



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2788115 C 2016/08/23

(11)(21) **2 788 115**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) **Date de dépôt PCT/PCT Filing Date:** 2011/02/08
(87) **Date publication PCT/PCT Publication Date:** 2011/08/11
(45) **Date de délivrance/Issue Date:** 2016/08/23
(85) **Entrée phase nationale/National Entry:** 2012/07/20
(86) **N° demande PCT/PCT Application No.:** US 2011/024024
(87) **N° publication PCT/PCT Publication No.:** 2011/097617
(30) **Priorité/Priority:** 2010/02/08 (US61/302,195)

(51) **Cl.Int./Int.Cl. A61K 8/34** (2006.01),
A61K 31/496 (2006.01), **A61K 31/505** (2006.01),
A61K 8/30 (2006.01), **A61P 17/00** (2006.01),
A61Q 1/00 (2006.01), **A61Q 19/02** (2006.01)
(72) **Inventeur/Inventor:**
YAROSH, DANIEL B., US
(73) **Propriétaire/Owner:**
ELC MANAGEMENT LLC, US
(74) **Agent:** OSLER, HOSKIN & HARCOURT LLP

(54) **Titre : COMPOSITIONS ET PROCEDES POUR REDUIRE L'APPARITION DE CERNES**
(54) **Title: COMPOSITIONS AND METHODS FOR REDUCING APPEARANCE OF UNDER-EYE DARK CIRCLES**

(57) **Abstrégé/Abstract:**

A cosmetic or dermatological composition is provided for reducing appearance of under-eye dark circles, which contains at least one bicyclic monoterpene diol and at least one skin lightening agent in a cosmetically or pharmaceutically acceptable carrier. The composition may further contain at least one anti-angiogenic agent and/or at least one anti-inflammatory agent.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
11 August 2011 (11.08.2011)

(10) International Publication Number
WO 2011/097617 A3

(51) International Patent Classification:

A61K 8/34 (2006.01) *A61Q 19/02* (2006.01)
A61K 8/30 (2006.01) *A61Q 1/00* (2006.01)
A61K 31/496 (2006.01) *A61P 17/00* (2006.01)
A61K 31/505 (2006.01)

(21) International Application Number:

PCT/US2011/024024

(22) International Filing Date:

8 February 2011 (08.02.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/302,195 8 February 2010 (08.02.2010) US

(71) Applicant (for all designated States except US): **ELC MANAGEMENT LLC** [US/US]; 767 Fifth Avenue, New York, New York 10153 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **YAROSH, Daniel B.** [US/US]; 2915 Shore Drive, Merrick, New York 11566 (US).

(74) Agents: **MCKELVEY, Idris N.** et al.; 155 Pinelawn Road Suite 345 South, Melville, New York 11747 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(88) Date of publication of the international search report:
8 December 2011

(54) Title: COMPOSITIONS AND METHODS FOR REDUCING APPEARANCE OF UNDER-EYE DARK CIRCLES

(57) Abstract: A cosmetic or dermatological composition is provided for reducing appearance of under-eye dark circles, which contains at least one bicyclic monoterpene diol and at least one skin lightening agent in a cosmetically or pharmaceutically acceptable carrier. The composition may further contain at least one anti-angiogenic agent and/or at least one anti-inflammatory agent.



WO 2011/097617 A3

COMPOSITIONS AND METHODS FOR REDUCING APPEARANCE OF UNDER-EYE DARK CIRCLES

5

FIELD OF THE INVENTION

The present invention relates to cosmetic or dermatological compositions comprising at least one bicyclic monoterpene diol and at least one skin lightening agent and methods of using such compositions for reducing appearance of under-eye dark circles.

10

BACKGROUND OF THE INVENTION

The eye contour (area around the eyes) has a very important aesthetic role since it immediately reflects fatigue, humor and age. In order to allow significant mobility of the eyelids, the epidermis surrounding the eyes is very thin (on the order of 0.33 to 0.36 mm, i.e., 3 to 5 times thinner than the rest of the skin of the face). Because of such extreme thinness, the skin around the eyes is easily dehydrated and is particularly vulnerable to adverse impact of external factors, such as heat, stress, tobacco, UV rays, and excessive facial expressions. Throughout the day, the skin tissues around the eye area can undergo multiple variations, such as vascularization, hydration and turgescence, which may contribute to swelling/puffiness and appearance of dark circles under the eyes, which are considered to be unattractive.

Most often the dark circles under the eyes have been attributed to hyperpigmentation. This is not necessarily the cause in all patients. Recently studies have revealed that the cause of under-eye dark circles tends to be multi-factorial and is more often the result of a combination of factors. Generally, there are main categories of factors that can be present in isolation or in combination, resulting in the appearance of under-eye dark circles: deep vascular congestion/superficial vascularity, hyperpigmentation, skin translucency, and structural shadowing. It is important to differentiate between these various factors in order to appropriately select treatment modalities to achieve a successful outcome.

A complex superficial vascular network exists within the dermis of the skin around the eyes. When these small, subcutaneous vessels become visible they lend a reddish discoloration to the area. Visibility may result from chronic eye rubbing, which creates repeated superficial trauma to the area and may also lead to deposition of pigment. Visible dark circles may also occur as a result of slowing blood microcirculation, especially at night,

which leads to formation of a transitory or permanent vascular congestion or reserve under the eyes and an accumulation of blood pigments in the conjunctive tissue.

Hyper-pigmentation occurs in a semicircular pattern around the eyes and may result from a multitude of focal or systemic conditions. Post inflammatory hyperpigmentation can
5 cause pigment accumulation in a superficial (more common) or deep (severe cases) pattern. Inflammatory conditions that disrupt the deep dermal-epidermal junction often heal with melanin deposition in the dermal macrophages where turnover of melanin is extremely slow. Hyper-pigmentation can also result from non-inflammatory lesions of the periorbital area. Examples of these conditions include melasma, ephelides, lentigo simplex, junctional nevi,
10 solar lentigines (“liver spots”), and nevi. systemic conditions that can lead to pigmentation of the periorbital area include various metabolic and endocrine disorders.

The skin of the eyelids and periorbital area is markedly thin in comparison to skin elsewhere on the face. Additionally, the skin becomes even thinner with aging, causing it to become more translucent. The vascular network underlying the surface becomes visible and
15 lends a reddish-blue hue to the periorbital area. This is especially true in the area of the infra-orbital rim wherein the lack of structural fat and muscle found elsewhere on the face places the coloration in relief against the underlying bone.

Further, multiple anatomical aspects of the periorbital area can create shadows in the infra-orbital area. Classically, deeply set orbits can cause shadowing resulting in discoloration
20 in the infra-orbital area. With prolapse of the infra-orbital fat and a prominent naso fugal fold, the double convex contour of the infra-orbital area creates a color change, which may be structural and vascular. This contour creates a shadow in the underlying tear trough. Shadows can also occur from other facial structures, such as a steep nasal bridge, prominent frontal bossing deeply set eyes, or enophthalmos.

25 The skin of the lower eyelid is contiguous with that of the upper cheek/malar area. With aging, the mid-face descends due to loss of support by the lateral component of the orbitomalar ligament and loss of volume. With this descent of the midface, a tear trough deformity is created and therefore a “dark circle.”

There is a multitude of cosmetic or skin care products on the market, many with
30 claims to reduce the appearance of under-eye dark circles. Further, there are various dermatological or surgical procedures, such as chemical peels, laser therapy, or electro-optical treatment, that are designed to reducing or minimizing the dark circles. However, most of these products or procedures target one of those causes described hereinabove, but fail to take

a comprehensive approach to address the multi-facet causes leading to the appearance of under-eye dark circles. Further, many of the currently available products or procedures are invasive and not suitable for long-term use due to undesirable side effects, such as skin/eye irritation.

5 There remains a need for cosmetic or dermatological compositions and methods which can reduce the appearance of dark circles around the eyes in a safe and effective manner.

SUMMARY OF THE INVENTION

10

This invention relates to cosmetic or dermatological compositions for safely and effectively reducing appearance of under-eye dark circles, and to methods of using such compositions.

15 In one aspect, the present invention relates to cosmetic or dermatological compositions comprising at least one bicyclic monoterpene diol and at least one skin lightening agent in a cosmetically or pharmaceutically acceptable carrier. Such compositions may further comprise at least one anti-angiogenic agent and/or at least one anti-inflammatory agent.

20 In another aspect, the present invention relates to a method for reducing appearance of under-eye dark circles by applying to an under-eye area with visible dark circles a cosmetic or dermatological composition comprising at least one bicyclic monoterpene diol and at least one skin lightening agent in a cosmetically or pharmaceutically acceptable carrier.

Other aspects and objectives of the present invention will become more apparent from the ensuing description, examples, and claims.

25

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term “at least one” means one or more and thus includes individual components as well as mixtures/combinations.

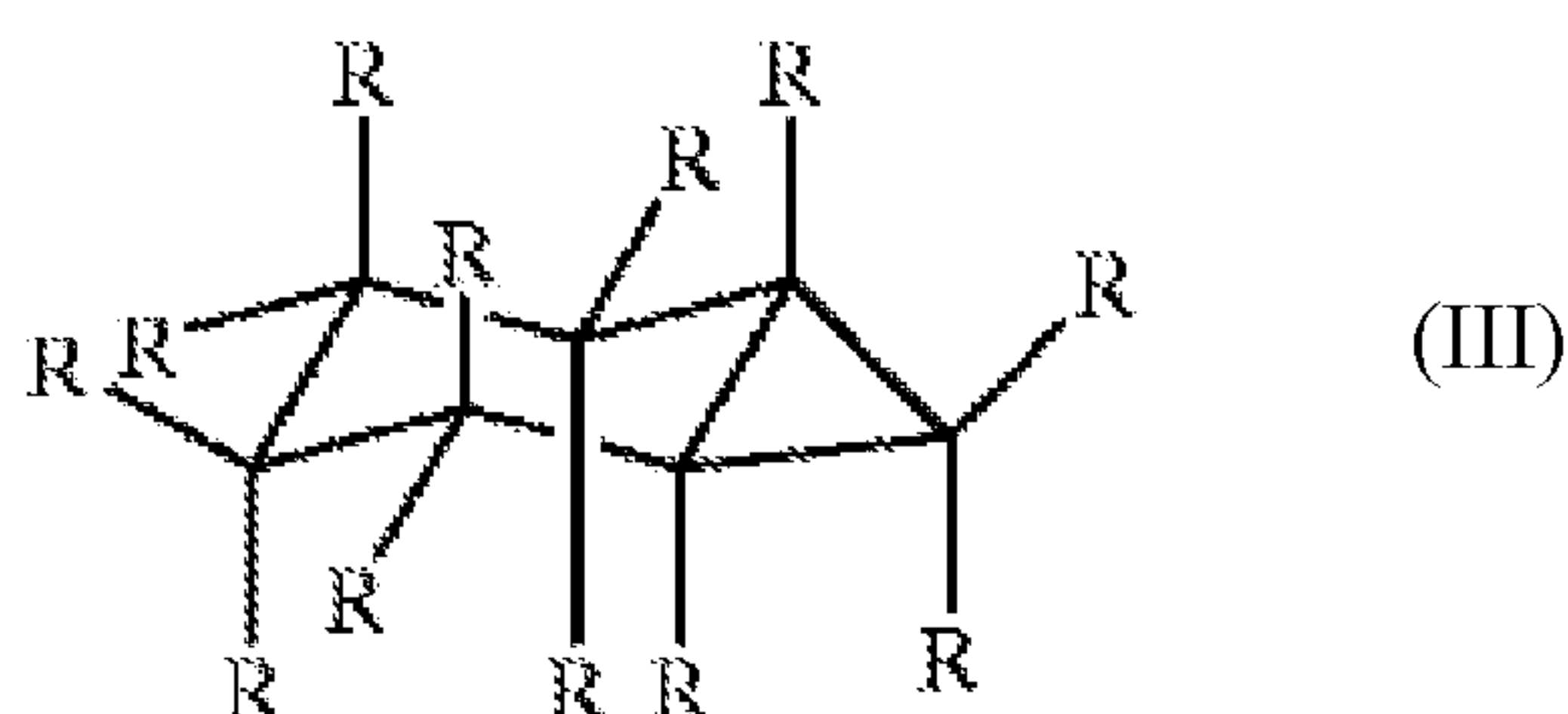
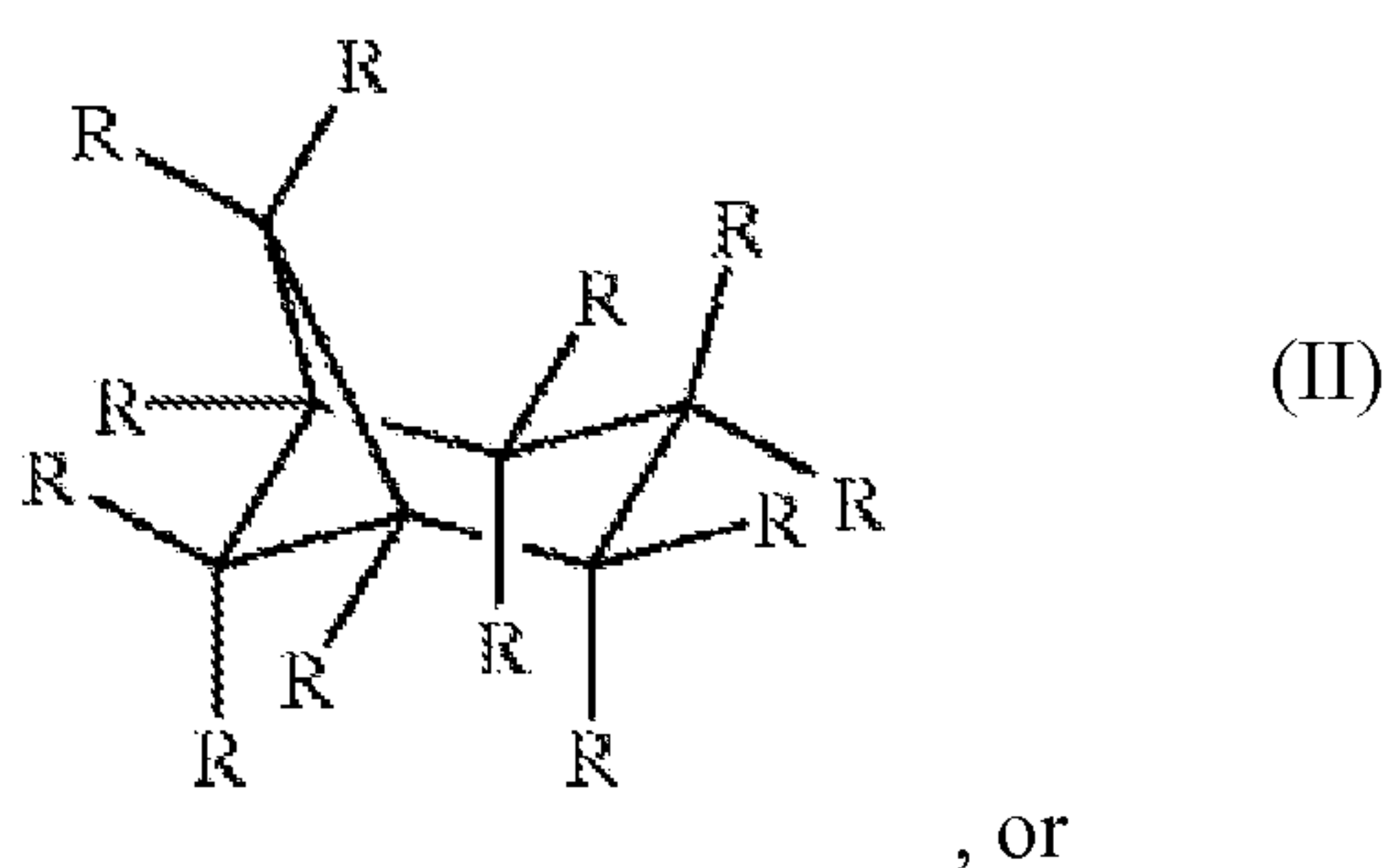
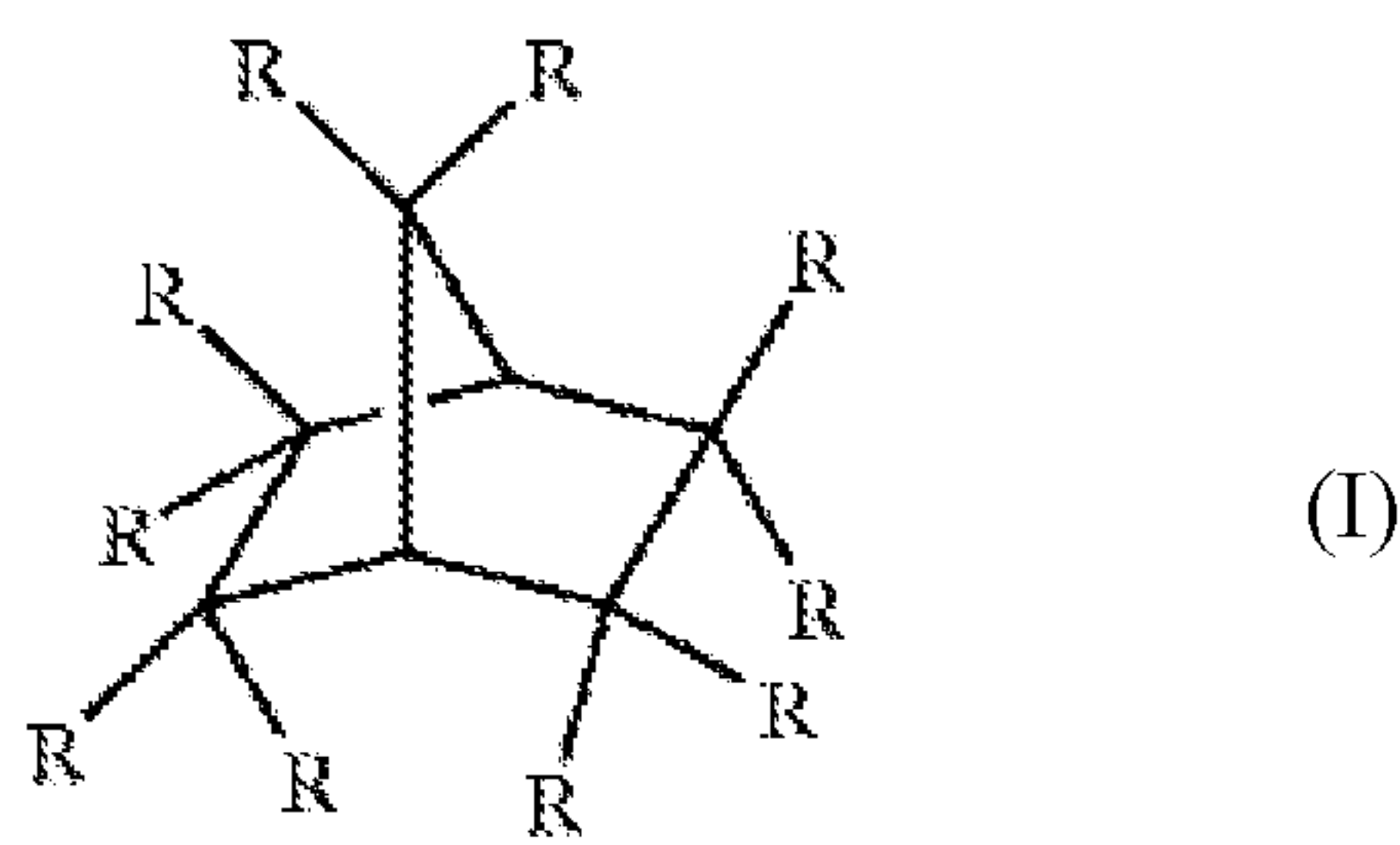
30 Unless otherwise specified, all percentages relating to the amounts or concentrations of ingredients as used herein refer to the percent by total weight of the final composition.

As used herein, the term “cosmetically or dermatologically acceptable” means suitable for use in contact with skin without undue toxicity, incompatibility, instability, irritation, allergic response, and the like, commensurate with a reasonable benefit/risk ratio.

As used herein, the term “skin-lightening” means decreasing melanin in skin, including overall lightening of skin tone and lightening of hyperpigmented regions, including age spots, melasma (chloasma), freckles, post-inflammatory hyperpigmentation or sun-induced pigmented blemishes, and the like.

The present invention is based on the discovery that the combination of certain bicyclic monoterpene diols with certain skin lightening agents surprisingly and unexpectedly achieves synergistic reduction of the appearance of under-eye dark circles, by simultaneously targeting vascular congestion in the dermis layer and hyperpigmentation in the epidermis layer of the skin. The term “diol” is referring to a compound having at least two, but permissibly more, -OH groups.

Preferably, the bicyclic monoterpene diols have the following generic formula:



wherein each R is independently selected from the group consisting of hydrogen, hydroxyl, methyl, hydroxymethyl, halogen, acyl, amino acyl, a group that is linear, branched, monocyclic, bicyclic, or polycyclic and contains from one atom to twenty atoms, at least one of which is carbon, nitrogen, oxygen, or sulfur, $-(CH_2)_n-OR'$, $-(CH_2)_n-[CH(OH)]_n-R'$, and -
 5 $(CH_2)_n-[CH(OH)]_n-(CH_2)_n-[CH(OH)]_n-R'$, wherein each n is independently an integer from 0-25 and R' is independently selected from the group consisting of hydrogen, hydroxyl, methyl, hydroxymethyl, halogen, acyl, amino acyl, and a group that is linear, branched, monocyclic, bicyclic, or polycyclic and contains from one atom to twenty atoms, at least one of which is carbon, nitrogen, oxygen, or sulfur, with the proviso that at least two of the Rs
 10 contain a hydroxyl group.

More preferably, the bicyclic monoterpene diols of the present invention is selected from the group consisting of 2,3-cis/exo-pinenediol, 2,3-trans-pinenediol, (1R)-(-)-trans-pinane-1,10-diol, and 2,3-cis/exo-camphanediol. Most preferably, the cosmetic or dermatological compositions of the present invention contain an equal molar mixture of 2,3-
 15 cis/exo-pinenediol and 2,3-cis/exo-camphanediol. It is believed that the bicyclic monoterpene diols of the present invention stimulate nitric oxide synthesis in epithelial cells of the skin. An increase in skin nitric oxide content is believed to lead to an increase in microcirculation, which facilitates dissipation of vascular congestion in the dermis layer of the skin and thereby reducing the under-eye dark circles caused by such congestion.

20 The bicyclic monoterpene diols may be present in the cosmetic or dermatological compositions of the present application at a total amount ranging from about 0.001% to about 20% by weight of the composition. More preferably, the bicyclic monoterpene diols are present at a total amount of about 0.01% to 5%, and most preferably about 0.1% to 3%, by weight of the composition.

25 The cosmetic or dermatological compositions of the present application also contain at least one skin lightening agent, such as ascorbic acid and its derivatives, e.g., magnesium ascorbyl phosphate, ascorbyl glucosamine, ascorbyl palmitate, adapalene, aloe extract, ammonium lactate, anethole derivatives, *Scutellaria baicalensis* root extract, *Pyrus malus* (apple) extract, *Cucumis sativus* (cucumber) extract, azelaic acid, ellagic acid and derivatives
 30 thereof, bamboo extract, bearberry extract, bletilla tuber, *Bupleurum falcatum* extract, burnet extract, butyl hydroxy anisole, butyl hydroxy toluene, deoxyarbutin, 1,3 diphenyl propane derivatives, 2,5 dihydroxybenzoic acid and its derivatives, 2-(4-acetoxyphenyl)-1,3 dithane, 2-(4-hydroxyphenyl)-1,3 dithane, ellagic acid, escinol, estragole derivatives, FADE OUT

(available from Pentapharm), Fangfeng, fennel extract, ganoderma extract, gaoben, GATULINE WHITENING (available from Gattlefosse), genistic acid and its derivatives, glabridin and its derivatives, gluco pyranosyl-1-ascorbate, gluconic acid, glycolic acid, green tea extract, placenta extract, 4-Hydroxy-5-methyl-3[2H]-furanone, 4 hydroxyanisole and its
5 derivatives, 4-hydroxy benzoic acid derivatives, hydroxycaprylic acid, inositol ascorbate, lactic acid, lemon extract, linoleic acid, MELA WHITE (available from Pentapharm), *Morus alba* extract, mulberry root extract, niacinamide, 5-octanoyl salicylic acid, parsley extract, *Phellinus linteus* extract, pyrogallol derivatives, retinoic acid, retinol, retinyl esters (acetate, propionate, palmitate, linoleate), 2,4 resorcinol derivatives, 3,5 resorcinol derivatives, rose
10 fruit extract, salicylic acid, 3,4,5 trihydroxybenzyl derivatives, tranexamic acid, vitamin D3 and its analogs, and mixtures thereof.

Preferably, but not necessarily, the cosmetic or dermatological compositions of the present application contain a mixture of *Scutellaria baicalensis* root extract, *Pyrus malus* (apple) extract, *Cucumis sativus* (cucumber) extract, which is commercially available from
15 BASF (Lyon, France) under the trademark Phytowhite®. The skin lightening agents may be present in the cosmetic or dermatological compositions of the present application at a total amount ranging from about 0.001% to about 10% by weight of the composition. More preferably, the skin lightening agents are present at a total amount of about 0.01% to 5%, and most preferably about 0.05% to 1%, by weight of the composition.

20 Cosmetic or dermatological compositions of the present inventions may be found in a variety of forms, such as anhydrous compositions, aqueous-based solutions, serums, gels, creams, lotions, mousses, sticks, sprays, ointments, essences, pastes, microcapsules, or color cosmetic compositions such as foundation, blush, eyeshadow, and the like. They may contain many other additional cosmetically and/or dermatologically acceptable ingredients, such as
25 anti-angiogenic agents, anti-inflammatory agents, antioxidants, botanicals, humectants, moisturizers, sunscreens, preservatives, colorants, perfumes, and the like.

Suitable serums or gels will generally comprise from about 1-99% water, and optionally from about 0.001-30% of an aqueous phase thickening agent. The other ingredients mentioned herein may be present in the percentage ranges set forth.

30 Typical skin creams or lotions comprise from about 5-98% water, 1-85% oil, and from about 0.1 to 20% of one or more surfactants. Preferably the surfactants are nonionic and may be in the form of silicones or organic nonionic surfactants.

Typical color cosmetic compositions such as foundations, blush, eyeshadow, and the like, will preferably contain from about 5-98% water, 1-85% oil, and from about 0.1 to 20% of one or more surfactants in addition to from about 0.1 to 65% of particulates that are pigments or a combination of pigments and powders.

5 In the case where the compositions are in the form of aqueous solutions, dispersions or emulsions, in addition to water the aqueous phase may contain one or more aqueous phase structuring agents, that is, an agent that increases the viscosity or thickens, the aqueous phase of the composition. Suitable ranges of aqueous phase structuring agent, if present, are from about 0.01 to 30%, preferably from about 0.1 to 20%, more preferably from about 0.5 to 15%
10 by weight of the total composition. Examples of such agents include various acrylate based thickening agents, natural or synthetic gums, polysaccharides, and the like, including but not limited to those set forth below. Such structuring agents may include the following:

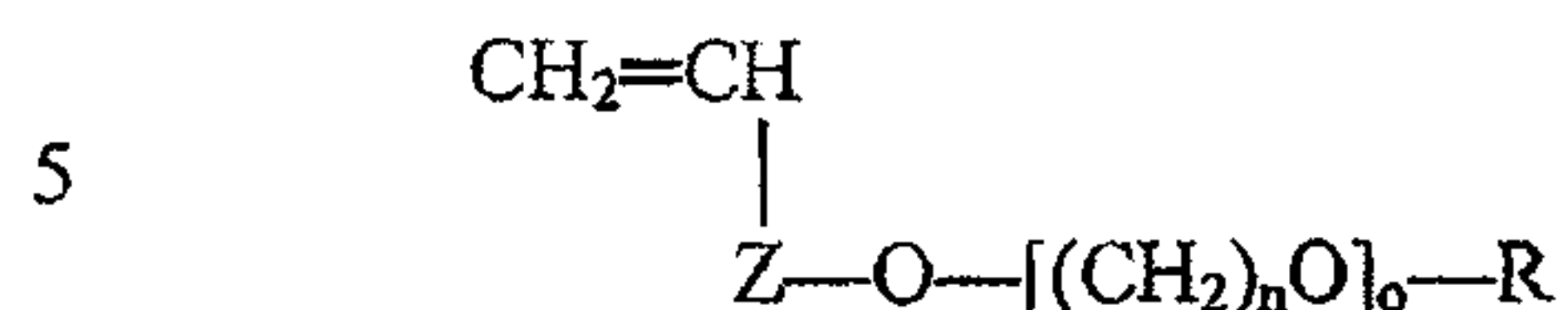
A. Polysaccharides

Polysaccharides may be suitable aqueous phase thickening agents. Examples of such
15 polysaccharides include naturally derived materials such as agar, agarose, aliccaligenes polysaccharides, algin, alginic acid, acacia gum, amylopectin, chitin, dextran, cassia gum, cellulose gum, gelatin, gellan gum, hyaluronic acid, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, pectin, sclerotium gum, xanthan gum, pectin, trehelose, gelatin, and so on.

B. Acrylate Polymers

20 Also suitable are different types of synthetic polymeric thickeners. One type includes acrylic polymeric thickeners comprised of monomers A and B wherein A is selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof; and B is selected from the group consisting of a C₁₋₂₂ alkyl acrylate, a C₁₋₂₂ alky methacrylate, and mixtures thereof are suitable. In one embodiment the A monomer comprises one or more of acrylic acid or
25 methacrylic acid, and the B monomer is selected from the group consisting of a C₁₋₁₀, most preferably C₁₋₄ alkyl acrylate, a C₁₋₁₀, most preferably C₁₋₄ alkyl methacrylate, and mixtures thereof. Most preferably the B monomer is one or more of methyl or ethyl acrylate or methacrylate. The acrylic copolymer may be supplied in an aqueous solution having a solids content ranging from about 10-60%, preferably 20-50%, more preferably 25-45% by weight of
30 the polymer, with the remainder water. The composition of the acrylic copolymer may contain from about 0. 1-99 parts of the A monomer, and about 0.1-99 parts of the B monomer. Acrylic polymer solutions include those sold by Seppic, Inc., under the tradename Capigel.

Also suitable are acrylic polymeric thickeners that are copolymer of A, B, and C monomers wherein A and B are as defined above, and C has the general formula:



wherein Z is $-(\text{CH}_2)_m$; wherein m is 1-10, n is 2-3, o is 2-200, and R is a C_{10-30} straight or branched chain alkyl. Examples of the secondary thickening agent above, are copolymers where A and B are defined as above, and C is CO, and wherein n, o, and R are as above defined. Examples of such secondary thickening agents include acrylates/steareth-20 methacrylate copolymer, which is sold by Rohm & Haas under the tradename Acrysol ICS-1.

Also suitable are acrylate based anionic amphiphilic polymers containing at least one hydrophilic unit and at least one allyl ether unit containing a fatty chain. Preferred are those where the hydrophilic unit contains an ethylenically unsaturated anionic monomer, more specifically a vinyl carboxylic acid such as acrylic acid, methacrylic acid or mixtures thereof, and where the allyl ether unit containing a fatty chain corresponds to the monomer of the formula:



in which R' denotes H or CH_3 , B denotes the ethylenoxy radical, n is zero or an integer ranging from 1 to 100, R denotes a hydrocarbon radical selected from alkyl, arylalkyl, aryl, alkylaryl and cycloalkyl radicals which contain from 8 to 30 carbon atoms, preferably from 10 to 24, and even more particularly from 12 to 18 carbon atoms. More preferred in this case is where R' denotes H, n is equal to 10 and R denotes a stearyl (C18) radical. Anionic amphiphilic polymers of this type are described and prepared in U.S. Patent Nos. 4,677,152 and 4,702,844.

Among these anionic amphiphilic polymers, polymers formed of 20 to 60% by weight acrylic acid and/or methacrylic acid, of 5 to 60% by weight lower alkyl methacrylates, of 2 to 50% by weight allyl ether containing a fatty chain as mentioned above, and of 0 to 1% by weight of a crosslinking agent which is a well-known copolymerizable polyethylenic unsaturated monomer, for instance diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene

glycol dimethacrylate and methylenebisacrylamide. Commercial examples of such polymers are crosslinked terpolymers of methacrylic acid, of ethyl acrylate, of polyethylene glycol (having 10 EO units) ether of stearyl alcohol or steareth-10, in particular those sold by the company Allied Colloids under the names *SALCARE* SC80 and *SALCARE* SC90, which are aqueous emulsions containing 30% of a crosslinked terpolymer of methacrylic acid, of ethyl acrylate and of steareth-10 allyl ether (40/50/10).

Also suitable are acrylate copolymers such as Polyacrylate-3 which is a copolymer of methacrylic acid, methylmethacrylate, methylstyrene isopropylisocyanate, and PEG-40 behenate monomers; Polyacrylate-10 which is a copolymer of sodium acryloyldimethyltaurate, sodium acrylate, acrylamide and vinyl pyrrolidone monomers; or Polyacrylate-11, which is a copolymer of sodium acryloyldimethylacryloyldimethyl taurate, sodium acrylate, hydroxyethyl acrylate, lauryl acrylate, butyl acrylate, and acrylamide monomers.

Also suitable are crosslinked acrylate based polymers where one or more of the acrylic groups may have substituted long chain alkyl (such as 6-40, 10-30, and the like) groups, for example acrylates/C₁₀₋₃₀ alkyl acrylate crosspolymer which is a copolymer of C₁₀₋₃₀ alkyl acrylate and one or more monomers of acrylic acid, methacrylic acid, or one of their simple esters crosslinked with the allyl ether of sucrose or the allyl ether of pentaerythritol. Such polymers are commonly sold under the Carbopol or Pemulen tradenames and have the CTFA name carbomer.

One particularly suitable type of aqueous phase thickening agent are acrylate based polymeric thickeners sold by Clariant under the Aristoflex trademark such as Aristoflex AVC, which is ammonium acryloyldimethyltaurate/VP copolymer; Aristoflex AVL which is the same polymer as found in AVC dispersed in a mixture containing caprylic/capric triglyceride, trilaureth-4, and polyglyceryl-2 sesquiisostearate; or Aristoflex HMB which is ammonium acryloyldimethyltaurate/beheneth-25 methacrylate crosspolymer, and the like.

C. High Molecular Weight PEG or Polyglycerins

Also suitable as the aqueous phase thickening agents are various polyethylene glycols (PEG) derivatives where the degree of polymerization ranges from 1,000 to 200,000. Such ingredients are indicated by the designation "PEG" followed by the degree of polymerization in thousands, such as PEG-45M, which means PEG having 45,000 repeating ethylene oxide units. Examples of suitable PEG derivatives include PEG 2M, 5M, 7M, 9M, 14M, 20M, 23M, 25M, 45M, 65M, 90M, 115M, 160M, 180M, and the like.

Also suitable are polyglycerins which are repeating glycerin moieties where the number of repeating moieties ranges from 15 to 200, preferably from about 20-100. Examples of suitable polyglycerins include those having the CTFA names polyglycerin-20, polyglycerin-40, and the like.

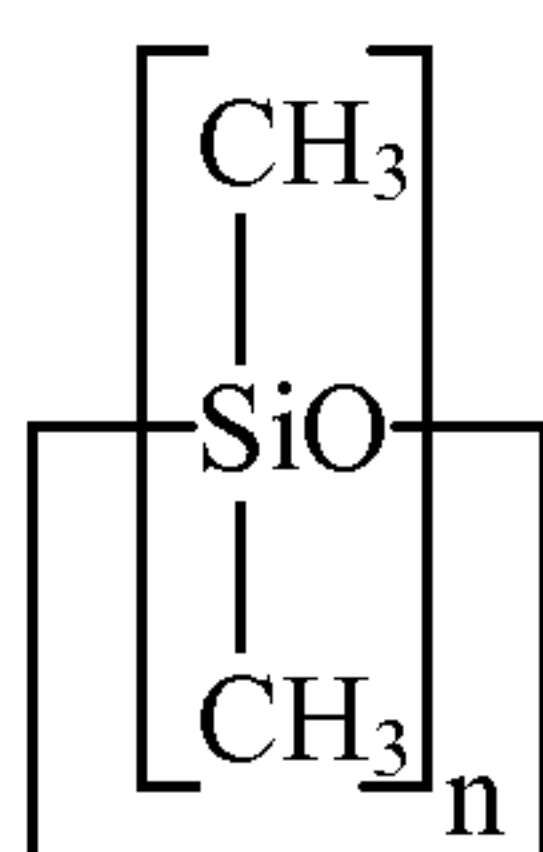
5 In the event the compositions of the invention are in anhydrous or emulsion form, the composition will comprise an oil phase. Oily ingredients are desirable for the skin moisturizing and protective properties. Suitable oils include silicones, esters, vegetable oils, synthetic oils, including but not limited to those set forth herein. The oils may be volatile or nonvolatile, and are preferably in the form of a pourable liquid at room temperature. The term
10 "volatile" means that the oil has a measurable vapor pressure or a vapor pressure of at least about 2 mm. of mercury at 20° C. The term "nonvolatile" means that the oil has a vapor pressure of less than about 2 mm. of mercury at 20° C. Suitable oils may include the following:

A. Volatile Oils

15 Suitable volatile oils generally have a viscosity ranging from about 0.5 to 5 centistokes 25° C. and include linear silicones, cyclic silicones, paraffinic hydrocarbons, or mixtures thereof. Volatile oils may be used to promote more rapid drying of the skin care composition after it is applied to skin. Volatile oils are more desirable when the skin care products containing the Type I H⁺, K⁺-ATPase inhibitor compound or derivative thereof are being
20 formulated for consumers that have combination or oily skin. The term "combination" with respect to skin type means skin that is oily in some places on the face (such as the T-zone) and normal in others.

1. Volatile Silicones

Cyclic silicones are one type of volatile silicone that may be used in the composition.
25 Such silicones have the general formula:



30

where n=3-6, preferably 4, 5, or 6.

Also suitable are linear volatile silicones, for example, those having the general formula:

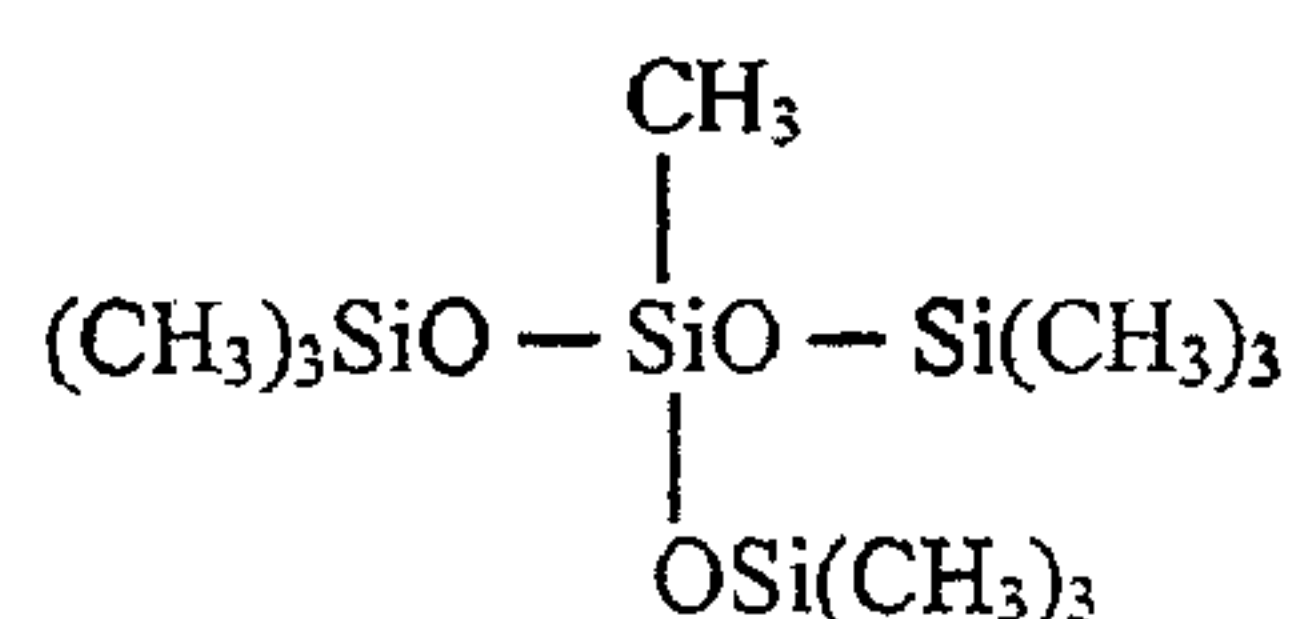


5 where $n=0, 1, 2, 3, 4$, or 5 , preferably $0, 1, 2, 3$, or 4 .

Cyclic and linear volatile silicones are available from various commercial sources including Dow Corning Corporation and General Electric. The Dow Corning linear volatile silicones are sold under the tradenames Dow Corning 244, 245, 344, and 200 fluids. These
10 fluids include hexamethyldisiloxane (viscosity 0.65 centistokes (abbreviated cst)), octamethyltrisiloxane (1.0 cst), decamethyltetrasiloxane (1.5 cst), dodecamethylpentasiloxane (2 cst) and mixtures thereof, with all viscosity measurements being at 25°C .

Suitable branched volatile silicones include alkyl trimethicones such as methyl trimethicone, a branched volatile silicone having the general formula:

15



Methyl trimethicone may be purchased from Shin-Etsu Silicones under the tradename
20 TMF-1.5, having a viscosity of 1.5 centistokes at 25°C .

2. Volatile Paraffinic Hydrocarbons

Also suitable as the volatile oils are various straight or branched chain paraffinic hydrocarbons having 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 carbon atoms, more preferably 8 to 16 carbon atoms. Suitable hydrocarbons include pentane, hexane,
25 heptane, decane, dodecane, tetradecane, tridecane, and C_{8-20} isoparaffins as disclosed in U.S. Pat. Nos. 3,439,088 and 3,818,105.

Preferred volatile paraffinic hydrocarbons have a molecular weight of 70-225, preferably 160 to 190 and a boiling point range of 30 to 320, preferably 60 to 260°C ., and a viscosity of less than about 10 cst. at 25°C . Such paraffinic hydrocarbons are available from
30 EXXON under the ISOPARS trademark, and from the Permethyl Corporation. Suitable C_{12} isoparaffins are manufactured by Permethyl Corporation under the tradename Permethyl 99A.

Various C₁₆ isoparaffins commercially available, such as isohexadecane (having the tradename Permethyl R), are also suitable.

B. Non-Volatile Oils

A variety of nonvolatile oils are also suitable for use in the compositions of the invention. The nonvolatile oils generally have a viscosity of greater than about 5 to 10 centistokes at 25° C., and may range in viscosity up to about 1,000,000 centipoise at 25° C. Examples of nonvolatile oils include, but are not limited to:

1. Esters

Suitable esters are mono-, di-, and triesters. The composition may comprise one or more esters selected from the group, or mixtures thereof.

(a) Monoesters

Monoesters are defined as esters formed by the reaction of a monocarboxylic acid having the formula R-COOH, wherein R is a straight or branched chain saturated or unsaturated alkyl having 2 to 45 carbon atoms, or phenyl; and an alcohol having the formula R-OH wherein R is a straight or branched chain saturated or unsaturated alkyl having 2-30 carbon atoms, or phenyl. Both the alcohol and the acid may be substituted with one or more hydroxyl groups. Either one or both of the acid or alcohol may be a "fatty" acid or alcohol, and may have from about 6 to 30 carbon atoms, more preferably 12, 14, 16, 18, or 22 carbon atoms in straight or branched chain, saturated or unsaturated form. Examples of monoester oils that may be used in the compositions of the invention include hexyl laurate, butyl isostearate, hexadecyl isostearate, cetyl palmitate, isostearyl neopentanoate, stearyl heptanoate, isostearyl isononanoate, stearyl lactate, stearyl octanoate, stearyl stearate, isononyl isononanoate, and so on.

(b). Diesters

Suitable diesters are the reaction product of a dicarboxylic acid and an aliphatic or aromatic alcohol or an aliphatic or aromatic alcohol having at least two substituted hydroxyl groups and a monocarboxylic acid. The dicarboxylic acid may contain from 2 to 30 carbon atoms, and may be in the straight or branched chain, saturated or unsaturated form. The dicarboxylic acid may be substituted with one or more hydroxyl groups. The aliphatic or aromatic alcohol may also contain 2 to 30 carbon atoms, and may be in the straight or branched chain, saturated, or unsaturated form. Preferably, one or more of the acid or alcohol is a fatty acid or alcohol, i.e. contains 12-22 carbon atoms. The dicarboxylic acid may also be an alpha hydroxy acid. The ester may be in the dimer or trimer form. Examples of diester

oils that may be used in the compositions of the invention include diisostearyl malate, neopentyl glycol dioctanoate, dibutyl sebacate, dicetearyl dimer dilinoleate, dicetyl adipate, diisocetyl adipate, diisononyl adipate, diisostearyl dimer dilinoleate, diisostearyl fumarate, diisostearyl malate, dioctyl malate, and so on.

5 (c). Triesters

Suitable triesters comprise the reaction product of a tricarboxylic acid and an aliphatic or aromatic alcohol or alternatively the reaction product of an aliphatic or aromatic alcohol having three or more substituted hydroxyl groups with a monocarboxylic acid. As with the mono- and diesters mentioned above, the acid and alcohol contain 2 to 30 carbon atoms, and
10 may be saturated or unsaturated, straight or branched chain, and may be substituted with one or more hydroxyl groups. Preferably, one or more of the acid or alcohol is a fatty acid or alcohol containing 12 to 22 carbon atoms. Examples of triesters include esters of arachidonic, citric, or behenic acids, such as triarachidin, tributyl citrate, triisostearyl citrate, tri C₁₂₋₁₃ alkyl citrate, tricaprylin, tricaprylyl citrate, tridecyl behenate, trioctyldodecyl citrate, tridecyl
15 behenate; or tridecyl cocoate, tridecyl isononanoate, and so on.

Esters suitable for use in the composition are further described in the C.T.F.A. Cosmetic Ingredient Dictionary and Handbook, Eleventh Edition, 2006, under the classification of "Esters" .

2. Hydrocarbon Oils

20 It may be desirable to incorporate one or more nonvolatile hydrocarbon oils into the composition. Suitable nonvolatile hydrocarbon oils include paraffinic hydrocarbons and olefins, preferably those having greater than about 20 carbon atoms. Examples of such hydrocarbon oils include C₂₄₋₂₈ olefins, C₃₀₋₄₅ olefins, C₂₀₋₄₀ isoparaffins, hydrogenated polyisobutene, polyisobutene, polydecene, hydrogenated polydecene, mineral oil,
25 pentahydrosqualene, squalene, squalane, and mixtures thereof. In one preferred embodiment such hydrocarbons have a molecular weight ranging from about 300 to 1000 Daltons.

3. Glyceryl Esters of Fatty Acids

Synthetic or naturally occurring glyceryl esters of fatty acids, or triglycerides, are also suitable for use in the compositions. Both vegetable and animal sources may be used.
30 Examples of such oils include castor oil, lanolin oil, C₁₀₋₁₈ triglycerides, caprylic/capric/triglycerides, sweet almond oil, apricot kernel oil, sesame oil, camelina sativa oil, tamanu seed oil, coconut oil, corn oil, cottonseed oil, linseed oil, ink oil, olive oil, palm

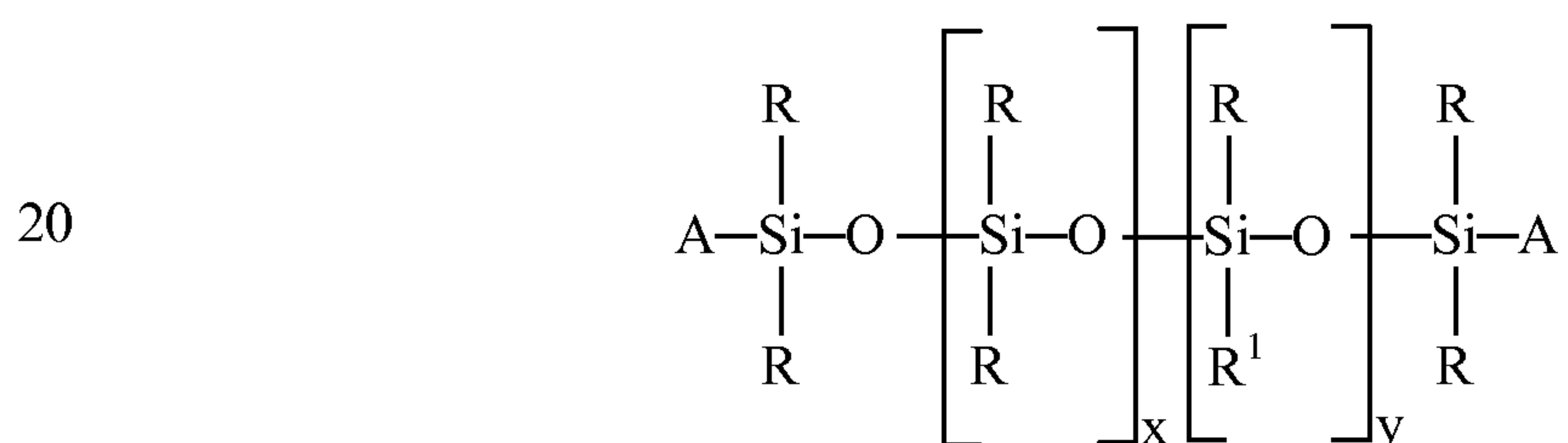
oil, illipe butter, rapeseed oil, soybean oil, grapeseed oil, sunflower seed oil, walnut oil, and the like.

Also suitable are synthetic or semi-synthetic glyceryl esters, such as fatty acid mono-, di-, and triglycerides which are natural fats or oils that have been modified, for example, mono-, di- or triesters of polyols such as glycerin. In an example, a fatty (C₁₂₋₂₂) carboxylic acid is reacted with one or more repeating glyceryl groups. glyceryl stearate, diglyceryl diiosostearate, polyglyceryl-3 isostearate, polyglyceryl-4 isostearate, polyglyceryl-6 ricinoleate, glyceryl dioleate, glyceryl diisostearate, glyceryl tetraisostearate, glyceryl trioctanoate, diglyceryl distearate, glyceryl linoleate, glyceryl myristate, glyceryl isostearate, PEG castor oils, PEG glyceryl oleates, PEG glyceryl stearates, PEG glyceryl tallowates, and so on.

4. Nonvolatile Silicones

Nonvolatile silicone oils, both water soluble and water insoluble, are also suitable for use in the composition. Such silicones preferably have a viscosity ranging from about greater than 5 to 800,000 cst, preferably 20 to 200,000 cst at 25° C. Suitable water insoluble silicones include amine functional silicones such as amodimethicone.

For example, such nonvolatile silicones may have the following general formula:



wherein R and R' are each independently C₁₋₃₀ straight or branched chain, saturated or unsaturated alkyl, phenyl or aryl, trialkylsiloxy, and x and y are each independently 1-1,000,000; with the proviso that there is at least one of either x or y, and A is alkyl siloxy endcap unit. Preferred is where A is a methyl siloxy endcap unit; in particular trimethylsiloxy, and R and R' are each independently a C₁₋₃₀ straight or branched chain alkyl, phenyl, or trimethylsiloxy, more preferably a C₁₋₂₂ alkyl, phenyl, or trimethylsiloxy, most preferably methyl, phenyl, or trimethylsiloxy, and resulting silicone is dimethicone, phenyl dimethicone, diphenyl dimethicone, phenyl trimethicone, or trimethylsiloxyphenyl

dimethicone. Other examples include alkyl dimethicones such as cetyl dimethicone, and the like wherein at least one R is a fatty alkyl (C₁₂, C₁₄, C₁₆, C₁₈, C₂₀, or C₂₂), and the other R is methyl, and A is a trimethylsiloxy endcap unit, provided such alkyl dimethicone is a pourable liquid at room temperature. Phenyl trimethicone can be purchased from Dow Corning Corporation under the tradename 556 Fluid. Trimethylsiloxyphenyl dimethicone can be purchased from Wacker-Chemie under the tradename PDM-1000. Cetyl dimethicone, also referred to as a liquid silicone wax, may be purchased from Dow Corning as Fluid 2502, or from DeGussa Care & Surface Specialties under the trade names Abil Wax 9801, or 9814.

5. Fluorinated Oils

Various types of fluorinated oils may also be suitable for use in the compositions including but not limited to fluorinated silicones, fluorinated esters, or perfluoropolyethers. Particularly suitable are fluorosilicones such as trimethylsilyl endcapped fluorosilicone oil, polytrifluoropropylmethoxysiloxanes, and similar silicones such as those disclosed in U.S. Pat. No. 5,118,496. Perfluoropolyethers include those disclosed in U.S. Pat. Nos. 5,183,589, 4,803,067, 5,183,588, which are commercially available from Montefluos under the trademark Fomblin.

In the case where the composition is anhydrous or in the form of an emulsion, it may be desirable to include one or more oil phase structuring agents in the cosmetic composition. The term "oil phase structuring agent" means an ingredient or combination of ingredients, soluble or dispersible in the oil phase, which will increase the viscosity, or structure, the oil phase. The oil phase structuring agent is compatible with the Type I H⁺, K⁺-ATPase inhibitor compound or derivative thereof, particularly if the Type I H⁺, K⁺-ATPase inhibitor compound or derivative thereof is soluble in the nonpolar oils forming the oil phase of the composition. The term "compatible" means that the oil phase structuring agent and Type I H⁺, K⁺-ATPase inhibitor compound or derivative thereof are capable of being formulated into a cosmetic product that is generally stable. The structuring agent may be present in an amount sufficient to provide a liquid composition with increased viscosity, a semi-solid, or in some cases a solid composition that may be self-supporting. The structuring agent itself may be present in the liquid, semi-solid, or solid form. Suggested ranges of structuring agent are from about 0.01 to 70%, preferably from about 0.05 to 50%, more preferably from about 0.1-35% by weight of the total composition. Suitable oil phase structuring agents include those that are silicone

based or organic based. They may be polymers or non-polymers, synthetic, natural, or a combination of both. Such oil structuring agents may include the following:

A. Silicone Structuring Agents

5 A variety of oil phase structuring agents may be silicone based, such as silicone elastomers, silicone gums, silicone waxes, and linear silicones having a degree of polymerization that provides the silicone with a degree of viscosity such that when incorporated into the cosmetic composition it is capable of increasing the viscosity of the oil phase. Examples of silicone structuring agents include, but are not limited to:

1. Silicone Elastomers

10 Silicone elastomers suitable for use in the compositions of the invention include those that are formed by addition reaction-curing, by reacting an SiH-containing diorganosiloxane and an organopolysiloxane having terminal olefinic unsaturation, or an alpha-omega diene hydrocarbon, in the presence of a platinum metal catalyst. Such elastomers may also be formed by other reaction methods such as condensation-curing organopolysiloxane
15 compositions in the presence of an organotin compound via a dehydrogenation reaction between hydroxyl-terminated diorganopolysiloxane and SiH-containing diorganopolysiloxane or alpha omega diene; or by condensation-curing organopolysiloxane compositions in the presence of an organotin compound or a titanate ester using a condensation reaction between an hydroxyl-terminated diorganopolysiloxane and a hydrolysable organosiloxane; peroxide-
20 curing organopolysiloxane compositions which thermally cure in the presence of an organoperoxide catalyst.

One type of elastomer that may be suitable is prepared by addition reaction-curing an organopolysiloxane having at least 2 lower alkenyl groups in each molecule or an alpha-omega diene; and an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in
25 each molecule; and a platinum-type catalyst. While the lower alkenyl groups such as vinyl, can be present at any position in the molecule, terminal olefinic unsaturation on one or both molecular terminals is preferred. The molecular structure of this component may be straight chain, branched straight chain, cyclic, or network. These organopolysiloxanes are exemplified by methylvinylsiloxanes, methylvinylsiloxane-dimethylsiloxane copolymers,
30 dimethylvinylsiloxyl-terminated dimethylpolysiloxanes, dimethylvinylsiloxyl-terminated dimethylsiloxane-methylphenylsiloxane copolymers, dimethylvinylsiloxyl-terminated dimethylsiloxane-diphenylsiloxane-methylvinylsiloxane copolymers, trimethylsiloxyl-terminated dimethylsiloxane-methylvinylsiloxane copolymers, trimethylsiloxyl-terminated

dimethylsiloxane-methylphenylsiloxane-methylvinylsiloxane copolymers,
dimethylvinylsiloxo-terminated methyl(3,3,3-trifluoropropyl) polysiloxanes, and
dimethylvinylsiloxo-terminated dimethylsiloxane-methyl(3,3-trifluoropropyl)siloxane
copolymers, decadiene, octadiene, heptadiene, hexadiene, pentadiene, or tetradiene, or
5 tridiene.

Curing proceeds by the addition reaction of the silicon-bonded hydrogen atoms in the
dimethyl methylhydrogen siloxane, with the siloxane or alpha-omega diene under catalysis
using the catalyst mentioned herein. To form a highly crosslinked structure, the methyl
hydrogen siloxane must contain at least 2 silicon-bonded hydrogen atoms in each molecule in
10 order to optimize function as a crosslinker.

The catalyst used in the addition reaction of silicon-bonded hydrogen atoms and
alkenyl groups, and is concretely exemplified by chloroplatinic acid, possibly dissolved in an
alcohol or ketone and this solution optionally aged, chloroplatinic acid-olefin complexes,
chloroplatinic acid-alkenylsiloxane complexes, chloroplatinic acid-diketone complexes,
15 platinum black, and carrier-supported platinum.

Examples of suitable silicone elastomers for use in the compositions of the invention
may be in the powder form, or dispersed or solubilized in solvents such as volatile or non-
volatile silicones, or silicone compatible vehicles such as paraffinic hydrocarbons or esters.
Examples of silicone elastomer powders include vinyl dimethicone/methicone silesquioxane
20 crosspolymers like Shin-Etsu's KSP-100, KSP-101, KSP-102, KSP-103, KSP-104, KSP-105,
hybrid silicone powders that contain a fluoroalkyl group like Shin-Etsu's KSP-200 which is a
fluoro-silicone elastomer, and hybrid silicone powders that contain a phenyl group such as
Shin-Etsu's KSP-300, which is a phenyl substituted silicone elastomer; and Dow Coming's DC
9506. Examples of silicone elastomer powders dispersed in a silicone compatible vehicle
25 include dimethicone/vinyl dimethicone crosspolymers supplied by a variety of suppliers
including Dow Corning Corporation under the tradenames 9040 or 9041, GE Silicones under
the tradename SFE 839, or Shin-Etsu Silicones under the tradenames KSG-15, 16, 18. KSG-
15 has the CTFA name cyclopentasiloxane/dimethicone/vinyl dimethicone crosspolymer.
KSG-18 has the INCI name phenyl trimethicone/dimethicone/phenyl vinyl dimethicone
30 crossopolymer. Silicone elastomers may also be purchased from Grant Industries under the
Gransil trademark. Also suitable are silicone elastomers having long chain alkyl substitutions
such as lauryl dimethicone/vinyl dimethicone crosspolymers supplied by Shin Etsu under the
tradenames KSG-31, KSG-32, KSG-41, KSG-42, KSG-43, and KSG-44. Cross-linked

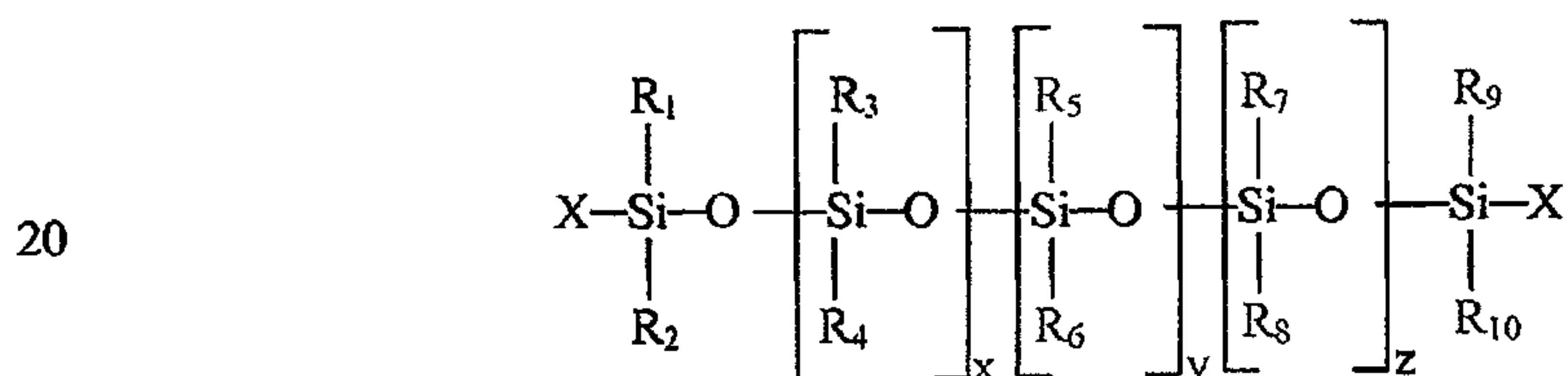
organopolysiloxane elastomers useful in the present invention and processes for making them are further described in U.S. Pat. No. 4,970,252; U.S. Pat. No. 5,760,116; U.S. Pat. No. 5,654,362; and Japanese Patent Application JP 61-18708.

It is particularly desirable to incorporate silicone elastomers into the compositions of the invention because they provide excellent "feel" to the composition, are very stable in cosmetic formulations, and relatively inexpensive.

2. Silicone Gums

Also suitable for use as an oil phase structuring agent are one or more silicone gums. The term "gum" means a silicone polymer having a degree of polymerization sufficient to provide a silicone having a gum-like texture. In certain cases the silicone polymer forming the gum may be crosslinked. The silicone gum typically has a viscosity ranging from about 500,000 to 100 million cst at 25° C., preferably from about 600,000 to 20 million, more preferably from about 600,000 to 12 million cst. All ranges mentioned herein include all subranges, e.g. 550,000; 925,000; 3.5 million.

The silicone gums that are used in the compositions include, but are not limited to, those of the general formula:



wherein R₁ to R₉ are each independently an alkyl having 1 to 30 carbon atoms, aryl, or aralkyl; and X is OH or a C₁₋₃₀ alkyl, or vinyl; and wherein x, y, or z may be zero with the proviso that no more than two of x, y, or z are zero at any one time, and further that x, y, and z are such that the silicone gum has a viscosity of at least about 500,000 cst, ranging up to about 100 million centistokes at 25° C. Preferred is where R is methyl or OH.

Such silicone gums may be purchased in pure form from a variety of silicone manufacturers including Wacker-Chemie or Dow Corning, and the like. Such silicone gums include those sold by Wacker-Belsil under the trade names CM3092, Wacker-Belsil 1000, or Wacker-Belsil DM 3096. A silicone gum where X is OH, also referred to as dimethiconol, is available from Dow Corning Corporation under the trade name 1401. The silicone gum may

also be purchased in the form of a solution or dispersion in a silicone compatible vehicle such as volatile or nonvolatile silicone. An example of such a mixture may be purchased from Barnet Silicones under the HL-88 tradename, having the INCI name dimethicone.

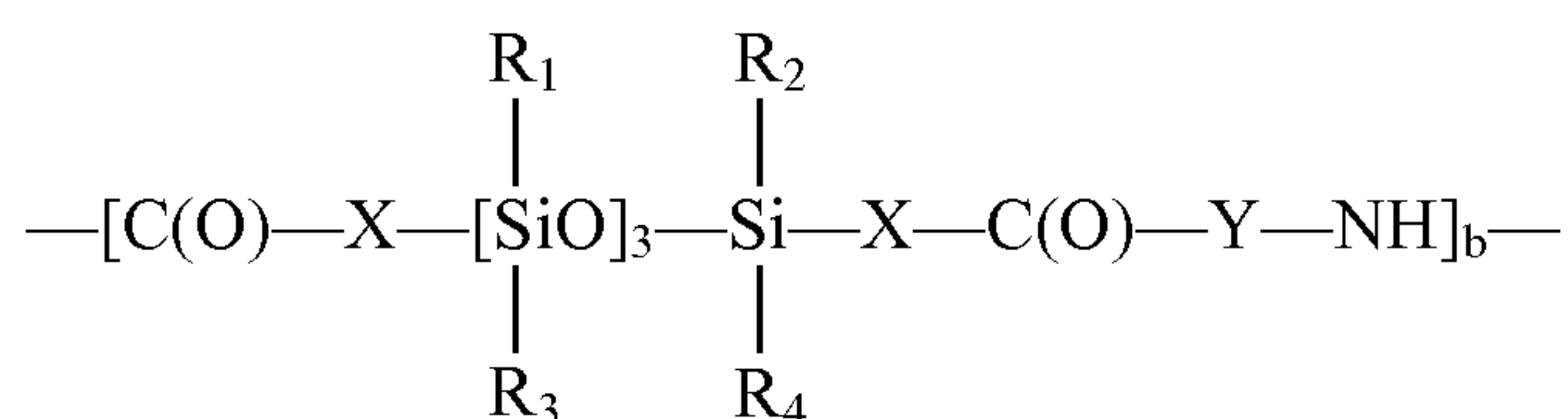
3. Silicone Waxes

Another type of oily phase structuring agent includes silicone waxes that are typically referred to as alkyl silicone waxes which are semi-solids or solids at room temperature. The term “alkyl silicone wax” means a polydimethylsiloxane having a substituted long chain alkyl (such as C16 to 30) that confers a semi-solid or solid property to the siloxane. Examples of such silicone waxes include stearyl dimethicone, which may be purchased from DeGussa Care & Surface Specialties under the tradename Abil Wax 9800 or from Dow Corning under the tradename 2503. Another example is bis-stearyl dimethicone, which may be purchased from Gransil Industries under the tradename Gransil A-18, or behenyl dimethicone, behenoxy dimethicone.

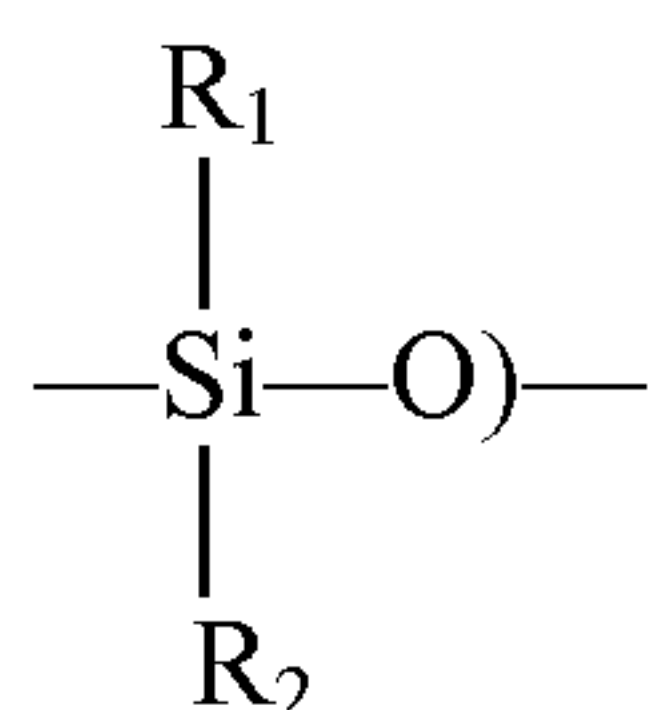
4. Polyamides or Silicone Polyamides

Also suitable as oil phase structuring agents are various types of polymeric compounds such as polyamides or silicone polyamides.

The term silicone polyamide means a polymer comprised of silicone monomers and monomers containing amide groups as further described herein. The silicone polyamide preferably comprises moieties of the general formula:



X is a linear or branched alkylene having from about 1-30 carbon atoms; R₁, R₂, R₃, and R₄ are each independently C₁₋₃₀ straight or branched chain alkyl which may be substituted with one or more hydroxyl or halogen groups; phenyl which may be substituted with one or more C₁₋₃₀ alkyl groups, halogen, hydroxyl, or alkoxy groups; or a siloxane chain having the general formula:



and Y is:

5

(a) a linear or branched alkylene having from about 1-40 carbon atoms which may be substituted with:

(i) one or more amide groups having the general formula R_1CONR_1 , or

(ii) C_{5-6} cyclic ring, or

10 (iii) phenylene which may be substituted with one or more C_{1-10} alkyl groups, or

(iv) hydroxy, or

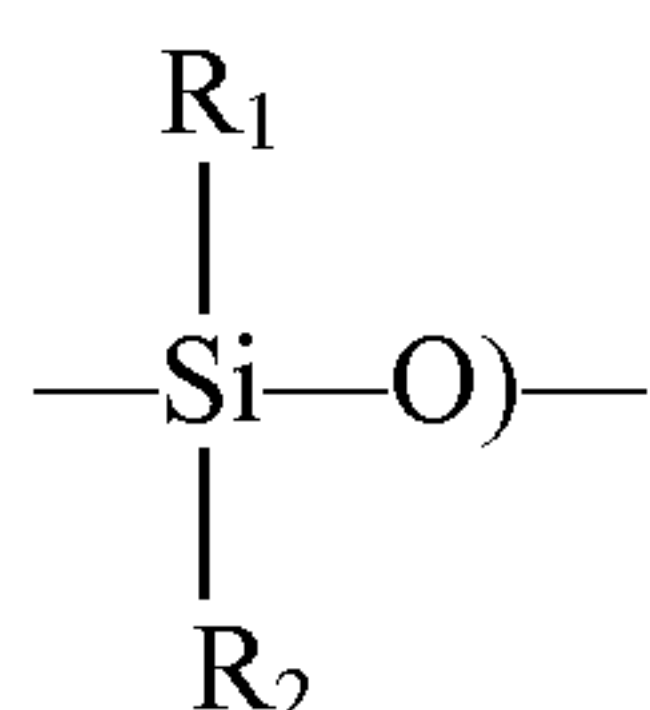
(v) C_{3-8} cycloalkane, or

(vi) C_{1-20} alkyl which may be substituted with one or more hydroxy groups, or

(vii) C_{1-10} alkyl amines; or

15 (b) $\text{TR}_5\text{R}_6\text{R}_7$

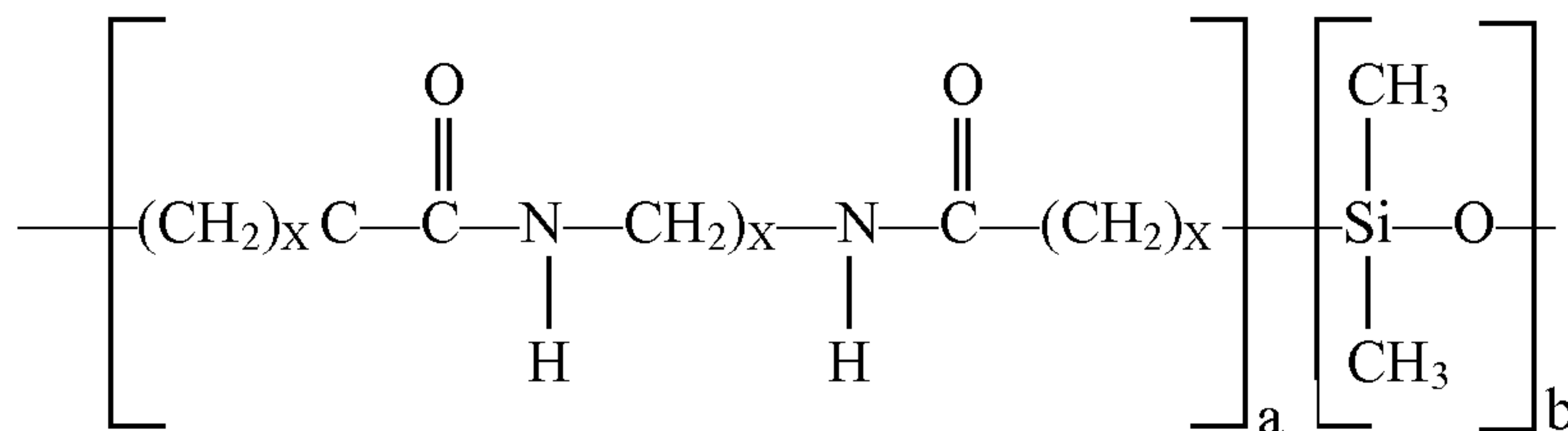
wherein R_5 , R_6 , and R_7 , are each independently a C_{1-10} linear or branched alkylenes, and T is CR_8 wherein R_8 is hydrogen, a trivalent atom N, P, or Al, or a C_{1-30} straight or branched chain alkyl which may be substituted with one or more hydroxyl or halogen groups; phenyl which
20 may be substituted with one or more C_{1-30} alkyl groups, halogen, hydroxyl, or alkoxy groups; or a siloxane chain having the general formula:



25

Preferred is where R_1 , R_2 , R_3 , and R_4 are C_{1-10} , preferably methyl; and X and Y are a linear or branched alkylene. Preferred are silicone polyamides having the general formula:

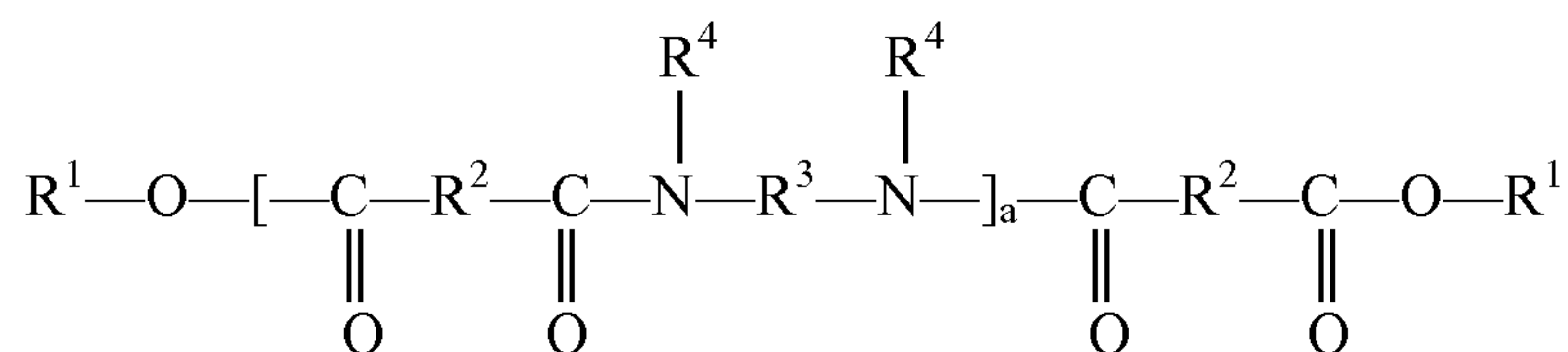
30



5

wherein a and b are each independently sufficient to provide a silicone polyamide polymer having a melting point ranging from about 60 to 120° C., and a molecular weight ranging from about 40,000 to 500,000 Daltons. One type of silicone polyamide that may be used in the compositions of the invention may be purchased from Dow Corning Corporation under the tradename Dow Corning 2-8178 gellant which has the CTFA name nylon-611/dimethicone copolymer which is sold in a composition containing PPG-3 myristyl ether.

Also suitable are polyamides such as those purchased from Arizona Chemical under the tradenames Uniclear and Sylvaclear. Such polyamides may be ester terminated or amide terminated. Examples of ester terminated polyamides include, but are not limited to those having the general formula:



20

wherein n denotes a number of amide units such that the number of ester groups ranges from about 10% to 50% of the total number of ester and amide groups; each R₁ is independently an alkyl or alkenyl group containing at least 4 carbon atoms; each R₂ is independently a C₄₋₄₂ hydrocarbon group, with the proviso that at least 50% of the R₂ groups are a C₃₀₋₄₂ hydrocarbon; each R₃ is independently an organic group containing at least 2 carbon atoms, hydrogen atoms and optionally one or more oxygen or nitrogen atoms; and each R₄ is independently a hydrogen atom, a C₁₋₁₀ alkyl group or a direct bond to R₃ or to another R₄, such that the nitrogen atom to which R₃ and R₄ are both attached forms part of a heterocyclic

structure defined by R_4-N-R_3 , with at least 50% of the groups R_4 representing a hydrogen atom.

General examples of ester and amide terminated polyamides that may be used as oil phase gelling agents include those sold by Arizona Chemical under the tradenames Sylvaclear A200V or A2614V, both having the CTFA name ethylenediamine/hydrogenated dimer dilinoleate copolymer/bis-di- C_{14-18} alkyl amide; Sylvaclear AF1900V; Sylvaclear C75V having the CTFA name bis-stearyl ethylenediamine/neopentyl glycol/stearyl hydrogenated dimer dilinoleate copolymer; Sylvaclear PA1200V having the CTFA name Polyamide-3; Sylvaclear PE400V; Sylvaclear WF1500V; or Uniclear, such as Uniclear 100VG having the INCI name ethylenediamine/stearyl dimer dilinoleate copolymer; or ethylenediamine/stearyl dimer ditallate copolymer. Other examples of suitable polyamides include those sold by Henkel under the Versamid trademark (such as Versamid 930, 744, 1655), or by Olin Mathieson Chemical Corp. under the brand name Onamid S or Onamid C.

5. Natural or Synthetic Organic Waxes

Also suitable as the oil phase structuring agent may be one or more natural or synthetic waxes such as animal, vegetable, or mineral waxes. Preferably such waxes will have a higher melting point such as from about 50 to 150° C., more preferably from about 65 to 100° C. Examples of such waxes include waxes made by Fischer-Tropsch synthesis, such as polyethylene or synthetic wax; or various vegetable waxes such as bayberry, candelilla, ozokerite, acacia, beeswax, ceresin, cetyl esters, flower wax, citrus wax, carnauba wax, jojoba wax, japan wax, polyethylene, microcrystalline, rice bran, lanolin wax, mink, montan, bayberry, ouricury, ozokerite, palm kernel wax, paraffin, avocado wax, apple wax, shellac wax, clary wax, spent grain wax, grape wax, and polyalkylene glycol derivatives thereof such as PEG6-20 beeswax, or PEG-12 carnauba wax; or fatty acids or fatty alcohols, including esters thereof, such as hydroxystearic acids (for example 12-hydroxy stearic acid), tristearin, tribehenin, and so on.

6. Montmorillonite Minerals

One type of structuring agent that may be used in the composition comprises natural or synthetic montmorillonite minerals such as hectorite, bentonite, and quaternized derivatives thereof, which are obtained by reacting the minerals with a quaternary ammonium compound, such as stearalkonium bentonite, hectorites, quaternized hectorites such as Quaternium-18 hectorite, attapulgite, carbonates such as propylene carbonate, bentones, and the like.

7. Silicas and Silicates

Another type of structuring agent that may be used in the compositions are silicas, silicates, silica silylate, and alkali metal or alkaline earth metal derivatives thereof. These silicas and silicates are generally found in the particulate form and include silica, silica
5 silylate, magnesium aluminum silicate, and the like.

The composition may contain one or more surfactants, especially if in the emulsion form. However, such surfactants may be used if the compositions are anhydrous also, and will assist in dispersing ingredients that have polarity, for example pigments. Such surfactants may be silicone or organic based. The surfactants will aid in the formation of stable emulsions of
10 either the water-in-oil or oil-in-water form. If present, the surfactant may range from about 0.001 to 30%, preferably from about 0.005 to 25%, more preferably from about 0.1 to 20% by weight of the total composition.

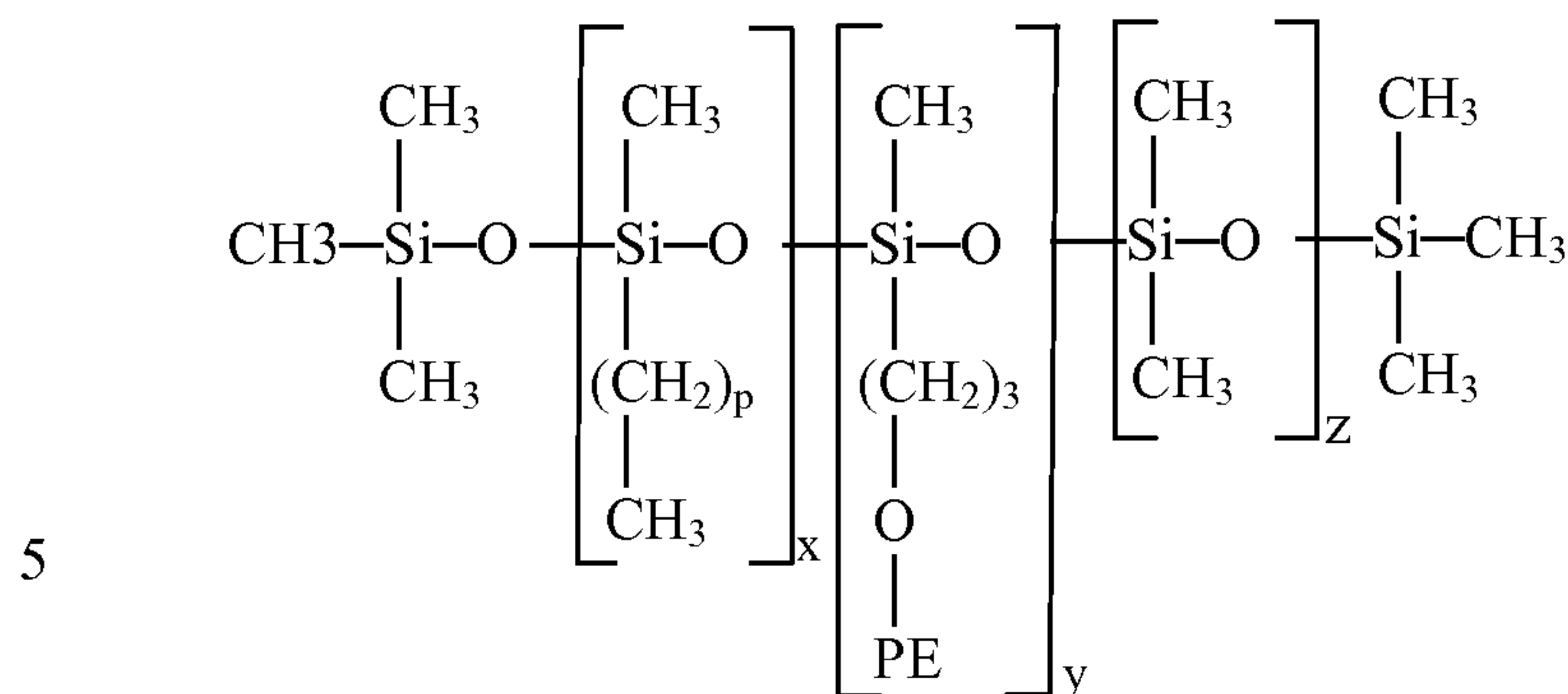
A. Silicone Surfactants

Suitable silicone surfactants include polyorganosiloxane polymers that have
15 amphiphilic properties, for example contain hydrophilic radicals and lipophilic radicals. These silicone surfactants may be liquids or solids at room temperature.

1. Dimethicone Copolyols or Alkyl Dimethicone Copolyols

One type of silicone surfactant that may be used is generally referred to as dimethicone copolyol or alkyl dimethicone copolyol. This surfactant is either a water-in-oil or oil-in-water
20 surfactant having an Hydrophile/Lipophile Balance (HLB) ranging from about 2 to 18. Preferably the silicone surfactant is a nonionic surfactant having an HLB ranging from about 2 to 12, preferably about 2 to 10, most preferably about 4 to 6. The term "hydrophilic radical" means a radical that, when substituted onto the organosiloxane polymer backbone, confers hydrophilic properties to the substituted portion of the polymer. Examples of radicals that will
25 confer hydrophilicity are hydroxy-polyethyleneoxy, hydroxyl, carboxylates, and mixtures thereof. The term "lipophilic radical" means an organic radical that, when substituted onto the organosiloxane polymer backbone, confers lipophilic properties to the substituted portion of the polymer. Examples of organic radicals that will confer lipophilicity are C₁₋₄₀ straight or branched chain alkyl, fluoro, aryl, aryloxy, C₁₋₄₀ hydrocarbyl acyl, hydroxy-polypropyleneoxy,
30 or mixtures thereof.

One type of suitable silicone surfactant has the general formula:



wherein p is 0-40 (the range including all numbers between and subranges such as 2, 3, 4, 13, 14, 15, 16, 17, 18, etc.), and PE is $(-\text{C}_2\text{H}_4\text{O})_a(-\text{C}_3\text{H}_6\text{O})_b\text{H}$ wherein a is 0 to 25, b is 0-25 with
 10 the proviso that both a and b cannot be 0 simultaneously, x and y are each independently ranging from 0 to 1 million with the proviso that they both cannot be 0 simultaneously. In one preferred embodiment, x, y, z, a, and b are such that the molecular weight of the polymer ranges from about 5,000 to about 500,000, more preferably from about 10,000 to 100,000, and is most preferably approximately about 50,000 and the polymer is generically referred to as
 15 dimethicone copolyol.

One type of silicone surfactant is wherein p is such that the long chain alkyl is cetyl or lauryl, and the surfactant is called, generically, cetyl dimethicone copolyol or lauryl dimethicone copolyol respectively.

In some cases the number of repeating ethylene oxide or propylene oxide units in the
 20 polymer are also specified, such as a dimethicone copolyol that is also referred to as PEG-15/PPG-10 dimethicone, which refers to a dimethicone having substituents containing 15 ethylene glycol units and 10 propylene glycol units on the siloxane backbone. It is also possible for one or more of the methyl groups in the above general structure to be substituted with a longer chain alkyl (e.g. ethyl, propyl, butyl, etc.) or an ether such as methyl ether, ethyl
 25 ether, propyl ether, butyl ether, and the like.

Examples of silicone surfactants are those sold by Dow Corning under the tradename Dow Corning 3225C Formulation Aid having the CTFA name cyclotetrasiloxane (and) cyclopentasiloxane (and) PEG/PPG-18 dimethicone; or 5225C Formulation Aid, having the CTFA name cyclopentasiloxane (and) PEG/PPG-18/18 dimethicone; or Dow Corning 190
 30 Surfactant having the CTFA name PEG/PPG-18/18 dimethicone; or Dow Corning 193 Fluid, Dow Corning 5200 having the CTFA name lauryl PEG/PPG-18/18 methicone; or Abil EM 90

having the CTFA name cetyl PEG/PPG-14/14 dimethicone sold by Goldschmidt; or Abil EM 97 having the CTFA name bis-cetyl PEG/PPG-14/14 dimethicone sold by Goldschmidt; or Abil WE 09 having the CTFA name cetyl PEG/PPG-10/1 dimethicone in a mixture also containing polyglyceryl-4 isostearate and hexyl laurate; or KF-6011 sold by Shin-Etsu
 5 Silicones having the CTFA name PEG-11 methyl ether dimethicone; KF-6012 sold by Shin-Etsu Silicones having the CTFA name PEG/PPG-20/22 butyl ether dimethicone; or KF-6013 sold by Shin-Etsu Silicones having the CTFA name PEG-9 dimethicone; or KF-6015 sold by Shin-Etsu Silicones having the CTFA name PEG-3 dimethicone; or KF-6016 sold by Shin-Etsu Silicones having the CTFA name PEG-9 methyl ether dimethicone; or KF-6017 sold by
 10 Shin-Etsu Silicones having the CTFA name PEG-10 dimethicone; or KF-6038 sold by Shin-Etsu Silicones having the CTFA name lauryl PEG-9 polydimethylsiloxylethyl dimethicone.

2. Crosslinked Silicone Surfactants

Also suitable are various types of crosslinked silicone surfactants that are often referred to as emulsifying elastomers. They are typically prepared as set forth above with
 15 respect to the section "silicone elastomers" except that the silicone elastomers will contain at least one hydrophilic moiety such as polyoxyalkylenated groups. Typically these polyoxyalkylenated silicone elastomers are crosslinked organopolysiloxanes that may be obtained by a crosslinking addition reaction of diorganopolysiloxane comprising at least one hydrogen bonded to silicon and of a polyoxyalkylene comprising at least two ethylenically
 20 unsaturated groups. In at least one embodiment, the polyoxyalkylenated crosslinked organopolysiloxanes are obtained by a crosslinking addition reaction of a diorganopolysiloxane comprising at least two hydrogens each bonded to a silicon, and a polyoxyalkylene comprising at least two ethylenically unsaturated groups, optionally in the presence of a platinum catalyst, as described, for example, in U.S. Pat. No. 5,236,986, U.S. Pat. No. 5,412,004, U.S. Pat. No.
 25 5,837,793 and U.S. Pat. No. 5,811,487.

Polyoxyalkylenated silicone elastomers that may be used in at least one embodiment of the invention include those sold by Shin-Etsu Silicones under the names KSG-21, KSG-20, KSG-30, KSG-31, KSG-32, KSG-33; KSG-210 which is dimethicone/PEG-10/15
 30 crosspolymer dispersed in dimethicone; KSG-310 which is PEG-15 lauryl dimethicone crosspolymer; KSG-320 which is PEG-15 lauryl dimethicone crosspolymer dispersed in isododecane; KSG-330 (the former dispersed in triethylhexanoin), KSG-340 which is a

mixture of PEG-10 lauryl dimethicone crosspolymer and PEG-15 lauryl dimethicone crosspolymer.

Also suitable are polyglycerolated silicone elastomers like those disclosed in PCT/WO 2004/024798. Such elastomers

5 include Shin-Etsu's KSG series, such as KSG-710 which is dimethicone/polyglycerin-3 crosspolymer dispersed in dimethicone; or lauryl dimethicone/polyglycerin-3 crosspolymer dispersed in a variety of solvent such as isododecane, dimethicone, triethylhexanoin, sold under the Shin-Etsu tradenames KSG-810, KSG-820, KSG-830, or KSG-840. Also suitable are silicones sold by Dow Corning under the tradenames 9010 and DC9011.

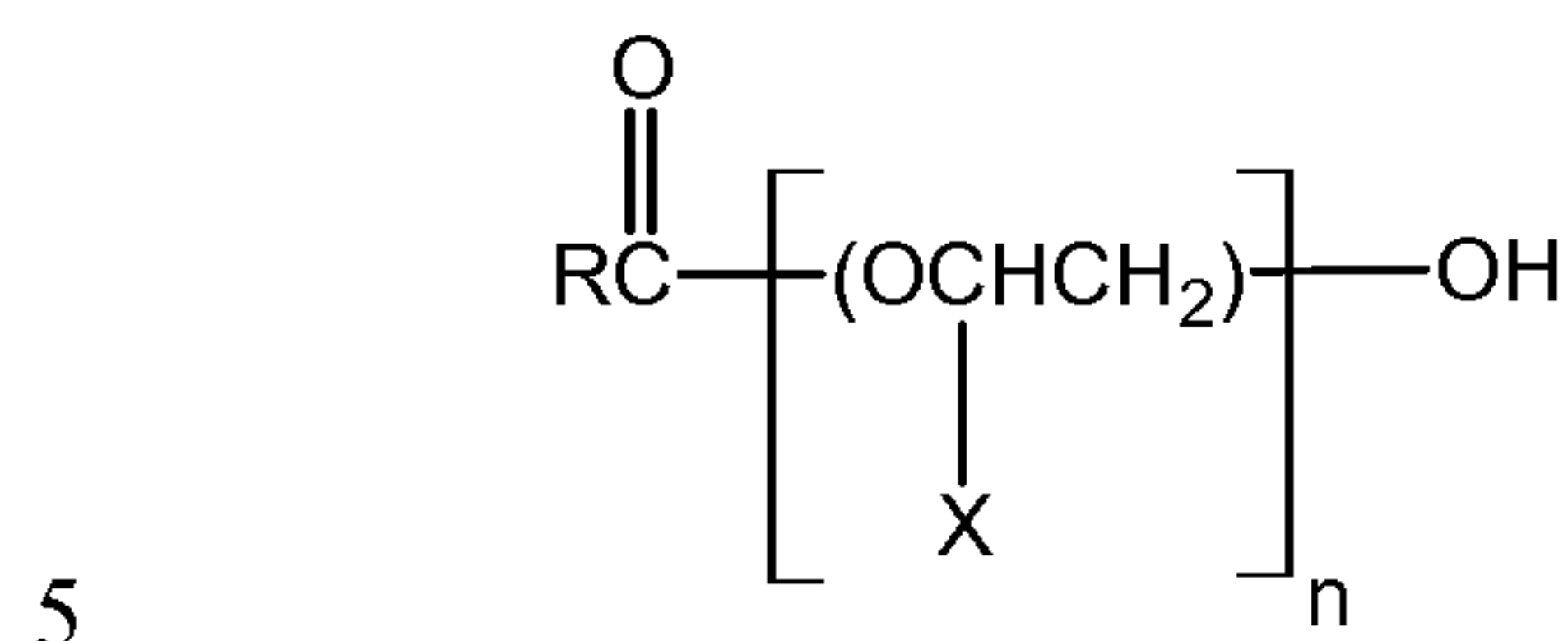
10 One preferred crosslinked silicone elastomer emulsifier is dimethicone/PEG-10/15 crosspolymer, which provides excellent aesthetics due to its elastomeric backbone, but also surfactancy properties.

B. Organic Nonionic Surfactants

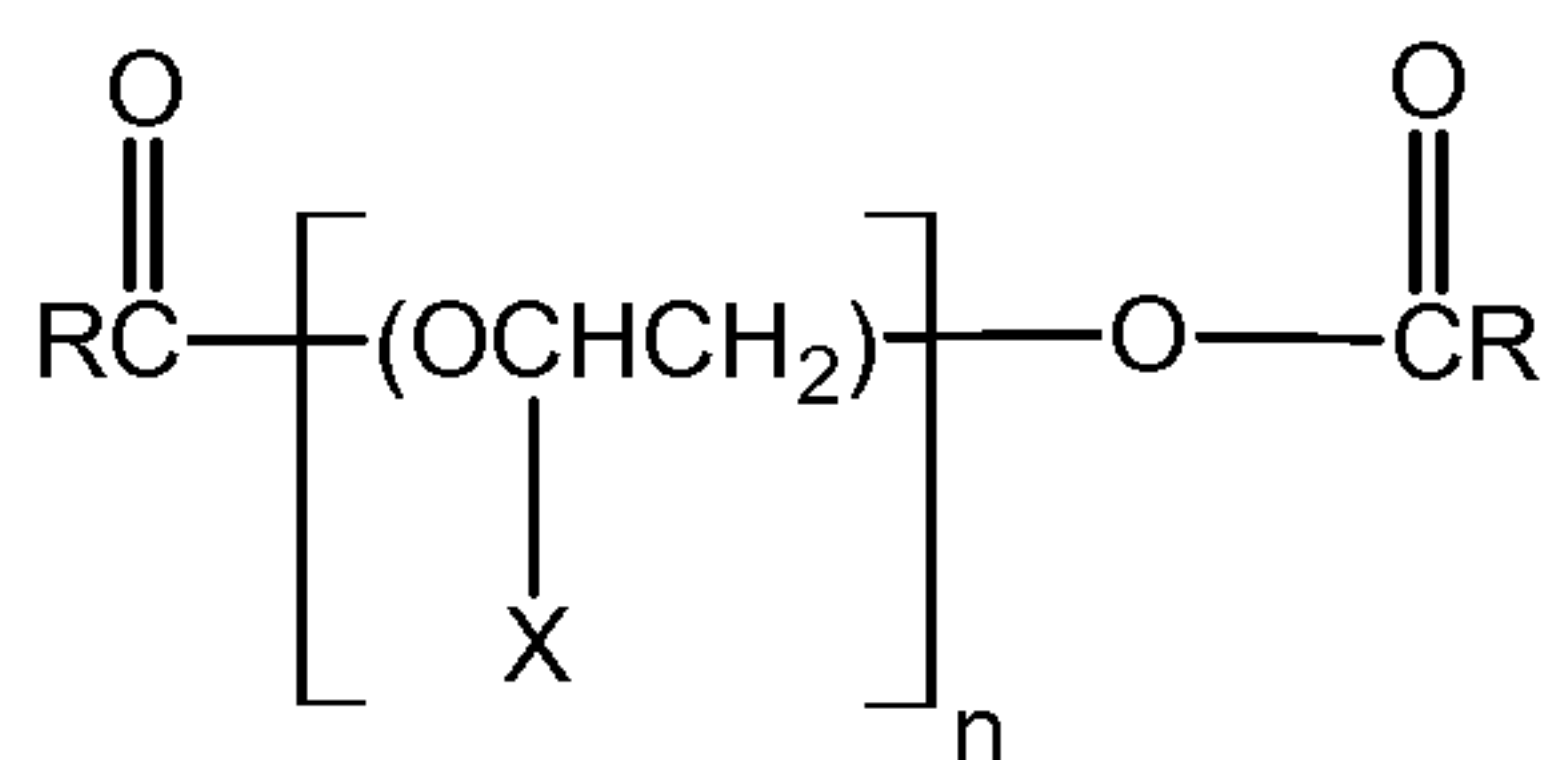
The composition may comprise one or more nonionic organic surfactants. Suitable
15 nonionic surfactants include alkoxylated alcohols, or ethers, formed by the reaction of an alcohol with an alkylene oxide, usually ethylene or propylene oxide. Preferably the alcohol is either a fatty alcohol having 6 to 30 carbon atoms. Examples of such ingredients include Steareth 2-100, which is formed by the reaction of stearyl alcohol and ethylene oxide and the number of ethylene oxide units ranges from 2 to 100; Beheneth 5-30 which is formed by the
20 reaction of behenyl alcohol and ethylene oxide where the number of repeating ethylene oxide units is 5 to 30; Cetareth 2-100, formed by the reaction of a mixture of cetyl and stearyl alcohol with ethylene oxide, where the number of repeating ethylene oxide units in the molecule is 2 to 100; Ceteth 1-45 which is formed by the reaction of cetyl alcohol and ethylene oxide, and the number of repeating ethylene oxide units is 1 to 45, and so on.

25 Other alkoxylated alcohols are formed by the reaction of fatty acids and mono-, di- or polyhydric alcohols with an alkylene oxide. For example, the reaction products of C₆₋₃₀ fatty carboxylic acids and polyhydric alcohols which are monosaccharides such as glucose, galactose, methyl glucose, and the like, with an alkoxylated alcohol. Examples include polymeric alkylene glycols reacted with glyceryl fatty acid esters such as PEG glyceryl
30 oleates, PEG glyceryl stearate; or PEG polyhydroxyalkanotes such as PEG dipolyhydroxystearate wherein the number of repeating ethylene glycol units ranges from 3 to 1000.

Also suitable as nonionic surfactants are those formed by the reaction of a carboxylic acid with an alkylene oxide or with a polymeric ether. The resulting products have the general formula:

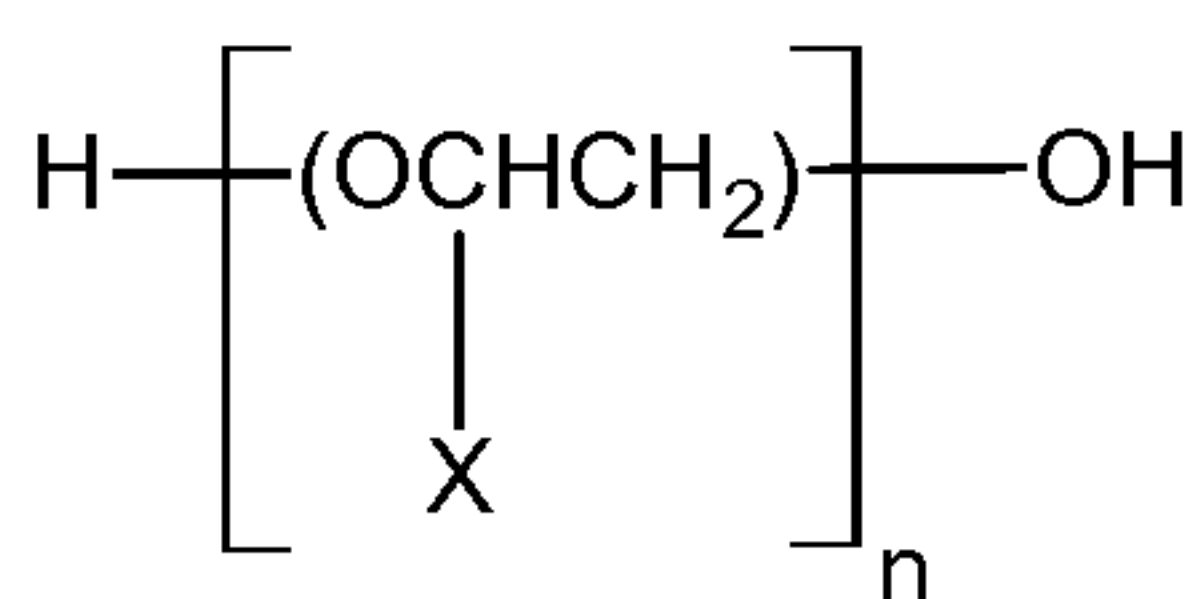


or



10 where RCO is the carboxylic ester radical, X is hydrogen or lower alkyl, and n is the number of polymerized alkoxy groups. In the case of the diesters, the two RCO-groups do not need to be identical. Preferably, R is a C6-30 straight or branched chain, saturated or unsaturated alkyl, and n is from 1-100.

15 Monomeric, homopolymeric, or block copolymeric ethers are also suitable as nonionic surfactants. Typically, such ethers are formed by the polymerization of monomeric alkylene oxides, generally ethylene or propylene oxide. Such polymeric ethers have the following general formula:



20 wherein R is H or lower alkyl and n is the number of repeating monomer units, and ranges from 1 to 500.

Other suitable nonionic surfactants include alkoxylated sorbitan and alkoxylated sorbitan derivatives. For example, alkoxylation, in particular ethoxylation of sorbitan provides polyalkoxylated sorbitan derivatives. Esterification of polyalkoxylated sorbitan provides sorbitan esters such as the polysorbates. For example, the polyalkoxyoxylated sorbitan can be esterified with C₆-30, preferably C₁₂-22 fatty acids. Examples of such ingredients include Polysorbates 20-85, sorbitan oleate, sorbitan sesquioleate, sorbitan palmitate, sorbitan sesquiisostearate, sorbitan stearate, and so on.

Certain types of amphoteric, zwitterionic, or cationic surfactants may also be used in the compositions. Descriptions of such surfactants are set forth in U.S. Pat. No. 5,843,193.

It may be desirable to include one or more penetration enhancers in the composition. Penetration enhancers are ingredients that enhance the penetration of the Type I H⁺, K⁺-ATPase inhibitor compound or derivative thereof into the keratinous surface to which the composition is applied. If present, suitable penetration enhancers may range from about 0.001 to 30%, preferably from about 0.005 to 25%, more preferably from about 0.01 to 20%. Suitable penetration enhancers include, but are not limited to lipophilic materials such as saturated or unsaturated C₆₋₄₀ straight or branched chain fatty acids, or saturated or unsaturated C₆₋₄₀ straight or branched chain fatty alcohols. Examples include oleic acid, linoleic acid, stearic acid, oleyl alcohol, linoleyl alcohol, and the like.

It may also be desirable to include one or more humectants in the composition. If present, such humectants may range from about 0.001 to 25%, preferably from about 0.005 to 20%, more preferably from about 0.1 to 15% by weight of the total composition. Examples of suitable humectants include glycols, sugars, and the like. Suitable glycols are in monomeric or polymeric form and include polyethylene and polypropylene glycols such as PEG 4-200, which are polyethylene glycols having from 4 to 200 repeating ethylene oxide units; as well as C₁₋₆ alkylene glycols such as propylene glycol, butylene glycol, pentylene glycol, and the like. Suitable sugars, some of which are also polyhydric alcohols, are also suitable humectants. Examples of such sugars include glucose, fructose, honey, hydrogenated honey, inositol, maltose, mannitol, maltitol, sorbitol, sucrose, xylitol, xylose, and so on. Also suitable is urea. Preferably, the humectants used in the composition of the invention are C₁₋₆, preferably C₂₋₄ alkylene glycols, most particularly butylene glycol.

It may be desirable to include one or more botanical extracts in the compositions. If so, suggested ranges are from about 0.0001 to 10%, preferably about 0.0005 to 8%, more

preferably about 0.001 to 5% by weight of the total composition. Suitable botanical extracts include extracts from plants (herbs, roots, flowers, fruits, seeds) such as flowers, fruits, vegetables, and so on, including yeast ferment extract, *Padina pavonica* extract, *Thermus thermophilis* ferment extract, *Camelina sativa* seed oil, *Boswellia serrata* extract, olive extract, 5 *Aribodopsis thaliana* extract, *Acacia dealbata* extract, *Acer saccharinum* (sugar maple), acidopholus, acorus, aesculus, agaricus, agave, agrimonia, algae, aloe, citrus, brassica, cinnamon, orange, apple, blueberry, cranberry, peach, pear, lemon, lime, pea, seaweed, caffeine, green tea, chamomile, willowbark, mulberry, poppy, and those set forth on pages 1646 through 1660 of the CTFA Cosmetic Ingredient Handbook, Eighth Edition, Volume 2.

10 Further specific examples include, but are not limited to, *Glycyrrhiza glabra*, *Salix nigra*, *Macrocystis pyrifera*, *Pyrus malus*, *Saxifraga sarmentosa*, *Vitis vinifera*, *Morus nigra*, *Scutellaria baicalensis*, *Anthemis nobilis*, *Salvia sclarea*, *Rosmarinus officianalis*, *Citrus medica Limonum*, *Panax*, *Ginseng*, *Siegesbeckia orientalis*, *Fructus mume*, *Ascophyllum nodosum*, Bifida Ferment lysate, *Glycine soja* extract, *Beta vulgaris*, *Haberlea rhodopensis*, 15 *Polygonum cuspidatum*, *Citrus Aurantium dulcis*, *Vitis vinifera*, *Selaginella tamariscina*, *Humulus lupulus*, *Citrus reticulata* Peel, *Punica granatum*, *Asparagopsis*, *Curcuma longa*, *Menyanthes trifoliata*, *Helianthus annuus*, *Hordeum vulgare*, *Cucumis sativus*, *Evernia prunastri*, *Evernia furfuracea*, and mixtures thereof.

It may be desirable to include one or more tyrosinase inhibiting agents in the 20 compositions of the invention. Such tyrosinase inhibitors may include kojic acid, arbutin and hydroquinone.

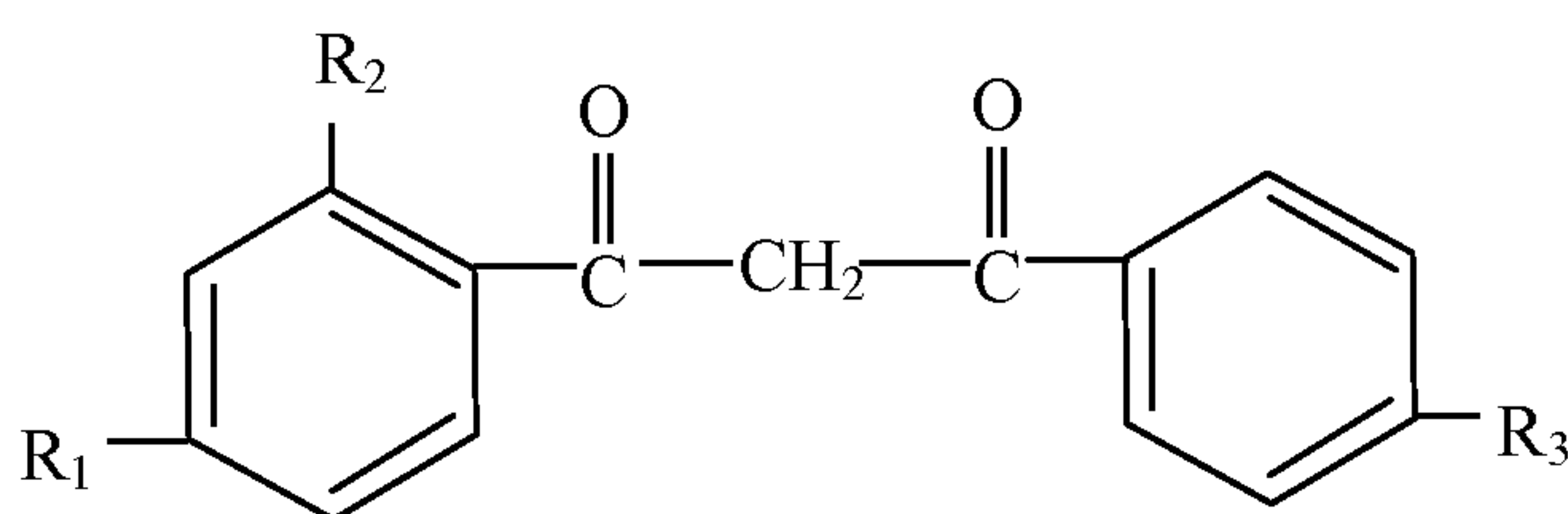
It may be desirable to include one or more additional skin-lightening compounds in the compositions of the present invention. Suitable skin-lightening compounds include ascorbic acid and its derivatives, e.g., magnesium ascorbyl phosphate, ascorbyl glucosamine, ascorbyl 25 palmitate. Other skin-lightening agents include adapalene, aloe extract, ammonium lactate, anethole derivatives, apple extract, azelaic acid, bamboo extract, bearberry extract, bletilla tuber, *Bupleurum falcatum* extract, burnet extract, butyl hydroxy anisole, butyl hydroxy toluene, deoxyarbutin, 1,3 diphenyl propane derivatives, 2,5 dihydroxybenzoic acid and its derivatives, 2-(4-acetoxyphenyl)-1,3 dithane, 2-(4-hydroxyphenyl)-1,3 dithane, ellagic acid, 30 escinol, estragole derivatives, FADE OUT (available from Pentapharm), Fangfeng, fennel extract, ganoderma extract, gaoben, GATULINE WHITENING (available from Gattlefosse), genistic acid and its derivatives, glabridin and its derivatives, gluco pyranosyl-1-ascorbate, gluconic acid, glycolic acid, green tea extract, placenta extract, 4-Hydroxy-5-methyl-3[2H]-

furanone, 4 hydroxyanisole and its derivatives, 4-hydroxy benzoic acid derivatives, hydroxycaprylic acid, inositol ascorbate, lactic acid, lemon extract, linoleic acid, MELA WHITE (available from Pentapharm), *Morus alba* extract, mulberry root extract, niacinamide, 5-octanoyl salicylic acid, parsley extract, phellinus linteus extract, pyrogallol derivatives, retinoic acid, retinol, retinyl esters (acetate, propionate, palmitate, linoleate), 2,4 resorcinol derivatives, 3,5 resorcinol derivatives, rose fruit extract, salicylic acid, 3,4,5 trihydroxybenzyl derivatives, tranexamic acid, vitamin D3 and its analogs, and mixtures thereof.

It may also be desirable to include one or more sunscreens in the compositions of the invention. Such sunscreens include chemical UVA or UVB sunscreens or physical sunscreens in the particulate form. Inclusion of sunscreens in the compositions containing the Type I H^+ , K^+ -ATPase inhibitor compound or derivative thereof will provide additional protection to skin during daylight hours and promote the effectiveness of the Type I H^+ , K^+ -ATPase inhibitor compound or derivative thereof on the skin. Such sunscreen compounds may include the following:

15 A. UVA Chemical Sunscreens

If desired, the composition may comprise one or more UVA sunscreens. The term "UVA sunscreen" means a chemical compound that blocks UV radiation in the wavelength range of about 320 to 400 nm. Preferred UVA sunscreens are dibenzoylmethane compounds having the general formula:

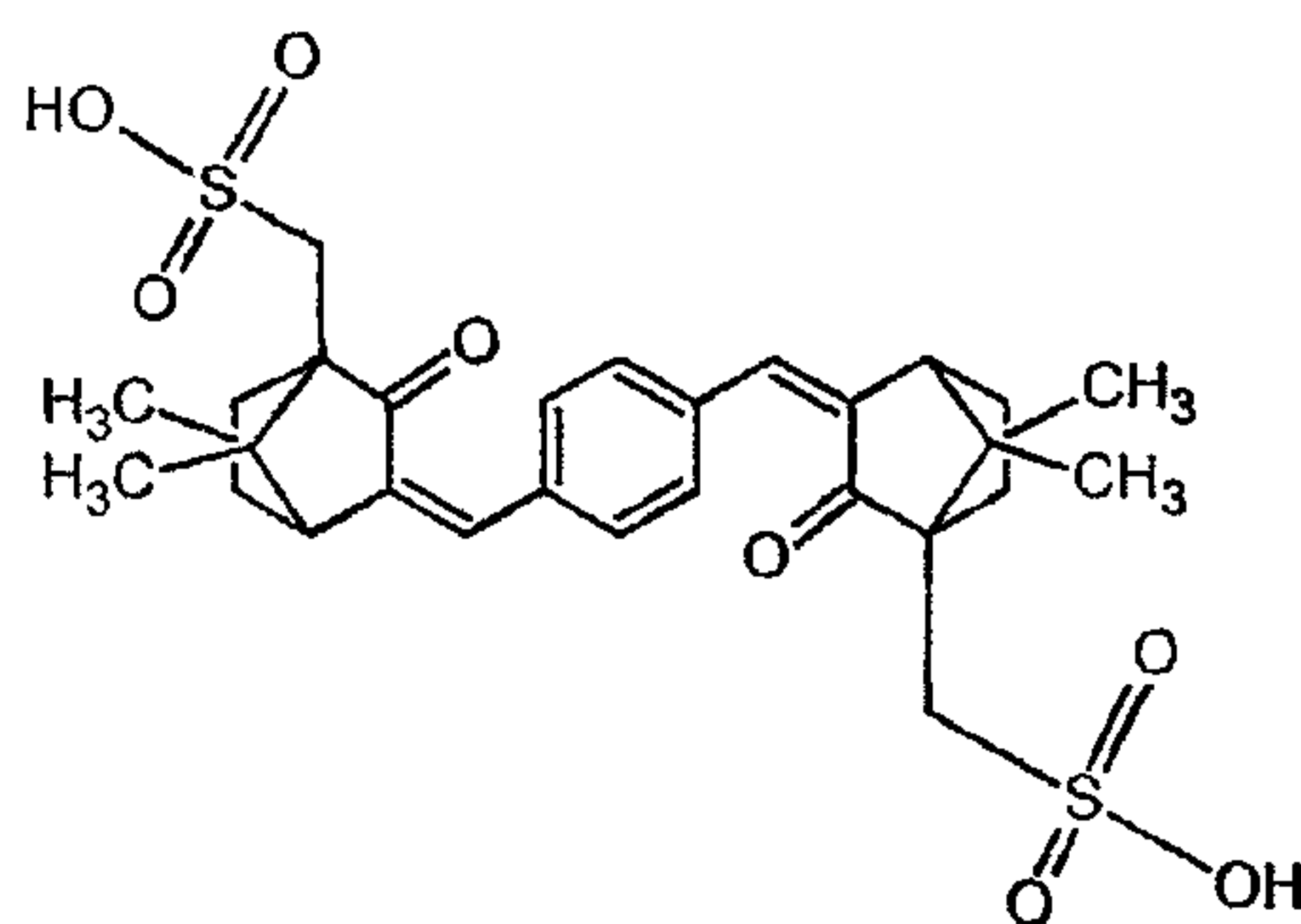


wherein R_1 is H, OR and NRR wherein each R is independently H, C_{1-20} straight or branched chain alkyl; R_2 is H or OH; and R_3 is H, C_{1-20} straight or branched chain alkyl.

Preferred is where R_1 is OR where R is a C_{1-20} straight or branched alkyl, preferably methyl; R_2 is H; and R_3 is a C_{1-20} straight or branched chain alkyl, more preferably, butyl.

Examples of suitable UVA sunscreen compounds of this general formula include 4-methyldibenzoylmethane, 2-methyldibenzoylmethane, 4-isopropyldibenzoylmethane, 4-tert-butyldibenzoylmethane, 2,4-dimethyldibenzoylmethane, 2,5-dimethyldibenzoylmethane, 4,4'-diisopropylbenzoylmethane, 4-tert-butyl-4'-methoxydibenzoylmethane, 4,4'-diisopropylbenzoylmethane, 2-methyl-5-isopropyl-4'-methoxydibenzoylmethane, 2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane, and so on. Particularly preferred is 4-tert-butyl-4'-methoxydibenzoylmethane, also referred to as Avobenzone. Avobenzone is commercial available from Givaudan-Roure under the trademark Parsol 1789, and Merck & Co. under the tradename Eusolex 9020.

Other types of UVA sunscreens include dicamphor sulfonic acid derivatives, such as ecamsule, a sunscreen sold under the trade name MexorylTM, which is terephthalylidene dicamphor sulfonic acid, having the formula:



15

The composition may contain from about 0.001-20%, preferably 0.005-5%, more preferably about 0.005-3% by weight of the composition of UVA sunscreen. In the preferred embodiment of the invention the UVA sunscreen is Avobenzone, and it is present at not greater than about 3% by weight of the total composition.

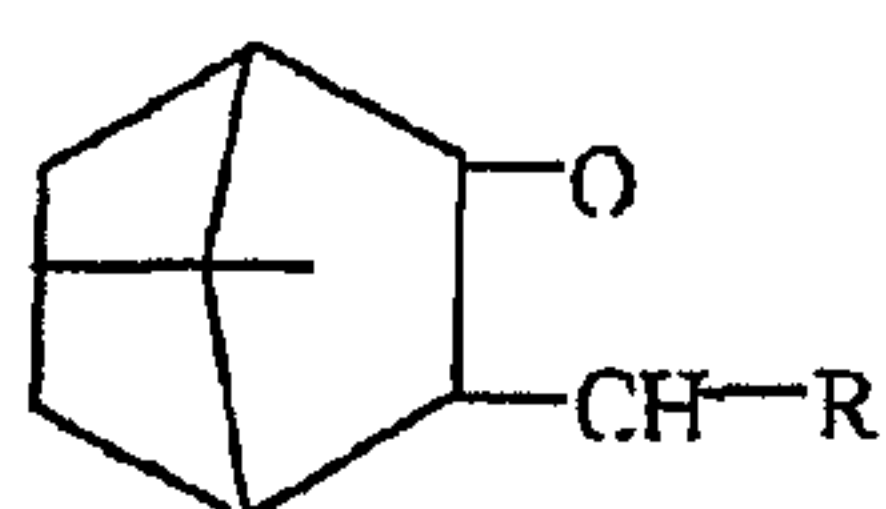
20 B. UVB Chemical Sunscreens

The term "UVB sunscreen" means a compound that blocks UV radiation in the wavelength range of from about 290 to 320 nm. A variety of UVB chemical sunscreens exist including alpha-cyano-beta,beta-diphenyl acrylic acid esters as set forth in U.S. Pat. No. 3,215,724. One particular example of an alpha-cyano-beta,beta-diphenyl acrylic acid ester is Octocrylene, which is 2-ethylhexyl 2-cyano-3,3-diphenylacrylate. In certain cases the composition may contain no more than about

110% by weight of the total composition of octocrylene. Suitable amounts range from about 0.001-10% by weight. Octocrylene may be purchased from BASF under the tradename Uvinul N-539.

Other suitable sunscreens include benzylidene camphor derivatives as set forth in U.S.

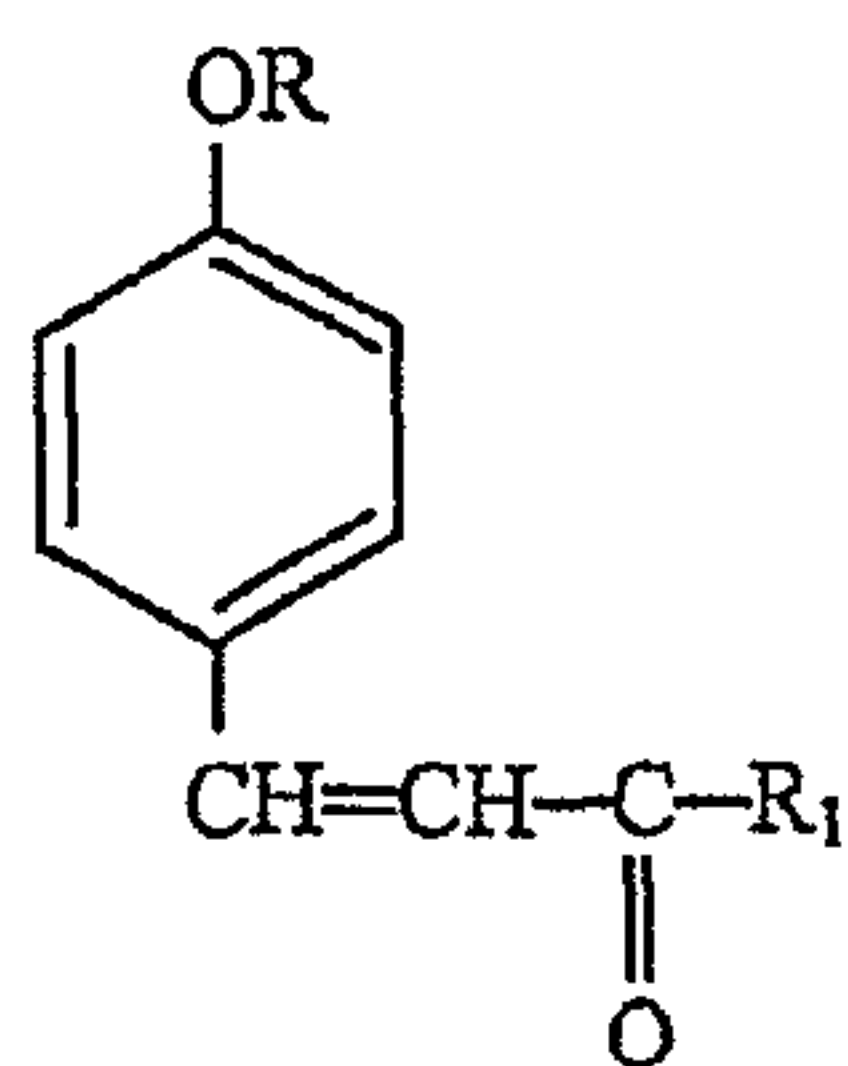
5 Pat. No. 3,781,417. Such benzylidene camphor derivatives have the general formula:



10

wherein R is p-tolyl or styryl, preferably styryl. Particularly preferred is 4-methylbenzylidene camphor, which is a lipid soluble UVB sunscreen compound sold under the tradename Eusolex 6300 by Merck.

15 Also suitable are cinnamate derivatives having the general formula:



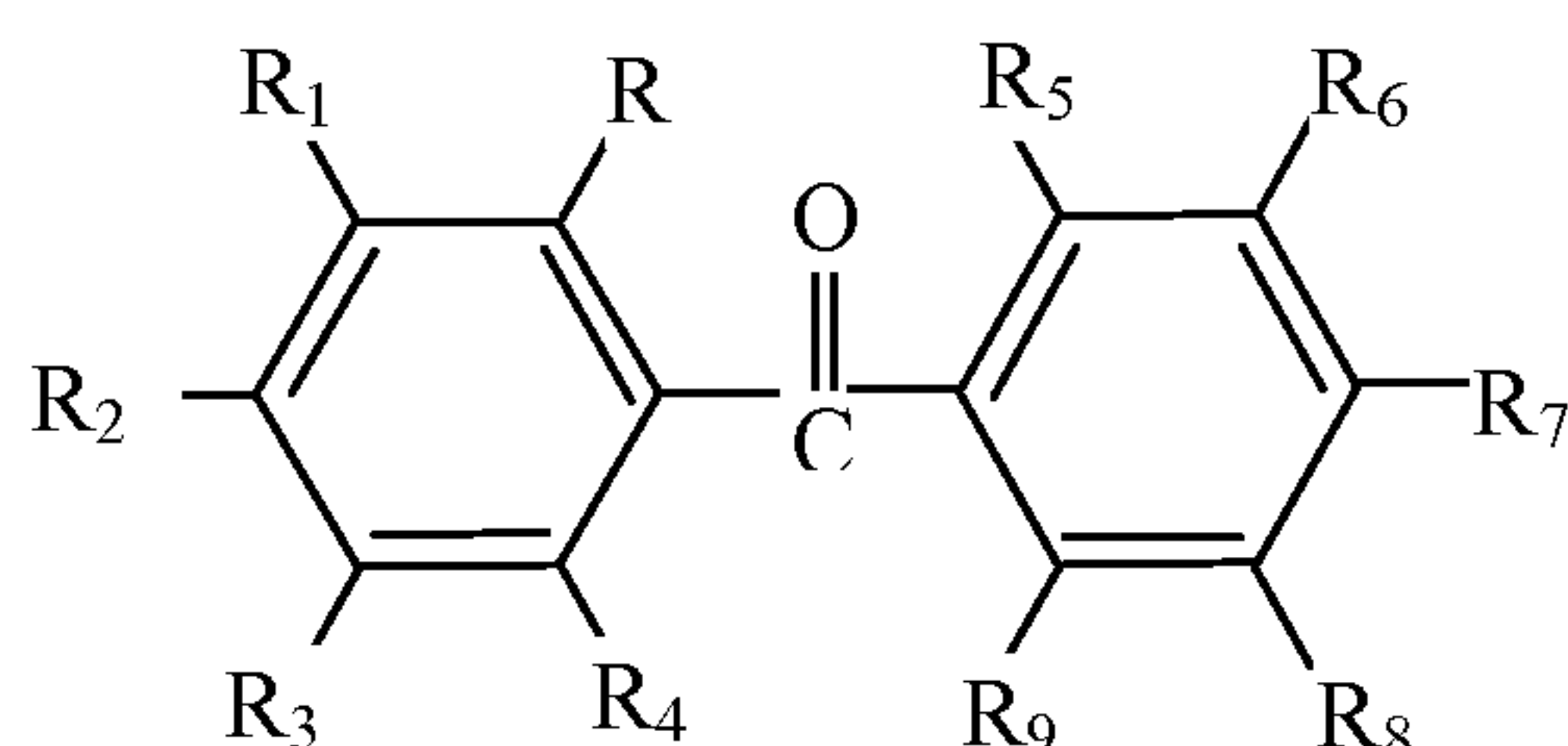
20

wherein R and R₁ are each independently a C₁₋₂₀ straight or branched chain alkyl. Preferred is where R is methyl and R₁ is a branched chain C₁₋₁₀, preferably C₈ alkyl. The preferred compound is ethylhexyl methoxycinnamate, also referred to as Octoxinate or octyl methoxycinnamate. The compound may be purchased from Givaudan Corporation under the tradename Parsol MCX, or BASF under the tradename Uvinul MC 80. Also suitable are mono-, di-, and triethanolamine derivatives of such methoxy cinnamates including

30

diethanolamine methoxycinnamate. Cinoxate, the aromatic ether derivative of the above compound is also acceptable. If present, the Cinoxate should be found at no more than about 3% by weight of the total composition.

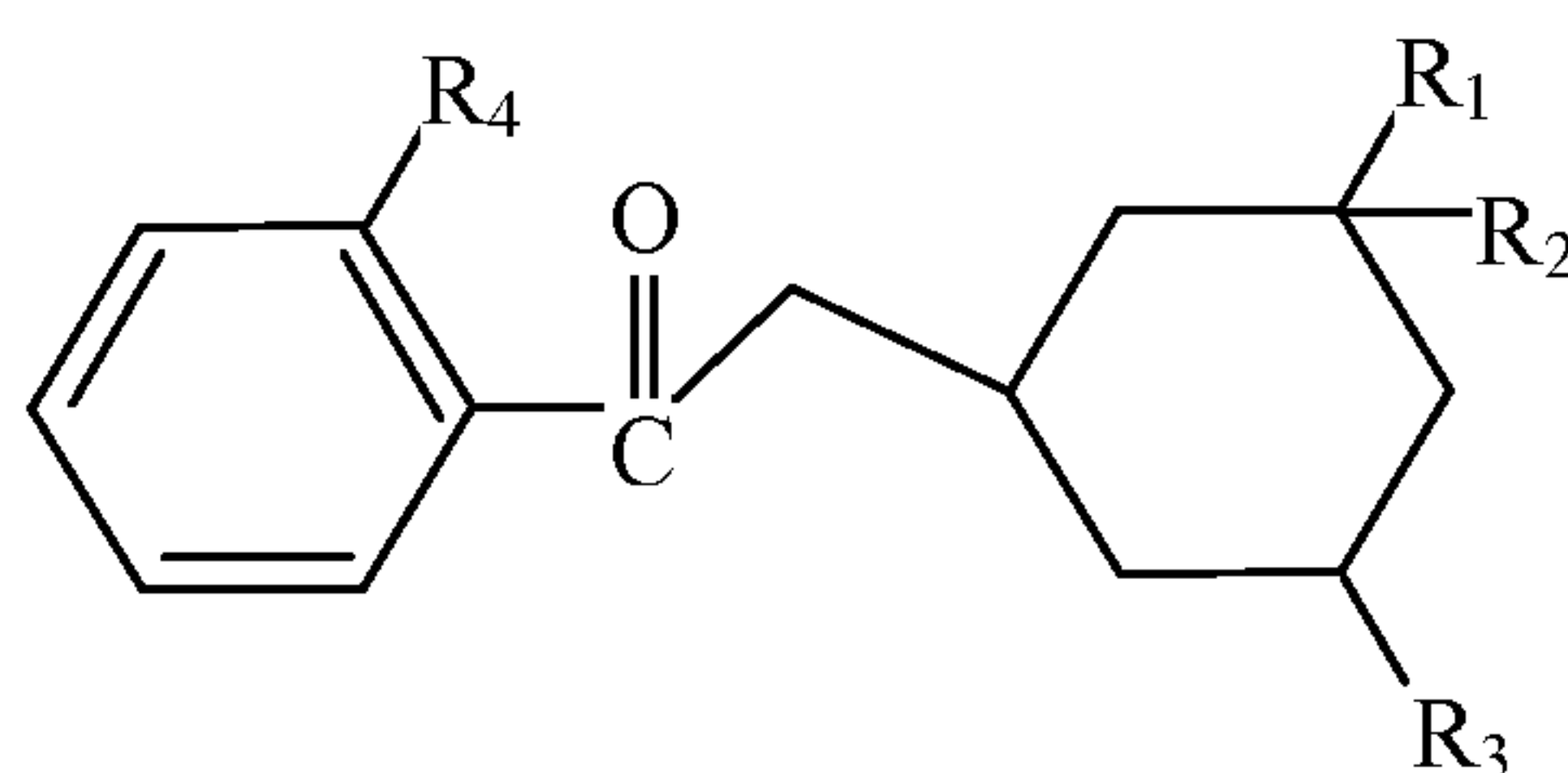
Also suitable as UVB screening agents are various benzophenone derivatives having
5 the general formula:



10

wherein R through R₉ are each independently H, OH, NaO₃S, SO₃H, SO₃Na, Cl, R'', OR'' where R'' is C₁₋₂₀ straight or branched chain alkyl. Examples of such compounds include Benzophenone 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12. Particularly preferred is where the
15 benzophenone derivative is Benzophenone 3 (also referred to as Oxybenzone), Benzophenone 4 (also referred to as Sulisobenzene), Benzophenone 5 (Sulisobenzene Sodium), and the like. Most preferred is Benzophenone 3.

Also suitable are certain menthyl salicylate derivatives having the general formula:



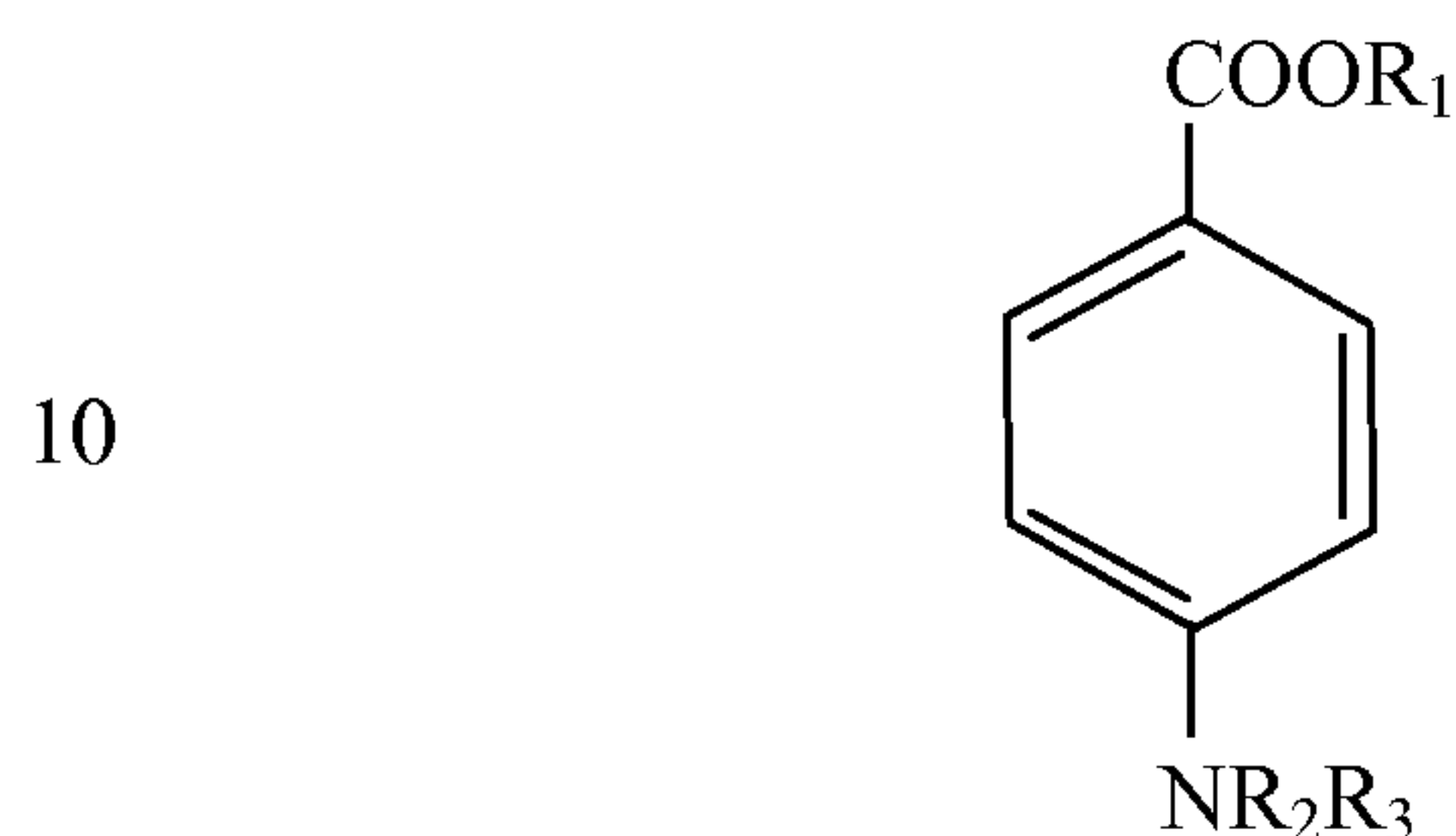
20

25

wherein R₁, R₂, R₃, and R₄ are each independently H, OH, NH₂, or C₁₋₂₀ straight or branched chain alkyl. Particularly preferred is where R₁, R₂, and R₃ are methyl and R₄ is hydroxyl or NH₂, the compound having the name homomenthyl salicylate (also known as Homosalate) or menthyl anthranilate. Homosalate is available commercially from Merck under the tradename

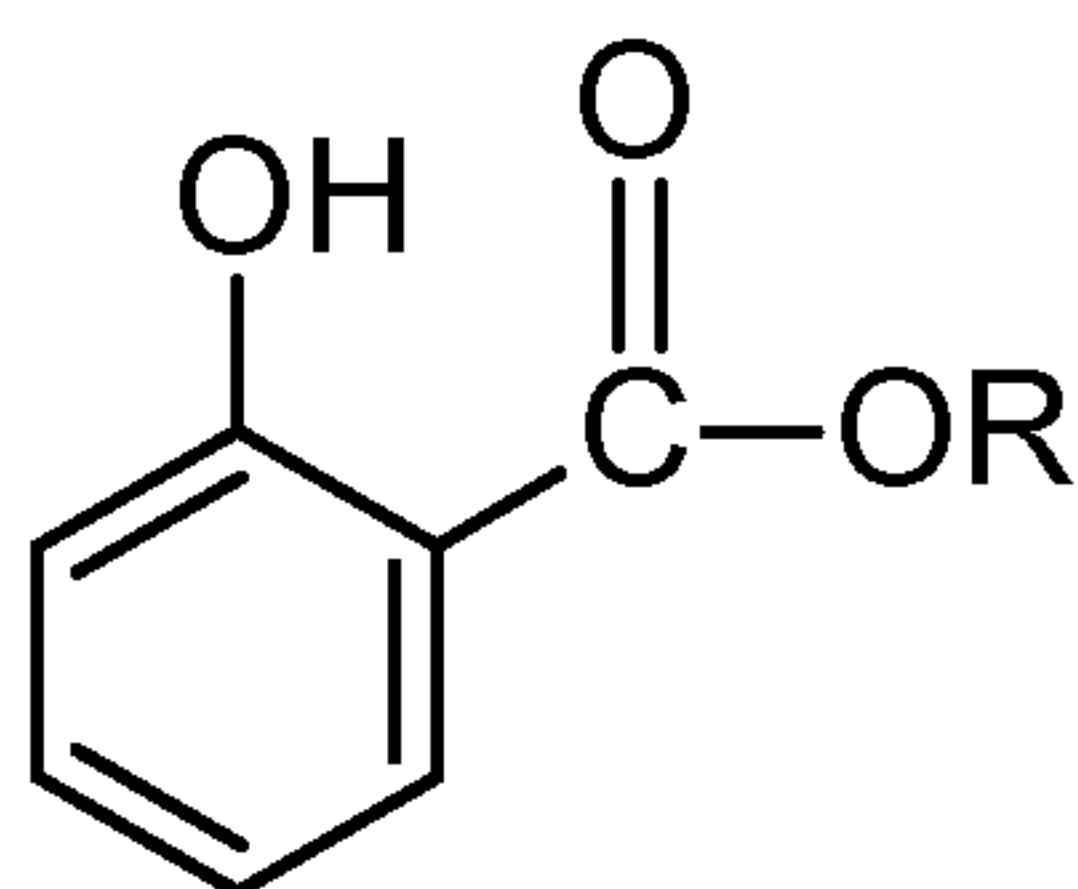
Eusolex HMS and menthyl anthranilate is commercially available from Haarmann & Reimer under the tradename Heliopan. If present, the Homosalate should be found at no more than about 15% by weight of the total composition.

Various amino benzoic acid derivatives are suitable UVB absorbers including those
5 having the general formula:



wherein R_1 , R_2 , and R_3 are each independently H, C_{1-20} straight or branched chain alkyl which
15 may be substituted with one or more hydroxy groups. Particularly preferred is wherein R_1 is H or C_{1-8} straight or branched alkyl, and R_2 and R_3 are H, or C_{1-8} straight or branched chain alkyl. Particularly preferred are PABA, ethyl hexyl dimethyl PABA (Padimate O), ethyldihydroxypropyl PABA, and the like. If present Padimate O should be found at no more than about 8% by weight of the total composition.

20 Salicylate derivatives are also acceptable UVB absorbers. Such compounds have the general formula:



wherein R is a straight or branched chain alkyl, including derivatives of the above compound formed from mono-, di-, or triethanolamines. Particular preferred are octyl salicylate, TEA-salicylate, DEA-salicylate, and mixtures thereof.

Generally, the amount of the UVB chemical sunscreen present may range from about
5 0.001-45%, preferably 0.005-40%, more preferably about 0.01-35% by weight of the total composition.

If desired, the compositions of the invention may be formulated to have a certain SPF (sun protective factor) values ranging from about 1-50, preferably about 2-45, most preferably about 5-30. Calculation of SPF values is well known in the art.

10 The compositions of the invention may contain particulate materials in the form of pigments, inert particulates, or mixtures thereof. If present, suggested ranges are from about 0.01-75%, preferably about 0.5-70%, more preferably about 0.1-65% by weight of the total composition. In the case where the composition may comprise mixtures of pigments and powders, suitable ranges include about 0.01-75% pigment and 0.1-75% powder, such weights
15 by weight of the total composition. Suitable particulate materials may include the following:

A. Powders

The particulate matter may be colored or non-colored (for example white) non-pigmented powders. Suitable non-pigmented powders include bismuth oxychloride, titanated mica, fumed silica, spherical silica, polymethylmethacrylate, micronized teflon, boron nitride,
20 acrylate copolymers, aluminum silicate, aluminum starch octenylsuccinate, bentonite, calcium silicate, cellulose, chalk, corn starch, diatomaceous earth, fuller's earth, glyceryl starch, hectorite, hydrated silica, kaolin, magnesium aluminum silicate, magnesium trisilicate, maltodextrin, montmorillonite, microcrystalline cellulose, rice starch, silica, talc, mica, titanium dioxide, zinc laurate, zinc myristate, zinc rosinate, alumina, attapulgite, calcium
25 carbonate, calcium silicate, dextran, kaolin, nylon, silica silylate, silk powder, sericite, soy flour, tin oxide, titanium hydroxide, trimagnesium phosphate, walnut shell powder, or mixtures thereof. The above mentioned powders may be surface treated with lecithin, amino acids, mineral oil, silicone, or various other agents either alone or in combination, which coat the powder surface and render the particles more lipophilic in nature.

B. Pigments

30 The particulate materials may comprise various organic and/or inorganic pigments. The organic pigments are generally various aromatic types including azo, indigoid, triphenylmethane, anthroquinone, and xanthine dyes which are designated as D&C and FD&C

blues, browns, greens, oranges, reds, yellows, etc. Organic pigments generally consist of insoluble metallic salts of certified color additives, referred to as the Lakes. Inorganic pigments include iron oxides, ultramarines, chromium, chromium hydroxide colors, and mixtures thereof. Iron oxides of red, blue, yellow, brown, black, and mixtures thereof are
5 suitable.

The composition may contain 0.001-8%, preferably 0.01-6%, more preferably 0.05-5% by weight of the total composition of preservatives. A variety of preservatives are suitable, including such as benzoic acid, benzyl alcohol, benzylhemiformal, benzylparaben, 5-bromo-5-nitro-1,3-dioxane, 2-bromo-2-nitropropane-1,3-diol, butyl paraben, phenoxyethanol, methyl
10 paraben, propyl paraben, diazolidinyl urea, calcium benzoate, calcium propionate, caprylyl glycol, biguanide derivatives, phenoxyethanol, captan, chlorhexidine diacetate, chlorhexidine digluconate, chlorhexidine dihydrochloride, chloroacetamide, chlorobutanol, p-chloro-m-cresol, chlorophene, chlorothymol, chloroxylenol, m-cresol, o-cresol, DEDM Hydantoin, DEDM Hydantoin dilaurate, dehydroacetic acid, diazolidinyl urea, dibromopropamidine
15 diisethionate, DMDM Hydantoin, and the like. In one preferred embodiment the composition is free of parabens.

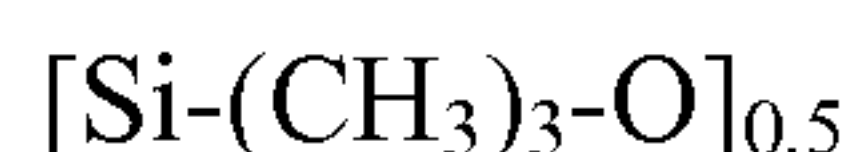
The compositions of the invention may contain vitamins and/or coenzymes, as well as antioxidants. If so, 0.001-10%, preferably 0.01-8%, more preferably 0.05-5% by weight of the total composition is suggested. Suitable vitamins include ascorbic acid and derivatives thereof
20 such as ascorbyl palmitate, tetrahexydecyl ascorbate, and so on; the B vitamins such as thiamine, riboflavin, pyridoxin, niacin, niacinamide, nicotinic acid, nicotinic acid dinucleotide, and so on, as well as coenzymes such as thiamine pyrophosphate, flavin adenine dinucleotide, folic acid, pyridoxal phosphate, tetrahydrofolic acid, and so on. Also Vitamin A and derivatives thereof are suitable. Examples are retinyl palmitate, retinol, retinoic acid, as well as
25 Vitamin A in the form of beta carotene. Also suitable is Vitamin E and derivatives thereof such as Vitamin E acetate, nicotinate, or other esters thereof. In addition, Vitamins D and K are suitable.

Suitable antioxidants are ingredients which assist in preventing or retarding spoilage. Examples of antioxidants suitable for use in the compositions of the invention are potassium
30 sulfite, sodium bisulfite, sodium erythrobate, sodium metabisulfite, sodium sulfite, propyl gallate, cysteine hydrochloride, butylated hydroxytoluene, butylated hydroxyanisole, and so on.

It may be desirable to include one or more film forming ingredients in the cosmetic compositions of the invention. Suitable film formers are ingredients that contribute to formation of a film on the keratinous surface. In some cases the film formers may provide films that provide long wearing or transfer resistant properties such that the cosmetic applied to the keratinous surface will remain for periods of time ranging from 3 to 16 hours. If present, such film formers may range from about 0.01 to 50%, preferably from about 0.1 to 40%, more preferably from about 0.5 to 35% by weight of the total composition. The film formers are most often found in the polymeric form and may be natural or synthetic polymers. If synthetic, silicone polymers, organic polymers or copolymers of silicones and organic groups may be acceptable. Suitable film formers include, but are not limited to:

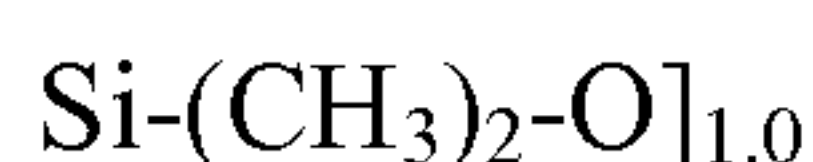
A. Silicone Resins

One particularly suitable type of silicone film former is a silicone resin. Silicone resins are generally highly crosslinked structures comprising combinations of M, D, T, and Q units. The term "M" means a monofunctional siloxy unit having the general formula:



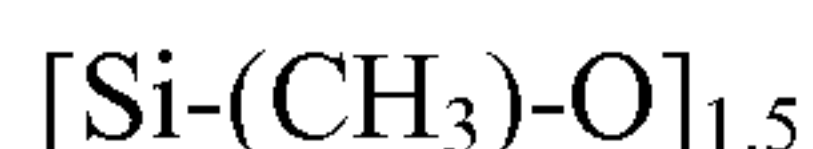
In cases where the M unit is other than methyl (such as ethyl, propyl, ethoxy, etc.) the M unit may have a prime after it, e.g. M'.

The term "D" means a difunctional siloxy unit having the general formula:



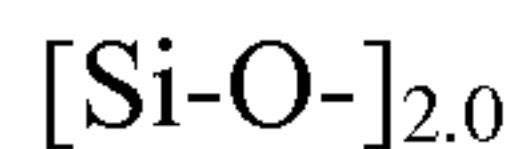
The difunctional unit may be substituted with alkyl groups other than methyl, such as ethyl, propyl, alkylene glycol, and the like, in which case the D unit may be referred to as D', with the prime indicating a substitution.

The term "T" means a trifunctional siloxy unit having the general formula:



The trifunctional unit may be substituted with substituents other than methyl, in which case it may be referred to as T'.

The term "Q" refers to a quadrifunctional siloxy unit having the general formula:

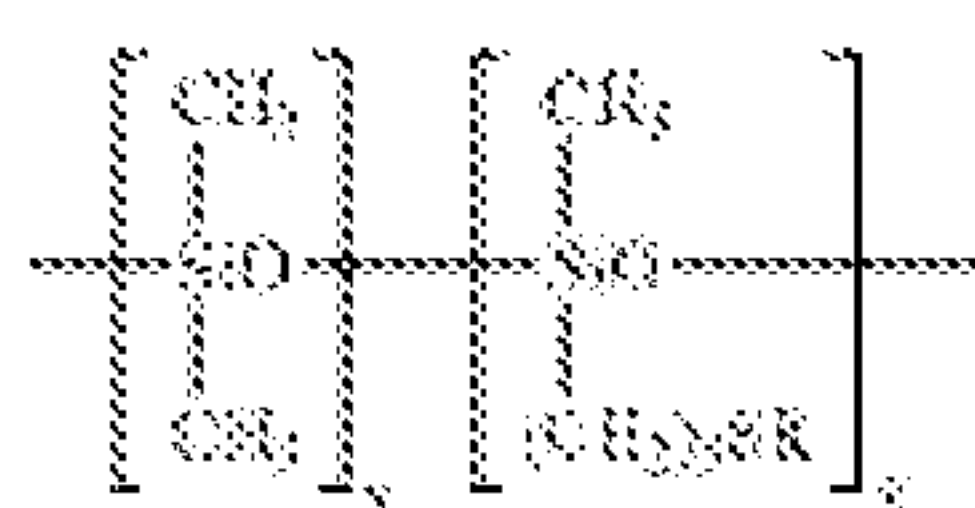


The silicone resins that may be used as film formers in the compositions of the invention preferably comprise highly crosslinked combinations of M, T, and Q units.

- 5 Examples of such resins include trimethylsiloxysilicate which can be purchased from Dow Corning Corporation as 749 Fluid, or from GE Silicones under the SR-1000 tradename. Also suitable is a silicone resin that contains a large percentage of T groups, such as MK resin sold by Wacker-Chemie, having the CTFA name polymethylsilsesquioxane.

B. Copolymers of Silicone and Organic Monomers

- 10 Also suitable for use as the film formers are copolymers of silicone and organic monomers such as acrylates, methacrylates, and the like. Examples of such suitable film forming polymers include those commonly referred to as silicone acrylate or vinyl silicone copolymers, such as those sold by 3M under the brand name "Silicone Plus" polymers such as SA-70, having the CTFA name Polysilicone-7 and is a copolymer of isobutylmethacrylate and
 15 n-butyl endblocked polydimethylsiloxane propyl methacrylate; or VS-70 having the CTFA name Polysilicone-6, which is a copolymer of dimethylsiloxane and methyl-3 mercaptopropyl siloxane reacted with isobutyl methacrylate; or VS-80, having the CTFA name Polysilicone-8, which has the general structure:



20

where R represents the acrylates copolymer radical.

C. Organic Polymers

- 25 Also suitable as film formers include various types of organic polymers such as polymers formed from acrylic acid, methacrylic acid, or their simple C₁₋₁₀ carboxylic acid esters, such as methyl methacrylate, methyl acrylate, and the like.

Also suitable are various types of natural polymers such as shellac, natural resins, chitin, and the like.

- 30 It may also be desirable to incorporate one or more DNA repair enzymes into the composition of the invention. Suggested ranges are from about 0.00001 to about 35%,

preferably from about 0.00005 to about 30%, more preferably from about 0.0001 to about 25% of one or more DNA repair enzymes.

DNA repair enzymes as disclosed in U.S. Patent Nos. 5,077,211; 5,190,762; 5,272,079; and 5,296,231 .

5 are suitable for use in the compositions and method of the invention. One example of such a DNA repair enzyme may be purchased from AGI Dermatics under the trade name Roxisomes®, and has the INCI name *Arabidopsis Thaliana* extract. It may be present alone or in admixture with lecithin and water. This DNA repair enzyme is known to be effective in repairing 8-oxo-diGuanine base mutation damage.

10 Another type of DNA repair enzyme that may be used is one that is known to be effective in repairing O6-methyl guanine base mutation damage. It is sold by AGI/Dermatics under the tradename Adasomes®, and has the INCI name *Lactobacillus* ferment, which may be added to the composition of the invention by itself or in admixture with lecithin and water.

Another type of DNA repair enzyme that may be used is one that is known to be
15 effective in repairing T-T dimers. The enzymes are present in mixtures of biological or botanical materials. Examples of such ingredients are sold by AGI/Dermatics under the tradenames Ultrasomes® or Photosomes®. Ultrasomes® comprises a mixture of *Micrococcus* lysate (an end product of the controlled lysis of a species of micrococcus), lecithin, and water. Photosomes® comprises a mixture of plankton extract (which is the extract of a biomass
20 which includes enzymes from one or more of the following organisms: thalassoplankton, green micro-algae, diatoms, greenish-blue and nitrogen-fixing seaweed), water, and lecithin.

Another type of DNA repair enzyme may be a component of various inactivated bacterial lysates such as *Bifida* lysate or *Bifida* ferment lysate, the latter a lysate from *Bifido* bacteria which contains the metabolic products and cytoplasmic fractions when *Bifido* bacteria
25 are cultured, inactivated and then disintegrated. This material has the INCI name *Bifida* Ferment Lysate.

Other suitable DNA repair enzymes include Endonuclease V, which may be produced by the denV gene of the bacteriophage T4. Also suitable are T4 endonuclease; O-6-methylguanine-DNA methyltransferases; photolyases, base glycosylases such as uracil- and
30 hypoxanthine-DNA glycosylases; apyrimidinic/apurinic endonucleases; DNA exonucleases, damaged-bases glycosylases (c.g., 3-methyladenine-DNA glycosylase); correndonucleases either alone or in complexes (e.g., *E. coli* uvrA/uvrB/uvrC endonuclease complex); APEX

nuclease, which is a multi-functional DNA repair enzyme often referred to as “APE”; dihydrofolate reductase; terminal transferase; polymerases; ligases; and topoisomerases.

Other types of suitable DNA repair enzymes may be categorized by the type of repair facilitated and include BER (base excision repair) or BER factor enzymes such as uracil-DNA glycosylase (UNG); single strand selective monofunctional uracil DNA glycosylase (SMUG1); 3,N(4)-ethenocytosine glycosylase (MBD4); thymine DNA-glycosylase (TDG); A/G-specific adenine DNA glycosylase (MUTYH); 8-oxoguanine DNA glycosylase (OGG1); endonuclease III-like (NTHL1); 3-methyladenine DNA glycosidase (MPG); DNA glycosylase/AP lyase (NEIL1 or 2); AP endonuclease (APEX 1 and 2), DNA ligase (LIG3), ligase accessory factor (XRCC1); DNA 5'-kinase/3'-phosphatase (PNKP); ADP-ribosyltransferase (PARP1 or 2).

Another category of DNA repair enzymes includes those that are believed to directly reverse damage such as O-6-MeG alkyl transferase (MGMT); 1-meA dioxygenase (ALKBH2 or ALKBH3).

Yet another category of enzymes operable to repair DNA/protein crosslinks includes Tyr-DNA phosphodiesterase (TDP1).

Also suitable are MMR (mismatch excision repair) DNA repair enzymes such as MutS protein homolog (MSH2); mismatch repair protein (MSH3); mutS homolog 4 (MSH4); MutS homolog 5 (MSH5); or G/T mismatch-binding protein (MSH6); DNA mismatch repair protein (PMS1, PMS2, MLH1, MLH3); Postmeiotic segregation increased 2-like protein (PMS2L3); or postmeiotic segregation increased 2-like 4 pseudogene (PMS2L4).

Also suitable are DNA repair enzymes are those known as nucleotide excision repair (NER) enzymes and include those such as Xeroderma Pigmentosum group C-complementing protein (XPC); RAD23 (S. cerevisiae) homolog (RAD23B); caltractin isoform (CETN2); RFA Protein 1, 2, of 3 (RPA1, 2, or 3); 3' to 5' DNA helicase (ERCC3); 5' to 3' DNA helicase (ERCC2); basic transcription factor (GTF2H1, GTF2H2, GTF2H3, GTF2H4, GTF2H5); CDK activating kinase (CDK7, CCNH); cyclin G1-interacting protein (MNAT1); DNA excision repair protein ERCC-1 or RAD-51; excision repair cross-complementing 1 (ERCC1); DNA ligase 1 (LIG1); ATP-dependent helicase (ERCC6); and the like.

Also suitable may be DNA repair enzymes in the category that facilitate homologous recombination and include, but are not limited to DNA repair protein RAD51 homolog (RAD51, RAD51L1, RAD51B etc.); DNA repair protein XRCC2; DNA repair protein

XRCC3; DNA repair protein RAD52; ATPase (RAD50); 3' exonuclease (MRE11A); and so on.

DNA repair enzymes that are DNA polymerases are also suitable and include DNA polymerase beta subunit (POLB); DNA polymerase gamma (POLG); DNA polymerase subunit delta (POLD1); DNA polymerase II subunit A (POLE); DNA polymerase delta
5 auxiliary protein (PCNA); DNA polymerase zeta (POLZ); MAD2 homolog (REV7); DNA polymerase eta (POLH); DNA polymerase kappa (POLK); and the like.

Various types of DNA repair enzymes that are often referred to as "editing and processing nucleases" include 3'-nuclease; 3'-exonuclease; 5'-exonuclease; endonuclease; and
10 the like.

Other examples of DNA repair enzymes include DNA helicases including such as ATP DNA helicase and so on.

The DNA repair enzymes may be present as components of botanical extracts, bacterial lysates, biological materials, and the like. For example, botanical extracts may
15 contain DNA repair enzymes.

The scope of the claims should not be limited by the preferred embodiments set forth in the Description, but should be given the broadest interpretation consistent with the Description as a whole.

The embodiments of the present invention for which an exclusive property or privilege is claimed are defined as follows:

1. A cosmetic or dermatological composition for reducing appearance of under-eye dark circles, comprising at least one bicyclic monoterpene diol selected from the group consisting of 2,3-cis/exo-pinandediol, 2,3-trans-pinandediol, (1R)-(-)-trans-pinane-1,10-diol, 2,3-cis/exo-camphanediol, and mixtures thereof in an amount ranging from about 0.001% to about 20% by total weight of the composition and at least one skin lightening agent selected from the group consisting of *Scutellaria baicalensis* root extract, *Pyrus malus* (apple) extract, *Cucumis sativus* (cucumber) extract, and mixtures thereof in an amount ranging from about 0.001% to about 10% by total weight of the composition in a cosmetically or pharmaceutically acceptable carrier.
2. The cosmetic or dermatological composition of claim 1, comprising an equal molar mixture of 2,3-cis/exo-pinandediol and 2,3-cis/exo-camphanediol.
3. The cosmetic or dermatological composition of any one of claims 1 to 2, wherein the at least one skin lightening agent is a mixture of *Scutellaria baicalensis* root extract, *Pyrus malus* (apple) extract, and *Cucumis sativus* (cucumber) extract.
4. The cosmetic or dermatological composition of any one of claims 1 to 3, further comprising at least one anti-angiogenic agent.
5. The cosmetic or dermatological composition of any one of claims 1 to 4, further comprising at least one anti-inflammatory agent.
6. Use of the cosmetic or dermatological composition according to any one of claims 1 to 5 for reducing appearance of under-eye dark circles in an under-eye area with visible dark circles.