C red 7 calcium lake[c]	1.00	-
Pearl pigment[d]	-	1.00
Brown iron oxide[c]	-	1.00
Yellow BC iron oxide[c]	-	1.50
	100.00	100.00

[a]Koster Keunen
[b]Dow Corning
[c]Whittaker, Clark & Daniels
[d]Rona

Procedure: Disperse pigments in orange wax in a beaker with a glass stirring rod. Once dispersed, add remainder of components, mix and melt. Pour into mold at approximately 60°C.

Exfoliating Cream

A natural exfoliating agent easily dispersed in this cream formula gives a non-irritating, abrasive quality.

A.	Orange wax[a]	3.50%
	White beeswax NF[a]	1.00
	Isostearic acid	3.00
	Almond oil	3.50
	Light mineral oil	4.00
	Glycerol monostearate	1.50
	Cetyl stearyl alcohol	1.00
	Octyl palmitate	3.00
B.	Water	65.60
	Propylene glycol	2.50
	Triethanolamine	1.00
	Polysorbate-60	0.20
	Carbomer 940	0.20
C.	Microgranulated carnauba, 20-60 mesh[a]	10.00
		100.00

[a]Koster Keunen

Procedure: Add mixed and uniform A to mixed and uniform B at 75°C under agitation. Continue mixing; cool to 50°C. Add C; mix until homogeneous.

ppm of any individual pesticide in lanolin.

The two laboratories showed concurring results. No individual pesticide was found in a concentration above 38 ppb. In such batches, most other pesticides were below detection limits of 10 ppb. Orange wax, for all practical purposes, is pesticide-free.

Toxicology/Anti-inflammatory Properties

Besides having functional properties to suit an array of cosmetic applications, a cosmetic raw material must be safe on the body. Orange wax has had the necessary safety testing performed on it to ensure its use in all types of applications.[e] Testing was not conducted on animals. Orange wax, tested 100%, showed:

- No irritation potential (human patch test),
- No phototoxicity (human test), and
- No irritation potential (in vitro toxicity).

Toxicology testing of orange wax has proven it to be safe; so, we are able to equate its non-irritation potential to the anti-inflammatory properties. Sterols and sterol esters have been shown to have anti-inflammatory properties in cosmetic and OTC preparations.[6] In the past, citrus products have produced slight irritation and phototoxic effects due to certain terpenes. Orange wax has no irritation potential and no phototoxicity largely due to the absence of those terpenes and to the anti-inflammatory properties of the sterols and sterol esters.

Conclusion

The multifunctional advantages of using orange wax are based on its chemistry. A series of sample formulas is given here to demonstrate some of its potential uses. Other products in which orange wax could be used to advantage include: lotions, mascaras, shampoos, conditioners, shaving creams and soaps. Properties associated with incorporation of orange wax into a formula are: moisturizing; emolliency; UVA and UVB sunscreen enhancement; natural anti-oxidancy by free-radical scavenging; mild antimicrobial activity; anti-

[e]Consumer Product Testing Co., Fairfield, NJ conducted all testing

inflammatory and analgesic activity; and virtually no irritation potential.

Orange wax is acceptable for cosmetic use in the United States and Europe, and has been submitted for approval as a cosmetic ingredient in Japan. Research on the total chemical composition and application potential of this wax continues. Orange wax is a "green" product, derived from a renewable plant source. It is biodegradable, thus in tune with the current marketing as well as global environment.

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C&T

Emollient Liquid Makeup

A.	Xanthan gum	0.33%
	Cellulose gum	0.23
	Water	50.55
	Triethanolamine	0.70
	PEG-1450	2.35
	Methylparaben	0.28
	Propylene glycol	1.88
	Polysorbate-60	0.47
B.	Titanium dioxide[a]	8.44
	Brown iron oxide[a]	2.35
	Yellow BC iron oxides[a]	0.94
	Orange wax[b]	6.10
	Cera bellina[b]	4.69
C.	Octyl palmitate	6.57
	Cyclomethicone (Silicone 245)[c]	2.00
	Isopropyl palmitate	6.10
	Hydrogenated castor oil	1.41
	Isostearic acid	1.50
	Jojoba oil	0.94
	Propylene glycol stearate	1.89
	Propylparaben	0.28
		100.00

[a] Whittaker, Clark & Daniels
[b] Koster Keunen
[c] Dow Corning

Procedure: Disperse pigments in orange wax and cera bellina in beaker with glass stirring rod. Mix, heat C to 75°C. When uniform, add to B under agitation; maintain temperature until homogeneous. Add mixed-and-melted BC to mixed-and-melted A. Continue mixing while cooling. Pour into containers at approximately 50°C.