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(54) **Title**: SUNLESS TANNING WITH PYRANONES AND FURANONES

(57) **Abstract**: A composition and method for imparting a sunless tan to skin is described. The composition and method make use of a sunless tanning agent like dihydroxyacetone in combination with an adjuvant which is a pyranone, furanone or a mixture thereof.

SUNLESS TANNING WITH PYRANONES AND FURANONES

FIELD OF THE INVENTION

The present invention is directed to a composition and method for imparting a sunless tan to skin. More particularly, the invention is directed to a composition and method that employ a sunless tanning agent as well as an adjuvant for the sunless tanning agent. The composition employs a pyranone furanone, derivative thereof or mixtures thereof as an adjuvant and, when applied, unexpectedly results in the consumer having skin with a brownish/tan coloration within a consumer acceptable time. Surprisingly, the composition does not result in color body generation even when the sunless tanning agent and adjuvant are stored together in a monophase.

BACKGROUND OF THE INVENTION

Sunless tanning agents are formulated into two types of cosmetic products. Of these, the most traditional is the self-tanning lotion. The imparted benefit is to achieve a skin coloration equivalent to that from basking in the sun. More recently, a second product category has arrived. Therein a sunless tanning agent in small amounts is added to a typical moisturizing lotion. A "glow or shine" is thereby imparted. Glow or shine is a major factor in the appearance of healthy looking skin.

Most prominent among the sunless tanning agents is dihydroxyacetone ("DHA" which is also chemically known as 1,3-dihydroxy-2-propanone). DHA, after application, is believed to exert its effect through interactions between its

hydroxyl groups and the amino groups of amino acids and peptides naturally occurring in the hydrolipid pellicle and first layers of the stratum corneum of the skin. These so-called Maillard reactions are believed (see, e.g., Bobin et al., J. Soc. Cosmet. Chem. 35: 255 (1984)) to lead to formation of brown pigments in the skin, thereby giving it an appearance similar to that of a naturally obtained tan.

Unfortunately, many sunless tanning products available on the market are not stable in that they turn a yellow and/or orange color after application, especially when exposed to UV light. Other sunless tanning products perform poorly and do not quickly impart a noticeable brown color after application. Such poorly performing products do not prevent "tan-happy" consumers from basking in the sun. Products that underperform, therefore, do not protect consumers from the sun's ultraviolet rays.

There is increasing interest to develop compositions and methods for imparting a sunless tan, and especially, compositions that are storage stable. This invention, therefore, is directed to a composition and method that employ a sunless tanning agent as well as an adjuvant for the sunless tanning agent. The composition employs a pyranone, furanone and/or a derivative thereof as an adjuvant and, when applied, unexpectedly results in the consumer having skin with a brownish/tan coloration within a consumer acceptable time. Surprisingly, such a composition does not result in color body generation even when the sunless tanning agent and adjuvant are stored together in a monophase.

Additional Information

Efforts have been disclosed for making self-tanning cosmetic compositions. In U.S. Patent Nos. 5,232,688 and 5,612,044, self-tanner compositions with DHA are described.

Other efforts have been disclosed for making self-tanning compositions. In U.S. Patent No. 5,750,092, compositions with DHA and secondary amines are described.

Still other efforts have been disclosed for making self-tanning compositions. In U.S. Patent No. 6,231,837, self tanning formulations comprising DHA, polyethoxyglycol and a polyol are described.

None of the additional information describes a method and/or composition that yield excellent sunless tanning results whereby the composition and method employ a sunless tanning agent and a pyranone, furanone, derivative thereof or mixture as an adjuvant.

SUMMARY OF THE INVENTION

In a first aspect, the present invention is directed to a composition comprising:

a) a sunless tanning agent; and
b) an adjuvant for the sunless tanning agent, the adjuvant comprising a pyranone, furanone, derivative thereof or mixture thereof.

In a second aspect, the present invention is directed to a method for generating a sunless tan comprising the step of applying to the skin the composition of the first aspect of this invention.

All other aspects of the present invention will more readily become apparent upon considering the detailed description and examples which follow.

Sunless tanning, as used herein, means obtaining the suntan look by applying a topical composition. The same can be interchanged with self-tanning. Composition, as used herein, is meant to include a substance applied to a human body for imparting a sunless tan where the composition is for example, a leave-on skin lotion, cream or mouse, shampoo, hair conditioner, shower gel, toilet bar, body wash, shaving cream, body wax, depilatory, mascara, sunscreen product or the like. Such a composition may also be put on body towelettes for application to the body. In a preferred embodiment, the composition of this invention is a lotion or cream. Consumer acceptable time means within about 3 to about 6 hours from application, and preferably, from about 1 to about 2 hours, and most preferably, from about 15 to about 30 minutes subsequent to application. A composition not resulting in color body generation means being storage stable where storage stable is defined to mean having no color bodies after about one (1) month of storage at room temperature and when formulated as a monophase product at a pH in a range from 3 to 6. Derivative thereof means derivative of a pyranone and/or furanone, and mixture thereof means any combination of a pyranone, furanone, a derivative of pyranone and a derivative of furanone.

Comprising, as used herein, is meant to include consisting essentially of and consisting of. All ranges identified herein are meant to include all ranges subsumed therein if, for example, reference to the same is not explicitly made.

DETAILED DESCRIPTION OF THE INVENTION

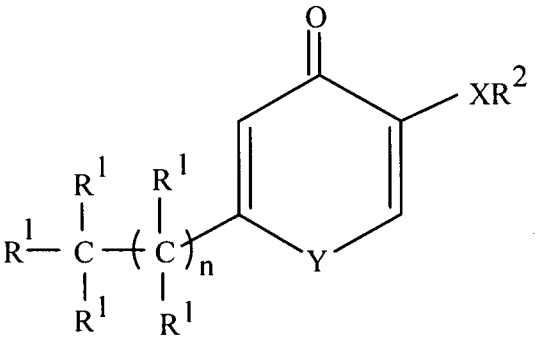
The sunless tanning agent suitable for use in this invention is only limited to the extent that it may be applied topically on humans to form pigmented components. Such materials may be alpha-hydroxyaldelydes and ketones, glyceraldehyde, troxerutin and related alcohol aldehydes, various indoles, imidazoles and derivatives thereof.

Illustrative yet non-limiting examples of the sunless tanning agents that may be used in this invention include dihydroxyacetone, melanin, mahakanni (eclipta alba), methyl glyoxal, erythrulose, alloxan, 2,3-dihydroxysuccindialdehyde, mixtures thereof, or the like. In a preferred embodiment, the sunless tanning agent used is dihydroxyacetone, erythrulose or a mixture thereof. In a most preferred embodiment, the sunless tanning agent is dihydroxyacetone.

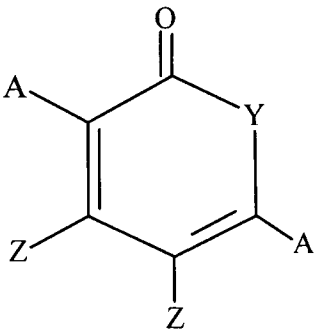
Typically, the sunless tanning agent makes up from about 0.025 to about 35%, and preferably, from about 0.05 to about 15%, and most preferably, from about 0.5 to about 10% by weight of the composition, based on total weight of the composition and including all ranges subsumed therein.

The adjuvant (i.e., pyranone, furanone and/or derivatives thereof) that may be used in this invention is limited only to the extent that the same may be used in a composition suitable for topical application to humans.

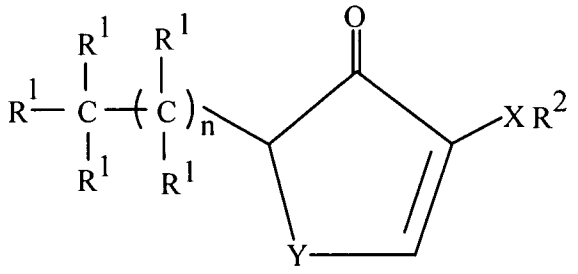
Typically, the adjuvant is represented by the formulae:



I

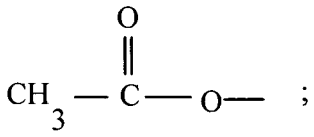


II



III

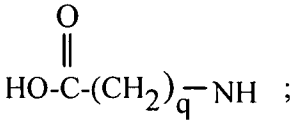
where each R^1 is independently H, Cl, OH, or



each A is independently R^2X- or H with the proviso that one A is R^2X-;

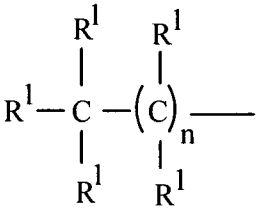
each R^2 is independently H, or C_{1-4} alkyl;

each X is independently NR^2, O, S or



each Y is independently O, NH, C_1-C_6 alkyl substituted N or S; and

each Z is independently



or H with the proviso that one Z is H; and
n is an integer from zero to 6, and q is an integer form 1 to 3.

In a most preferred embodiment, the sunless tanning adjuvant used in this invention is 3-hydroxy-6-methyl, 4-pyrone, often known commonly as Allomatol. Typically, the adjuvant makes up from about 0.025 to about 35%, and preferably, from about 0.05 to about 15%, and most preferably, from about 0.5 to about 8% by weight of the composition, including all ranges subsumed therein. It is also within the scope of this invention to employ mixtures of adjuvant represented by formulae I and II. Such adjuvants may be obtained from fungi like *Aspergillus oryzae* or by art recognized techniques including those which are initiated with a Kojic acid precursor. An illustrative example of the Synthesis of Allomatol, for example, is described in Japanese patent 4036217.

Compositions of the present invention will typically include a cosmetically acceptable carrier. Water is the most preferred carrier. Amounts of water may range from about 1 to about 99%, and preferably, from about 5 to about 90%, and most preferably, from about 35 to about 80% and optimally from about 40 to about 75% by weight, based on total weight of the composition and including all ranges subsumed therein. Ordinarily the compositions will be water and oil emulsions, most preferably, of the oil-in-water variety. Water-in-oil emulsions, and especially, those generally classified as water-in-oil and high internal phase emulsions are, however, an option. Illustrative examples of the high internal

phase emulsions suitable to carry the actives and adjuvants of this invention described in commonly owned U.S. Patent Application Publication Nos. 2008/0311058 and 2009/0247445, the disclosures of which are incorporated herein by reference.

Other cosmetically acceptable carriers may include mineral oils, silicone oils, synthetic or natural esters, fatty acids and alcohols. Amounts of these materials may range from about 0.1 to about 50%, and preferably, from about 0.1 to about 30%, and most preferably, from about 1 to about 20% by weight of the composition, including all ranges subsumed therein.

Silicone oils may be divided into the volatile and non-volatile variety. The term "volatile" as used herein refers to those materials which have a measurable vapor pressure at ambient temperature. Volatile silicone oils are preferably chosen from cyclic or linear polydimethylsiloxanes containing from about 3 to about 9, and preferably, from about 4 to about 5 silicon atoms.

Linear volatile silicone materials generally have viscosities less than about 5 centistokes at 25°C while cyclic materials typically have viscosities of less than about 10 centistokes.

Nonvolatile silicone oils useful as carrier material include polyalkyl siloxanes, polyalkylaryl siloxanes and polyether siloxane copolymers. The essentially non-volatile polyalkyl siloxanes useful herein include, for example, polydimethylsiloxanes (like dimethicone) with viscosities of from about 5 to about 100,000 centistokes at 25°C.

An often preferred silicone source is a cyclopentasiloxane and dimethiconol solution.

Among suitable esters are:

(1) Alkenyl or alkyl esters of fatty acids having 10 to 20 carbon atoms like isopropyl palmitate, isopropyl isostearate, isononyl isonanonoate, oleyl myristate, oleyl stearate, and oleyl oleate;

(2) Ether-esters such as fatty acid esters of ethoxylated fatty alcohols;

(3) Polyhydric alcohol esters such as ethylene glycol mono- and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol (200-6000) mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol 2000 monooleate, polypropylene glycol 2000 monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxy-ethylene sorbitan fatty acid esters;

(4) Wax esters such as beeswax, spermaceti, myristyl myristate, stearyl stearate; and

(5) Sterol esters, of which soya sterol and cholesterol fatty acid esters are examples thereof.

Fatty acids having from 10 to 30 carbon atoms may be included in the compositions of this invention. Illustrative of this category are pelargonic, lauric, myristic, palmitic, stearic, isostearic, hydroxystearic, oleic, linoleic, ricinoleic, arachidic, behenic and erucic acids.

Emulsifiers may be present in the compositions of the present invention. Total concentration of the emulsifier may range from about 0.1 to about 40%, and preferably, from about 1 to about 20%, and most preferably, from about 1 to about 5% by weight of the composition, including all ranges subsumed therein. The emulsifier may be selected from the group consisting of anionic, nonionic, cationic and amphoteric actives. Particularly preferred nonionic actives are those with a C_{10}-C_{20} fatty alcohol or acid hydrophobe condensed with from about 2 to about 100 moles of ethylene oxide or propylene oxide per mole of hydrophobe; C_2-C_{10} alkyl phenols condensed with from 2 to 20 moles of alkylene oxide; mono- and di- fatty acid esters of ethylene glycol; fatty acid monoglyceride; sorbitan, mono- and di- C_8-C_{20} fatty acids; and polyoxyethylene sorbitan as well as combinations thereof. Alkyl polyglycosides and saccharide fatty amides (e.g. methyl gluconamides) are also suitable nonionic emulsifiers.

Preferred anionic emulsifiers include soap, alkyl ether sulfate and sulfonates, alkyl sulfates and sulfonates, alkylbenzene sulfonates, alkyl and dialkyl sulfosuccinates, C_8-C_{20} acyl isethionates, C_8-C_{20} alkyl ether phosphates, alkylethercarboxylates and combinations thereof.

Cationic emulsifiers that may be used include, for example, palmitamidopropyltrimonium chloride, distearyldimonium chloride and mixtures thereof. Useful amphoteric emulsifiers include cocoamidopropyl betaine, C_{12}-C_{20} trialkyl betaines, sodium lauroamphoacetate, and sodium laurodiamphoacetate or a mixture thereof.

Other generally preferred emulsifiers include glyceryl stearate, glycol stearate, stearamide AMP, PEG-100 stearate, cetyl alcohol as well as emulsifying/thickening additives like hydroxyethylacrylate/sodium acryloyldimethyl taurates copolymer/squalane and mixtures thereof.

Preservatives can desirably be incorporated into the compositions comprising the sunless tanning agent and adjuvant of this invention to protect against the growth of potentially harmful microorganisms. Suitable traditional preservatives for compositions of this invention are alkyl esters of para-hydroxybenzoic acid. Other preservatives which have more recently come into use include hydantoin derivatives, propionate salts, and a variety of quaternary ammonium compounds. Cosmetic chemists are familiar with appropriate preservatives and routinely choose them to satisfy the preservative challenge test and to provide product stability. Particularly preferred preservatives are iodopropynyl butyl carbamate, phenoxyethanol, methyl paraben, propyl paraben, imidazolidinyl urea, sodium dehydroacetate and benzyl alcohol. The preservatives should be selected having regard for the use of the composition and possible incompatibilities between the preservatives and other ingredients in the emulsion. Preservatives are preferably employed in amounts ranging from about 0.01% to about 2% by weight of the composition, including all ranges subsumed therein.

Thickening agents may be included in compositions of the present invention. Particularly useful are the polysaccharides. Examples include starches, natural/synthetic gums and cellulosics. Representative of the starches are chemically modified starches such as sodium hydroxypropyl starch phosphate and aluminum starch octenylsuccinate. Suitable gums include xanthan, sclerotium, pectin, karaya, arabic, agar, guar, carrageenan, alginate and combinations thereof. Suitable cellulosics include hydroxypropyl cellulose, hydroxypropyl methylcellulose, ethylcellulose and sodium carboxy methylcellulose. Synthetic polymers are yet another class of effective thickening agent. This category includes crosslinked polyacrylates such as the Carbomers, polyacrylamides such as Sepigel® 305 and taurate copolymers such as Simulgel EG® and Aristoflex®

AVC, the copolymers being identified by respective INCI nomenclature as Sodium Acrylate/Sodium Acryloyldimethyl Taurate and Acryloyl Dimethyltaurate/Vinyl Pyrrolidone Copolymer.

Amounts of the thickener may range from about 0.001 to about 5%, and preferably, from about 0.1 to about 2%, and most preferably, from about 0.2 to about 0.5% by weight of the composition including all ranges subsumed therein.

Fragrances, fixatives and abrasives may optionally be included in compositions of the present invention. Each of these substances may range from about 0.05 to about 5%, preferably between 0.1 and 3% by weight.

To enhance skin moisturization, cationic ammonium compounds may optionally be used in the compositions of this invention. Such compounds include salts of hydroxypropyltri (C_1-C_3 alkyl) ammonium mono-substituted-saccharide, salts of hydroxypropyltri (C_1-C_3 alkyl) ammonium mono-substituted polyols, dihydroxypropyltri (C_1-C_3 alkyl) ammonium salts, dihydroxypropyldi (C_1-C_3 alkyl) mono(hydroxyethyl) ammonium salts, guar hydroxypropyl trimonium salts, 2,3-dihydroxypropyl tri(C_1-C_3 alkyl or hydroxalkyl) ammonium salts or mixtures thereof. In a most preferred embodiment and when desired, the cationic ammonium compound employed in this invention is the quaternary ammonium compound 1,2-dihydroxypropyltrimonium chloride. If used, such compounds typically make up from about 0.01 to about 30%, and preferably, from about 0.1 to about 15% by weight of the composition.

When cationic ammonium compounds are used, preferred additives for use with the same are moisturizing agents such as substituted ureas like hydroxymethyl urea, hydroxyethyl urea, hydroxypropyl urea; bis(hydroxymethyl) urea; bis(hydroxyethyl) urea; bis(hydroxypropyl) urea; N,N'-dihydroxymethyl

urea; N,N'-di-hydroxyethyl urea; N,N'-di-hydroxypropyl urea; N,N,N'-tri-hydroxyethyl urea; tetra(hydroxymethyl) urea; tetra(hydroxyethyl) urea; tetra(hydroxypropyl) urea; N-methyl-N'-hydroxyethyl urea; N-ethyl-N,N-N'-hydroxyethyl urea; N-hydroxypropyl-N'-hydroxyethyl urea and N,N'-dimethyl-N-hydroxyethyl urea or mixtures thereof. Where the term hydroxypropyl appears, the meaning is generic for either 3-hydroxy-n-propyl, 2-hydroxy-n-propyl, 3-hydroxy-i-propyl or 2-hydroxy-i-propyl radicals. Most preferred is hydroxyethyl urea. The latter is available as a 50% aqueous liquid from the National Starch & Chemical Division of ICI under the trademark Hydrovance.

Amounts of substituted urea, when used, in the composition of this invention range from about 0.01 to about 20%, and preferably, from about 0.5 to about 15%, and most preferably, from about 2 to about 10% based on total weight of the composition and including all ranges subsumed therein.

When cationic ammonium compound and substituted urea are used, in a most especially preferred embodiment at least from about 0.01 to about 25%, and preferably, from about 0.2 to about 20%, and most preferably, from about 1 to about 15% humectant, like glycerine, is used, based on total weight of the composition and including all ranges subsumed therein.

Conventional humectants may be employed in the present invention. These are generally polyhydric alcohol-type materials. Typical polyhydric alcohols include glycerol (i.e., glycerine or glycerin), propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,3-butylene glycol, isoprene glycol, 1,2,6-hexanetriol, ethoxylated glycerol, propoxylated glycerol and mixtures thereof. Most preferred is glycerin, propylene glycol or a mixture thereof. The

amount of humectant employed may range anywhere from 0.5 to 50%, preferably between 1 and 15% by weight of the composition.

Compositions of the present invention may include vitamins. Illustrative vitamins are Vitamin A (retinol), Vitamin B_2, Vitamin B_3 (niacinamide), Vitamin B_6, Vitamin C, Vitamin E, Folic Acid and Biotin. Derivatives of the vitamins may also be employed. For instance, Vitamin C derivatives include ascorbyl tetraisopalmitate, magnesium ascorbyl phosphate and ascorbyl glycoside. Derivatives of Vitamin E include tocopheryl acetate, tocopheryl palmitate and tocopheryl linoleate. DL-panthenol and derivatives may also be employed. Total amount of vitamins when present in compositions according to the present invention may range from 0.001 to 10%, preferably from 0.01% to 1%, optimally from 0.1 to 0.5% by weight of the end use composition.

Desquamation promoters may be present. Illustrative are the alpha-hydroxycarboxylic acids and beta-hydroxycarboxylic acids. The term "acid" is meant to include not only the free acid but also salts and C_1-C_{30} alkyl or aryl esters thereof and lactones generated from removal of water to form cyclic or linear lactone structures. Representative acids are glycolic, lactic and malic acids. Salicylic acid is representative of the beta-hydroxycarboxylic acids. Amounts of these materials when present may range from about 0.01 to about 15% by weight of the end use composition.

A variety of herbal extracts may optionally be included in compositions of this invention. The extracts may either be water soluble or water-insoluble carried in a solvent which respectively is hydrophilic or hydrophobic. Water and ethanol are the preferred extract solvents. Illustrative extracts include those from green tea, yarrow, chamomile, licorice, aloe vera, grape seed, citrus unshui, willow bark, sage, thyme and rosemary.

Also optionally suitable for use include materials like lipoic acid, retinoxytrimethylsilane (available from Clariant Corp. under the Silcare 1M-75 trademark), dehydroepiandrosterone (DHEA) and combinations thereof. Ceramides (including Ceramide 1, Ceramide 3, Ceramide 3B and Ceramide 6) as well as pseudoceramides may also be useful. Amounts of these materials may range from about 0.000001 to about 10%, preferably from about 0.0001 to about 1% by weight of the composition.

Conventional buffers/pH modifiers may be used. These include commonly employed additives like sodium hydroxide, hydrochloric acid, citric acid and citrate/citric acid buffers. In an especially preferred embodiment, the pH of the composition of this invention is from about 3 to about 4.75, and preferably, from about 3.25 to about 4, and most preferably, from about 3.25 to about 3.75, including all ranges subsumed therein.

Colorants, opacifiers, chelators (like tetrasodium EDTA) and abrasives may also be included in the compositions of the present invention. Each of these substances may range from about 0.05 to about 5%, preferably between 0.1 and 3% by weight of the composition.

In an especially preferred embodiment, the composition of the present invention comprises less than about 5%, and preferably, from 0.01 to 4% glycine, and most preferably, no glycine.

A wide variety of packaging can be employed to store and deliver the compositions. Packaging is often dependent upon the type of personal care end-use. For instance, leave-on skin lotions and creams, shampoos, conditioners and shower gels generally employ plastic containers with an opening at a dispensing end covered by a closure. Typical closures are screw-caps, non-aerosol pumps

and flip-top hinged lids. Packaging for antiperspirants, deodorants and depilatories may involve a container with a roll-on ball on a dispensing end. Alternatively these types of personal care products may be delivered in a stick composition formulation in a container with propel-repel mechanism where the stick moves on a platform towards a dispensing orifice. Metallic cans pressurized by a propellant and having a spray nozzle serve as packaging for antiperspirants, shave creams and other personal care products. Toilette bars may have packaging constituted by a cellulosic or plastic wrapper or within a cardboard box or even encompassed by a shrink wrap plastic film.

Optionally, the composition of this invention may be divided so that a first portion may carry sunless tanning agent and a second portion may carry adjuvant. When dividing the composition, each portion should be packaged separately from each other and not come into contact with each other until application to the body. The packaging for dual compositions is known and commercially available. Upon application, the make up of the composition (i.e., the combined portions) is as described herein.

When making the composition of the present invention, ingredients may be combined in no particular order. Typically the ingredients are combined and mixed under conditions of moderate shear and at ambient temperature with pressure being atmospheric conditions. In a most preferred embodiment, DHA and adjuvant are not added at a time when mixing and heating are desired. When applied by the consumer, typically from about 1 to 5 mg, and preferably, from about 1 to 4 mg, and preferably, from about 1.5 to 2.5 mg per square centimeter of composition is applied to body surface (like skin) and including all ranges subsumed therein.

The following examples are provided to facilitate an understanding of the present invention. The examples are not intended to limit the scope of the claims.

Example 1

Illustrative adjuvant suitable for use in this invention was made in the following way:

Kojic acid (2.6 g) was dissolved in distilled thionylchloride (10 mL). The resulting mixture was stirred for about one hour at room temperature. The formed yellow crystalline mass was filtered and washed with petroleum ether and water sequentially to yield a chlorinated Kojic acid derivative. Such derivative (1.6 g) was added to 5 mL of distilled water and the resulting mixture was heated to 50°C with stirring. Zinc dust (1.3 g) was added and followed by the addition of concentrated hydrochloric acid (3 mL) with vigorous stirring. The resulting reaction mixture was stirred for an additional three (3) hours at 70°C. Excess zinc was removed by hot filtration and the filtrate was extracted with dichloromethane.

Resulting extract was dried over anhydrous sodium sulphate, filtered and concentrated in vacuum to yield product which was purified via column chromatography or by isopropanol recrystallization. The desired adjuvant, Allomatol, was obtained.

Example 2

Illustrative adjuvant suitable for use in this invention was made in the following way:

Allomatol (126 mg) and 4 mL of toluene were combined with glycine methyl ester hydrochloride (138 mg) and toluene-4-sulfonic acid monohydrate. The reaction mixture was stirred under reflux for a few days and concentrated in vacuo whereby the resulting residue was chromatographed on a silica gel column with petroleum/ethyl acetate. The resulting Kojic acid/Allomatol derivative (20 mg) was mixed in a solvent of methanol/water (2 mL, 3:1) and 5 mg of potassium hydroxide was added. The resulting reaction system was stirred at room temperature for one (1) hour. Hydrochloric acid solution (2N, 100 microliters) was added to adjust pH to circa 4. The mixture produced was dried over anhydrous magnesium sulfate and filtered to recover the desired adjuvant, Allomatol derivative with $NHCH_2COOH$ in lieu of OH.

Example 3

Compositions comprising Allomatol were made by mixing the following:

Sample*	DHA (wt. %)	Glycine** (wt. %)	Allomatol (wt. %)
1 (Control)	5	5	-
2	5	5	0.5
3	5	5	1
4	5	5	2
5	5	5	3***

* = compositions having a balance of water
** = glycine was provided to mimic amino acid condition of skin.
*** = circa 95% Allomatol was dissolved.

Visual observations and photographs of the above Samples revealed that tanning rate (color formation) was enhanced when Allomatol was added and the rate was related to the dosage of Allomatol employed.

Color development for the above was also assessed using a spectrophotometer set at a wavelength of 400 nm. The results from such assessment indicated that the color development at 3% Allomatol was 20% greater than at 2%, 40% greater than at 1% and 45% greater than at 0.5% Allomatol after 20 hours of mixing. The results also indicated that color development was 60% greater when a composition with 3% Allomatol was compared to a composition deplete of adjuvant (with all results obtained after 20 hours of mixing the compositions).

Example 4

Compositions as described below were thoroughly mixed and stored for about 10 hours at 35°C and 55°C.

Sample 1: DHA (5 wt. %) and glycine (5 wt. %) in 0.1 M citric acid buffer (pH=5.5)

Sample 2: Allomatol (5 wt. %) and glycine (5 wt. %) in 0.1 M citric acid buffer (pH=5.5)

Sample 3: Allomatol (5 wt. %) and dihydroxyacetone (5 wt. %) in 0.1 M citric acid buffer (pH=5.5)

Visual observations and photographs revealed that only Sample 1 developed a color change within the first 10 hours at both temperatures. The other two samples did not exhibit obvious color changes during the period. The results indicate that Allomatol and dihydroxyacetone, unexpectedly, did not produce visual coloration (i.e., color bodies) during storage, thus meaning that adjuvant according to this invention may be formulated with dihydroxyacetone in a monophase product.

Example 5

Color development of the Samples of Example 3 was also monitored using Macbeth® Color-Eye 7000A which characterizes the color of an object in terms of L*, a*, and b*. Composition (2mL each) was measured after dilution with 8 ml deionized water after 27 hours of stirring. The results for the Samples are presented below. The same indicate that ΔL* increased when adjuvant according to this invention was used.

Sample	ΔL*
1 (Control)	52
2	62
3	68
4	80
5	85

- delta L* = color difference after stirring was completed versus initial.

Example 6

Compositions comprising Kojic acid or Allomatol were made by mixing the following ingredients at room temperature. Mixing was achieved with moderate shear and the balance of the compositions made was water.

Sample	DHA %	Glycine %	Kojic acid %	Allomatol %
1	5	5	0.5	-
2	5	5	1	-
3	5	5	2	-
4	5	5	3	-
5	5	5	-	1
6 (Control)	5	5	-	-

Visual observation and photographs after 6 hours of mixing at room temperature showed clear color development in the Samples. Samples 1 through 5 were shown to out perform the control by 93%, 130%, 203%, 256% and 193%, respectively, as determined by assessing the Samples with a spectrophotometer, wavelength 400 nm.

Visual observation and photographs were taken after 27 hours of mixing. Samples 1-5 were shown to out perform the control by 16%, 22%, 35%, 38% and 19%, respectively, as determined by assessing the Samples with a Spectrophotometer, wavelength 400 nm. These results illustrate the enhancement in tanning achieved with Kojic acid and Allomatol.

Example 7

Compositions were made by mixing the following ingredients at room temperatures. Mixing was achieved with moderate shear and the balance of the compositions made was water. All percents are by weight.

Sample	DHA %	Glycine %	Chlorinated Adjuvant*	Kojic acid
1 (Control)	5	5	--	--
2	5	5	--	0.25
3	5	5	0.25	--
4	5	5	0.5	--
5	5	5	1.5	--
6	--	5	0.25	--

*Kojic acid derivative with CH_2Cl in lieu of CH_2OH.

The Samples were assessed for color development (with a Spectrophometer, 400 nm wavelength) three (3) days after mixing. The results revealed Samples 2 through 5 out performed the control by 23%, 20%, 25% and 32%, respectively. No color body generation was observed when the chlorinated adjuvant was mixed with glycine and no DHA.

Example 8

The following compositions were mixed in a manner similar to the one described in Example 7.

Sample	DHA %	Glycine %	Nitrogen comprising Allomatol derivative* (adjuvant)	Allomatol
1 (Control)	5	5	--	--
2	5	5	--	0.5
3	5	5	0.5	--
4	5	5	1	--
5	5	5	2	--
6	--	5	0.5	--

*Allomatol derivative with $NHCH_2COOH$ in lieu of OH.

The Samples were assessed (with a Spectrophotometer, 400 nm wavelength) fifteen (15) hours after mixing. The results revealed Samples 2 through 5 out performed the control by 40%, 17%, 2%, 6%, respectively. No color body generation was observed when the adjuvant was mixed with glycine and no DHA.

Example 9

Synthetic skin, VITRO-SKIN®, was purchased from IMS Inc. The same is conventionally known to mimic the surface properties of human skin.

About 6 mL solvent (Glycerin:H_2O=15:85 (w:w)) was used to dissolve material to make a total weight stock solution of 6g and pH 5.7 was controlled with citric buffer. The substrate was cut into squares and treated with 20 microliters of the solution which was then spread smoothly within a 4.5 cm^2 circular area. The pieces of substrate were then stored in a desiccator containing an equimolar mixture of glycerol and water at 35°C (50% relative humidity). Color developed on the synthetic skin substrate was monitored. The Compositions assessed are described below and were prepared by mixing all ingredients at ambient temperature under conditions of moderate shear. The balance of the compositions was water and all percents are by weight.

Sample	DHA %	Glycine %	Allomatol %	Kojic acid %
1	3	--	--	--
2 (Control)	3	2.5	--	--
3	3	2.25	0.5	--
4	3	2.5	1	--
5	3	2.5	2	--
6	3	2.5	--	0.5
7	3	2.5	--	1
8	3	2.5	--	2

A colorimeter was used to obtain ΔL* values for each Sample at 4, 22 and 51 hours.

Sample	ΔL^{*i}
1	3, 12, 14
2	17, 27, 26
3	21, 33, 32
4	22, 34, 36
5	23, 36, 37
6	22, 33, 35
7	21, 33, 34
8	23, 32, 38

i = ΔL^* values at 4, 22 and 51 hours, read left to right.

The results demonstrate color enhancement was achieved on artificial skin.

What is claimed is:

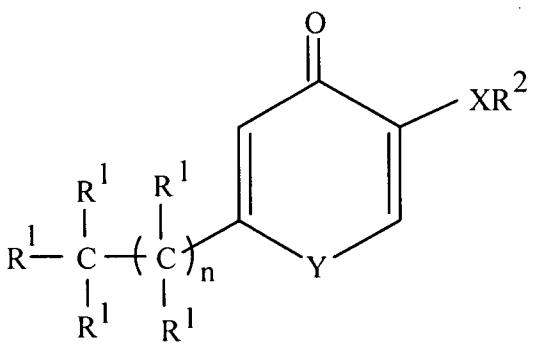
1. A composition comprising:

a) a sunless tanning agent; and

b) an adjuvant for the sunless tanning agent, the adjuvant comrpising a pyranone, furanone, derivative thereof or a mixture thereof.

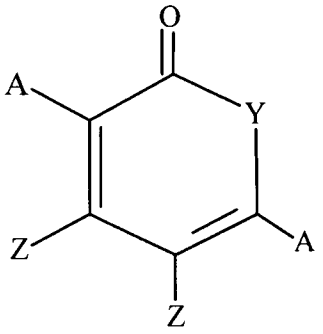
2. The composition according to claim 1 wherein the sunless tanning agent is dihydroxyacetone, melanin, mahakanni (eclipta alba), methyl glyoxal, erythrulose, alloxan, 2,3-dihydroxysuccindialdehyde or a mixture thereof.

3. The composition according to claim 1 wherein the adjuvant is represented by the formula:

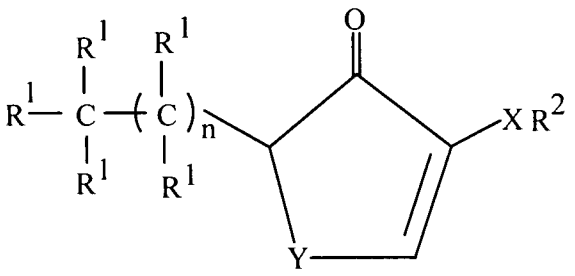


I

or

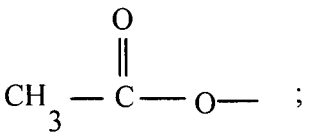


II



III

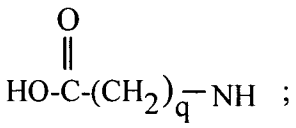
where each R^1 is independently H, Cl, OH, or



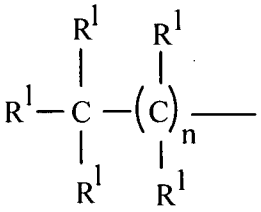
each A is independently R^2X- or H with the proviso that one A is R^2X-;

each R^2 is independently H, or C_{1-4} alkyl;

each X is independently NR^2, O, S or



each Y is independently O, NH, C_1-C_6 alkyl substituted N or S; and
each Z is independently



or H with the proviso that one Z is H; and
n is an integer from zero to 6, and q is an integer form 1 to 3.

4. The composition according to claim 1 wherein the adjuvant is 3-hydroxy-6-methyl,4-pyrone.

5. The composition according to claim 1 wherein the sunless tanning agent is alloxan, dihydroxyacetone, erythrulose or a mixture thereof.

6. The composition according to claim 1 wherein the sunless tanning agent is dihydroxyacetone.

7. The composition according to claim 1 wherein the composition further comprises a cosmetically acceptable carrier.

8. The composition according to claim 1 wherein the cosmetically acceptable carrier is an oil-in-water emulsion.

9. The composition according to claim 1 wherein the composition further comprises a cationic ammonium compound.

10. The composition according to claim 9 wherein the cationic ammonium compound is 1,2-dihydroxypropyltrimoniumn chloride.

11. The composition according to claim 1 wherein the sunless tanning agent makes up from about 0.025 to about 35% by weight of the composition.

12. The composition according to claim 1 wherein the adjuvant makes up from about 0.025 to about 35% by weight of the composition.

13. The composition according to claim 1 wherein the composition has a pH from about 3 to about 4.75.

14. The composition according to claim 1 wherein the composition is in a dual compartment package comprising at least two compartments.

15. The composition according to claim 14 wherein the first compartment comprises sunless tanning agent and the second compartment comprises adjuvant.

16. The composition according to claim 1 wherein the composition is a monophase composition in a single compartment package.

17. A method for imparting a sunless tan comprising the step of topically applying to skin the composition of claim 1.

Form PCT/ISA /210 (continuation of first sheet (3)) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2009/001544

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC:A61K, A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC, CNPAT, CNKI, CAS-online: sunless tanning; self-tanning; tanning; artificial tanning; pyranone; pyrone; furanone; furaneol; dha; dihydroxyacetone; melanin; mahakanni; eclipta alba; methyl glyoxal; erythrulose; alloxan; 2,3-dihydroxysuccindialdehyde; allomaltol; kojic acid; 3-hydroxy-6-methyl; 4-pyrone;

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO9955303A1 (The Procter & Gamble Company) , 04 Nov.1999(04.11.1999), claims 1,4,6,23	1-17 (partial)
A	CN101068528A(The Procter & Gamble Company), 07 Nov.2007(07.11.2007), see the whole document	1-17 (partial)
A	CN1816316A(The Procter & Gamble Company), 09 Aug.2006(09.8.2006), see the whole document	1-17 (partial)

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 Aug. 2010 (25.08.2010)	**28 Oct. 2010 (28.10.2010)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer Guo Yixin Telephone No. (86-10)62411139

Form PCT/ISA /210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2009/001544

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-17(partial)
The scopes of "a sunless tanning agent" and "the adjuvant comprising a pyranone, furanone, derivative thereof or a mixture" are vague and unclear. Therefore, the subject-matters of claims 1-17 do not meet the requirement of Article 6 PCT.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2009/001544

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
WO9955303A1	04-11-1999	AU2952499A	16-11-1999
		BR9909629A	19-12-2000
		EP1071396A1	31-01-2001
		CZ20003900A3	14-02-2001
		KR20010043002A	25-05-2001
		US6338855B1	15-01-2002
		JP2002512944T	08-05-2002
		MXPA00010386A	01-07-2001
		CA2332948A1	04-11-1999
		KR100450333B	01-10-2004
		MX225836B	26-01-2005
		CN1198581C	27-04-2005
		CN1298293A	06-06-2001
		AU756691B	23-01-2003
CN101068528A	07-11-2007	US2005238595A1	27-10-2005
		WO2005102010A2	03-11-2005
		EP1763333A2	21-03-2007
		MXPA06012190 A	01-01-2007
CN1816316A	09-08-2006	EP1493430A1	05-01-2005
		WO2005004833A1	20-01-2005
		MXPA05013665A	01-03-2006
		AU2004255271A1	20-01-2005
		BRPI0412150A	22-08-2006
		KR20060023173A	13-03-2006
		JP2007524642T	30-08-2007
		KR100746058B1	03-08-2007
		EP1493430B1	11-11-2009
		MX267579B	18-06-2009
		CA2529305C	08-12-2009
		CN100508938C	08-07-2009
		DE60329994E	24-12-2009

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2009/001544

1.CLASSIFICATION OF SUBJECT MATTER

A61K8/49(2006.01) i

A61K8/35(2006.01) i

A61Q9/04(2006.01) i

2.THE SUBJECT-MATTERS WHICH HAVE BEEN SEARCHED

The search for claim 1 is restricted to those claimed compositions which are clear, wherein the compound a) was restricted within those compounds defined by claim 2, and the compound b) was restricted within those compounds defined by claim 3.

The search for the dependent claims 2-17 are restricted accordingly.