



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

<p>(51) International Patent Classification <sup>6</sup> : <b>A61K 7/42</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 97/28785</b></p> <p>(43) International Publication Date: 14 August 1997 (14.08.97)</p>
<p>(21) International Application Number: PCT/US97/01170</p> <p>(22) International Filing Date: 24 January 1997 (24.01.97)</p> <p>(30) Priority Data: 08/599,202                      9 February 1996 (09.02.96)                      US</p> <p>(71) Applicant: THE PROCTER &amp; GAMBLE COMPANY [US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventors: TANNER, Paul, Robert; 1101 Seapine Court, Maineville, OH 45039 (US). WAGNER, Julie, Ann; 7931 Harrison Avenue, Cincinnati, OH 45231 (US).</p> <p>(74) Agents: REED, David, T. et al.; The Procter &amp; Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p>		<p>(81) Designated States: AU, CA, CN, CZ, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: PHOTOPROTECTIVE COMPOSITIONS</p>		
<p>(57) Abstract</p> <p>The present invention relates to leave on, skin care compositions, comprising: (a) from about 0.1 % to about 30 % of a sunscreen active, (b) from about 0.5 % to about 20 % of a hydrophobic, structuring agent, (c) from about 0.2 % to about 10 % of a hydrophilic surfactant, (d) from about 0.1 % to about 5 % of a thickening agent, and (e) water. These compositions are useful for providing protection to human skin from the harmful effects of ultraviolet radiation.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LR	Liberia	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	MN	Mongolia	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

## PHOTOPROTECTIVE COMPOSITIONS

### TECHNICAL FIELD

The present invention relates to compositions which are useful for providing protection to the skin of humans from the harmful effects of ultraviolet radiation. In particular it relates to stable, cosmetic, aqueous-containing compositions having gel networks, liquid crystalline phases, or both. These compositions also contain a thickening agent. Without being limited by theory, it is believed that the aqueous phase of these compositions contain relatively-low levels of free water. In other words, the water is believed to be bound as part of the gel network or liquid crystals. These compositions are found to be especially useful for delivering sunscreen actives to the skin.

### BACKGROUND OF THE INVENTION

The damaging effects of sunlight on skin are well documented. Contrary to what most people believe, it is not necessary that one sunbathe to suffer the ill-effects of excessive UV exposure. In fact, significant damage can be done just by routine day to day activities in sunlight. The major short term hazard of prolonged exposure to sunlight is erythema, i.e. sunburn. In addition to the short term hazard are long term hazards such as malignant changes in the skin surface. Numerous epidemiologic studies demonstrate a strong relationship between sunlight exposure and human skin cancer. Another long term hazard of ultraviolet radiation is premature aging of the skin. This condition is characterized by wrinkling and pigment changes of the skin, along with other physical changes such as cracking, telangiectasis, solar dermatoses, ecchymoses, and loss of elasticity. The adverse effects associated with exposure to UV radiation are more fully discussed in DeSimone, "Sunscreen and Suntan Products," *Handbook of Nonprescription Drugs*, 7th Ed., Chapter 26, pp. 499-511 (American Pharmaceutical Association, Washington, D.C.; 1982); Grove and Forbes, "A Method for Evaluating the Photoprotection Action of Sunscreen Agents Against UV-A Radiation," *International Journal of Cosmetic Science*, 4, pp. 15-24 (1982); and U.S. Patent No. 4,387,089, DePolo, issued June 7, 1983; all of these references being incorporated by reference herein in their entirety. Hence, although the immediate effects of ultraviolet radiation may be cosmetically and socially gratifying, the long term hazards are cumulative and potentially serious.

The fact that these effects are taken seriously by the general public is suggested by considering the sun protection product market. This market has grown considerably in recent years and many new products are introduced each year. What used to be looked upon as a seasonal business is no longer seen as such. Sunscreen agents are now included in a diversity of personal care products, particularly cosmetic type products which are worn on a daily basis.

Sunscreen formulas are generally based on oil-in-water and water-in-oil emulsion systems. However, many conventional systems suffer from disadvantages such as inefficient UV protection, chemical and physical instability, and unattractive aesthetic properties when applied to the skin. It

has surprisingly been found that the photoprotective compositions of the present invention overcome these disadvantages. These compositions comprise a sunscreen active, a stable, hydrophobic, structuring agent, a hydrophilic surfactant, a thickening agent, and water. Without being limited by theory, it is believed that these compositions contain gel network structures, liquid crystal structures, or both. It is believed that these gel networks and liquid crystals tend to bind the available water in the composition, thereby rendering the water less available for contributing to the instability and decomposition of the active ingredients. It is also found that these compositions are well-suited for formulating with highly polar materials, e.g., inorganic sunscreen agents such as titanium dioxide, zinc oxide, and iron oxide, which are often used to enhance or boost the UV protection effects of organic type sunscreen agents. Additionally, it is found that these compositions have good aesthetic, i.e. skin feel properties.

Therefore, it is an object of the present invention to provide novel compositions for providing protection from the harmful effects of UV radiation to the skin.

It is a further object of the present invention to provide photoprotective compositions comprising water, and having gel networks, liquid crystals or both.

It is a further object of the present invention to provide photoprotective compositions which are both chemically and physically stable.

It is a further objective of the present invention to provide photoprotective compositions which have an aesthetically appealing feel when applied to the skin.

These and other objects will become readily apparent from the detailed description which follows.

#### SUMMARY OF THE INVENTION

The present invention relates to photoprotective compositions that are useful for protecting human skin from the harmful effects of UV radiation comprising:

- (a) from about 0.1% to about 30% of a sunscreen active;
- (b) from about 0.5% to about 20% of a hydrophobic, structuring agent selected from the group consisting of saturated C<sub>16</sub> to C<sub>30</sub> fatty alcohols, saturated C<sub>16</sub> to C<sub>30</sub> fatty alcohols containing from about 1 to about 5 moles of ethylene oxide, saturated C<sub>16</sub> to C<sub>30</sub> diols, saturated C<sub>16</sub> to C<sub>30</sub> monoglycerol ethers, saturated C<sub>16</sub> to C<sub>30</sub> hydroxy fatty acids, and mixtures thereof, having a melting point of at least about 40°C;
- (c) from about 0.2 % to about 10% of a hydrophilic surfactant selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, zwitterionic surfactants, amphoteric surfactants, and mixtures thereof;
- (d) from about 0.1% to about 5% of a thickening agent selected from the group consisting of carboxylic acid polymers, crosslinked polyacrylate polymers, polyacrylamide polymers, polysaccharides, gums, crosslinked vinyl ether/maleic anhydride copolymers, crosslinked poly(N-vinylpyrrolidones), and mixtures thereof, and

(e) from about 25% to about 99.1% water.

In further embodiments, the present invention also relates to methods for providing protection to human skin from the harmful effects of UV radiation.

All percentages and ratios used herein are by weight of the total composition. All measurements made are at 25°C, unless otherwise designated. All weight percentages, unless otherwise indicated, are on an actives weight basis. The invention hereof can comprise, consist of, or consist essentially of, the essential as well as optional ingredients and components described herein.

#### DETAILED DESCRIPTION OF THE INVENTION

The compositions of the present invention are useful for providing protection to human skin from the harmful effects of ultraviolet radiation. These compositions are in the form of oil-in-water emulsions whereby the oil phase and the water phase can contain, in addition to the essential components described herein, a variety of ingredients known in the art. These compositions are in the form of topical, leave-on compositions. The compositions herein are useful for topical application to the skin.

The term "topical application," as used herein, means to apply or spread the compositions to the surface of the skin.

The term "pharmaceutically acceptable," as used herein, means that the compositions or components thereof so described are suitable for use in contact with human skin without undue toxicity, incompatibility, instability, allergic response, and the like.

The compositions of the present invention have complex rheological characteristics. These compositions have physical properties characteristic of oil-in-water emulsions, liquid crystals, and crystalline gel networks. Without being limited by theory, it is believed that these compositions have low levels of free water, such that most of the water is bound up with liquid crystals or gel networks. It is found that these compositions are useful as vehicles for compositions which are labile in aqueous solution or dispersion. It is also found that these compositions are useful for formulating with actives which are highly polar, such as physical sunscreen agents such as titanium dioxide, zinc oxide, iron oxide, and the like.

The nature of liquid crystals, the formation of liquid crystals, the properties and advantages of liquid crystals, and gel networks are described further in G. Dahms, "Properties of O/W Emulsions with Anisotropic Lamellar Phases," 101 Cosmetics & Toiletries 113-115, (1986); P. Loll, "Liquid Crystals in Cosmetic Emulsions," ICI Surfactants' Publication RP94-93E; and G.M. Eccleston, "Multiple-Phase Oil-In-Water Emulsion," 41 J. Soc. Cosmet. Chem. 1-22, (January/February 1990); all of which are incorporated herein by reference in their entirety.

The compositions herein have desirable aesthetic and elegant properties, such as a rich and creamy, yet non-greasy, skin feel. These compositions can span a broad range of consistencies from thin lotions to heavy creams. These compositions typically have viscosities ranging from about 100 cps to about 500,000 cps, preferably from about 3,000 cps to about 200,000 cps, more preferably

from about 5000 cps to about 150,000 cps, as measured at a temperature of 25°C with a Brookfield Synchro-Lectric Viscometer Model D. The compositions can span a wide range of pH values. Even though buffers can be utilized to help maintain the pH of the emulsion compositions, these are not required components, but are merely optional ingredients.

The compositions of the present invention comprise the following essential components. These components should be pharmaceutically acceptable.

#### Sunscreen Agent

The compositions of the present invention comprise from about 0.1% to about 30%, more preferably from about 0.5% to about 25%, and most preferably from about 1% to about 20% of the compositions of the present invention. Mixtures of sunscreen agents can also be used. Exact amounts of sunscreen agent will vary depending upon the sunscreen or sunscreens chosen and the desired Sun Protection Factor (SPF) to be achieved. SPF is a commonly used measure of photoprotection of a sunscreen against erythema. The SPF is defined as the ratio of the ultraviolet energy required to produce minimal erythema on protected skin to that required to produce the same minimal erythema on unprotected skin in the same individual. See Federal Register, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978, which is incorporated herein by reference in its entirety.

A wide variety of sunscreen agents are useful herein. These sunscreen agents include both organic compounds and their salts as well as inorganic particulate materials. Without being limited by theory, it is believed that sunscreen agents provide protection from ultraviolet radiation by one or more of the following mechanisms including absorption, scattering, and reflection of the ultraviolet radiation. Nonlimiting examples of these sunscreen agents are described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 5,073,372, to Turner et al., issued December 17, 1991; U.S. Patent No. 5,073,371, to Turner et al. issued December 17, 1991; U.S. Patent No. 5,160,731, to Sabatelli et al., issued November 3, 1992; U.S. Patent No. 5,138,089, to Sabatelli, issued August 11, 1992; U.S. Patent No. 5,041,282, to Sabatelli, issued August 20, 1991; U.S. Patent No. 4,999,186, to Sabatelli et al., issued March 12, 1991; U.S. Patent No. 4,937,370, to Sabatelli, issued June 26, 1990; and Segarin, et al., at Chapter VIII, pages 189 et seq., of Cosmetics Science and Technology; all of these documents being incorporated herein by reference in their entirety. Preferred among the sunscreen agents are those selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, octyl salicylate, octocrylene, oxybenzone, 2-ethylhexyl N,N-dimethylaminobenzoate, p-aminobenzoic acid, 2-phenyl-benzimidazole-5-sulfonic acid, homomenthyl salicylate, DEA p-methoxycinnamate, 4,4'-methoxy-t-butylidibenzoylmethane, 4-isopropylidibenzoylmethane, 3-(4-methylbenzylidene) camphor, 3-benzylidene camphor, 4-N,N-dimethylaminobenzoic acid ester with 2,4-dihydroxybenzophenone, 4-N,N-dimethylaminobenzoic acid ester with 2-hydroxy-4-(2-hydroxyethoxy)benzophenone, 4-N,N-dimethylaminobenzoic acid ester with 4-hydroxydibenzoyl- methane, 4-N,N-dimethylaminobenzoic acid ester with 4-(2-hydroxyethoxy)dibenzoylmethane, 4-N,N-di(2-ethylhexyl)- aminobenzoic acid ester with 2,4-

dihydroxybenzophenone, 4-N,N-di(2-ethylhexyl)aminobenzoic acid ester with 2-hydroxy-4-(2-hydroxyethoxy)benzophenone, 4-N,N-di(2-ethylhexyl)aminobenzoic acid ester with 4-hydroxydibenzoylmethane, 4-N,N-di(2-ethylhexyl)aminobenzoic acid ester with 4-(2-hydroxyethoxy)dibenzoylmethane, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 2,4-dihydroxybenzophenone, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 2-hydroxy-4-(2-hydroxyethoxy)benzophenone, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 4-hydroxydibenzoylmethane, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 4-(2-hydroxyethoxy)dibenzoylmethane, titanium dioxide, zinc oxide, iron oxide, and mixtures thereof.

More preferred for use in the compositions described herein are the sunscreen agents selected from the group consisting of 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, 2-ethylhexyl p-methoxycinnamate, octocrylene, octyl salicylate, homomenthyl salicylate, p-aminobenzoic acid, oxybenzone, 2-phenylbenzimidazole-5-sulfonic acid, DEA p-methoxycinnamate, 4,4'-methoxy-t-butylidibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-(4-methylbenzylidene) camphor, 3-benzylidene camphor, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 4-(2-hydroxyethoxy)dibenzoylmethane, titanium dioxide, zinc oxide, iron oxide, and mixtures thereof.

Even more preferred for use in the compositions described herein are the sunscreen agents selected from the group consisting of 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, 2-ethylhexyl p-methoxycinnamate, octocrylene, octyl salicylate, oxybenzone, 2-phenylbenzimidazole-5-sulfonic acid, 4,4'-methoxy-t-butylidibenzoylmethane, 3-(4-methylbenzylidene) camphor, 3-benzylidene camphor, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 4-(2-hydroxyethoxy)dibenzoylmethane, titanium dioxide, zinc oxide, iron oxide, and mixtures thereof.

Most preferred for use in the compositions of the present invention are the sunscreen agents selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, 4,4'-methoxy-t-butylidibenzoylmethane, zinc oxide, and mixtures thereof.

### Structuring Agent

The present invention comprises from about 0.5% to about 20%, preferably from about 1% to about 10%, and more preferably from about 1% to about 5%, of a hydrophobic, structuring agent selected from the group consisting of saturated C<sub>16</sub> to C<sub>30</sub> fatty alcohols, saturated C<sub>16</sub> to C<sub>30</sub> fatty alcohols containing from about 1 to about 5 moles of ethylene oxide, saturated C<sub>16</sub> to C<sub>30</sub> diols, saturated C<sub>16</sub> to C<sub>30</sub> monoglycerol ethers, saturated C<sub>16</sub> to C<sub>30</sub> hydroxy fatty acids, and mixtures thereof, having a melting point of at least about 40°C. Without being limited by theory, it is believed that these structuring agents are useful to assist in the formation of the rheological characteristic of the composition which contribute to the hydrolytic stability of the composition of the present invention. In particular structuring agents assist in the formation of the liquid crystalline gel network structures.

The preferred structuring agents of the present invention are selected from the group consisting of stearyl alcohol, cetyl alcohol, behenyl alcohol, stearic acid, palmitic acid, the polyethylene glycol ether of stearyl alcohol having an average of about 1 to about 5 ethylene oxide units, the polyethylene glycol ether of cetyl alcohol having an average of about 1 to about 5 ethylene oxide units, and mixtures thereof. More preferred structuring agents of the present invention are selected from the group consisting of stearyl alcohol, cetyl alcohol, behenyl alcohol, the polyethylene glycol ether of stearyl alcohol having an average of about 2 ethylene oxide units (steareth-2), the polyethylene glycol ether of cetyl alcohol having an average of about 2 ethylene oxide units, and mixtures thereof. Even more preferred structuring agents are selected from the group consisting of stearyl alcohol, cetyl alcohol, behenyl alcohol, steareth-2, and mixtures thereof. Hydrophilic Surfactant

The compositions of the present invention comprise from about 0.2% to about 10%, preferably from about 0.2% to about 6%, and more preferably from about 0.2% to about 3% of at least one hydrophilic surfactant. Without being limited by theory, it is believed that the hydrophilic surfactant disperses the hydrophobic materials, i.e. the structuring agent, in the water phase. The surfactant, at a minimum, must be hydrophilic enough to disperse in water.

The surfactants useful herein can include any of a wide variety of cationic, anionic, zwitterionic, and amphoteric surfactants disclosed in prior patents and other references. See McCutcheon's, Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation; U.S. Patent No. 5,011,681 to Ciotti et al., issued April 30, 1991; U.S. Patent No. 4,421,769 to Dixon et al., issued December 20, 1983; and U.S. Patent No. 3,755,560 to Dickert et al., issued August 28, 1973; these four references are incorporated herein by reference in their entirety.

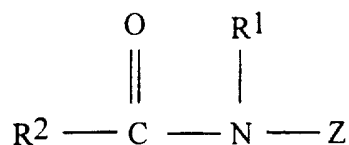
The exact surfactant chosen will depend upon the pH of the composition and the other components present.



Preferred for use herein are nonionic surfactants. Among the nonionic surfactants that are useful herein are those that can be broadly defined as condensation products of long chain alcohols, e.g. C8-30 alcohols, with sugar or starch polymers, i.e., glycosides. These compounds can be represented by the formula  $(S)_n-O-R$  wherein S is a sugar moiety such as glucose, fructose, mannose, and galactose; n is an integer of from about 1 to about 1000, and R is a C8-30 alkyl group. Examples of long chain alcohols from which the alkyl group can be derived include decyl alcohol, cetyl alcohol, stearyl alcohol, lauryl alcohol, myristyl alcohol, oleyl alcohol, and the like. Preferred examples of these surfactants include those wherein S is a glucose moiety, R is a C8-20 alkyl group, and n is an integer of from about 1 to about 9. Commercially available examples of these surfactants include decyl polyglucoside (available as APG 325 CS from Henkel) and lauryl polyglucoside (available as APG 600 CS and 625 CS from Henkel).

Other useful nonionic surfactants include the condensation products of alkylene oxides with fatty acids (i.e. alkylene oxide esters of fatty acids). These materials have the general formula  $RCO(X)_nOH$  wherein R is a C10-30 alkyl group, X is  $-OCH_2CH_2-$  (i.e. derived from ethylene glycol or oxide) or  $-OCH_2CHCH_3-$  (i.e. derived from propylene glycol or oxide), and n is an integer from about 6 to about 100. Other nonionic surfactants are the condensation products of alkylene oxides with 2 moles of fatty acids (i.e. alkylene oxide diesters of fatty acids). These materials have the general formula  $RCO(X)_nOOCR$  wherein R is a C10-30 alkyl group, X is  $-OCH_2CH_2-$  (i.e. derived from ethylene glycol or oxide) or  $-OCH_2CHCH_3-$  (i.e. derived from propylene glycol or oxide), and n is an integer from about 6 to about 100. Other nonionic surfactants are the condensation products of alkylene oxides with fatty alcohols (i.e. alkylene oxide ethers of fatty alcohols). These materials have the general formula  $R(X)_nOR'$  wherein R is a C10-30 alkyl group, X is  $-OCH_2CH_2-$  (i.e. derived from ethylene glycol or oxide) or  $-OCH_2CHCH_3-$  (i.e. derived from propylene glycol or oxide), and n is an integer from about 6 to about 100 and R' is H or a C10-30 alkyl group. Still other nonionic surfactants are the condensation products of alkylene oxides with both fatty acids and fatty alcohols [i.e. wherein the polyalkylene oxide portion is esterified on one end with a fatty acid and etherified (i.e. connected via an ether linkage) on the other end with a fatty alcohol]. These materials have the general formula  $RCO(X)_nOR'$  wherein R and R' are C10-30 alkyl groups, X is  $-OCH_2CH_2-$  (i.e. derived from ethylene glycol or oxide) or  $-OCH_2CHCH_3-$  (derived from propylene glycol or oxide), and n is an integer from about 6 to about 100. Nonlimiting examples of these alkylene oxide derived nonionic surfactants include ceteth-6, ceteth-10, ceteth-12, cetareth-6, cetareth-10, cetareth-12, steareth-6, steareth-10, steareth-12, PEG-6 stearate, PEG-10 stearate, PEG-12 stearate, PEG-20 glyceryl stearate, PEG-80 glyceryl tallowate, PPG-10 glyceryl stearate, PEG-30 glyceryl cocoate, PEG-80 glyceryl cocoate, PEG-200 glyceryl tallowate, PEG-8 dilaurate, PEG-10 distearate, and mixtures thereof.

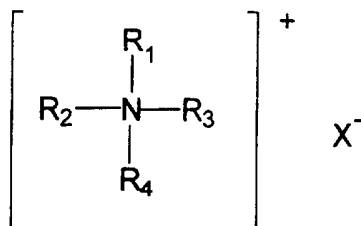
Still other useful nonionic surfactants include polyhydroxy fatty acid amide surfactants corresponding to the structural formula:



wherein:  $\text{R}^1$  is H,  $\text{C}_1$ - $\text{C}_4$  alkyl, 2-hydroxyethyl, 2-hydroxy-propyl, preferably  $\text{C}_1$ - $\text{C}_4$  alkyl, more preferably methyl or ethyl, most preferably methyl;  $\text{R}^2$  is  $\text{C}_5$ - $\text{C}_{31}$  alkyl or alkenyl, preferably  $\text{C}_7$ - $\text{C}_{19}$  alkyl or alkenyl, more preferably  $\text{C}_9$ - $\text{C}_{17}$  alkyl or alkenyl, most preferably  $\text{C}_{11}$ - $\text{C}_{15}$  alkyl or alkenyl; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with a least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably is a sugar moiety selected from the group consisting of glucose, fructose, maltose, lactose, galactose, mannose, xylose, and mixtures thereof. An especially preferred surfactant corresponding to the above structure is coconut alkyl N-methyl glucoside amide (i.e., wherein the  $\text{R}^2\text{CO}$ - moiety is derived from coconut oil fatty acids). Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd.; U.S. Patent No. 2,965,576, to E.R. Wilson, issued December 20, 1960; U.S. Patent No. 2,703,798, to A.M. Schwartz, issued March 8, 1955; and U.S. Patent No. 1,985,424, to Piggott, issued December 25, 1934; which are incorporated herein by reference in their entirety.

Preferred among the nonionic surfactants are those selected from the group consisting of steareth-21, cetareth-20, cetareth-12, sucrose cocoate, steareth-100, PEG-100 stearate, and mixtures thereof.

A wide variety of cationic surfactants useful herein are disclosed in U.S. Patent No. 5,151,209, to McCall et al., issued September 29, 1992; U.S. Patent No. 5,151,210, to Steuri et al., issued September 29, 1992; U.S. Patent No. 5,120,532, to Wells et al., issued June 9, 1992; U.S. Patent No. 4,387,090, to Bolich, issued June 7, 1983; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent No. 3,929,678, to Laughlin et al., issued December 30, 1975; U.S. Patent No. 3,959,461, to Bailey et al., issued May 25, 1976; McCutcheon's, Detergents & Emulsifiers, (North American edition 1979) M.C. Publishing Co.; and Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; all of these documents being incorporated herein by reference in their entirety. The cationic surfactants useful herein include cationic ammonium salts such as those having the formula:



wherein  $R_1$ , is an alkyl group having from about 12 to about 30 carbon atoms, or an aromatic, aryl or alkaryl groups having from about 12 to about 30 carbon atoms;  $R_2$ ,  $R_3$ , and  $R_4$  are independently selected from hydrogen, an alkyl group having from about 1 to about 22 carbon atoms, or aromatic, aryl or alkaryl groups having from about 12 to about 22 carbon atoms; and  $X$  is any compatible anion, preferably selected from the group consisting of chloride, bromide, iodide, acetate, phosphate, nitrate, sulfate, methyl sulfate, ethyl sulfate, tosylate, lactate, citrate, glycolate, and mixtures thereof. Additionally, the alkyl groups of  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  can also contain ester and/or ether linkages, or hydroxy or amino group substituents (e.g., the alkyl groups can contain polyethylene glycol and polypropylene glycol moieties).

More preferably,  $R_1$  is an alkyl group having from about 12 to about 22 carbon atoms;  $R_2$  is selected from H or an alkyl group having from about 1 to about 22 carbon atoms;  $R_3$  and  $R_4$  are independently selected from H or an alkyl group having from about 1 to about 3 carbon atoms; and  $X$  is as described previously.

Most preferably,  $R_1$  is an alkyl group having from about 12 to about 22 carbon atoms;  $R_2$ ,  $R_3$ , and  $R_4$  are selected from H or an alkyl group having from about 1 to about 3 carbon atoms; and  $X$  is as described previously.

Alternatively, other useful cationic emulsifiers include amino-amides, wherein in the above structure  $R_1$  is alternatively  $R_5\text{CONH}-(\text{CH}_2)_n-$ , wherein  $R_5$  is an alkyl group having from about 12 to about 22 carbon atoms, and  $n$  is an integer from about 2 to about 6, more preferably from about 2 to about 4, and most preferably from about 2 to about 3. Nonlimiting examples of these cationic emulsifiers include stearamidopropyl PG-dimonium chloride phosphate, behenamidopropyl PG dimonium chloride, stearamidopropyl ethyldimonium ethosulfate, stearamidopropyl dimethyl (myristyl acetate) ammonium chloride, stearamidopropyl dimethyl cetaryl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof. Especially preferred is behenamidopropyl PG dimonium chloride.

Nonlimiting examples of quaternary ammonium salt cationic surfactants include those selected from the group consisting of cetyl ammonium chloride, cetyl ammonium bromide, lauryl ammonium chloride, lauryl ammonium bromide, stearyl ammonium chloride, stearyl ammonium bromide, cetyl dimethyl ammonium chloride, cetyl dimethyl ammonium bromide, lauryl dimethyl ammonium chloride, lauryl dimethyl ammonium bromide, stearyl dimethyl ammonium chloride, stearyl dimethyl ammonium bromide, cetyl trimethyl ammonium chloride, cetyl trimethyl ammonium bromide, lauryl trimethyl ammonium chloride, lauryl trimethyl ammonium bromide,

stearyl trimethyl ammonium chloride, stearyl trimethyl ammonium bromide, lauryl dimethyl ammonium chloride, stearyl dimethyl cetyl ditallow dimethyl ammonium chloride, dicetyl ammonium chloride, dicetyl ammonium bromide, dilauryl ammonium chloride, dilauryl ammonium bromide, distearyl ammonium chloride, distearyl ammonium bromide, dicetyl methyl ammonium chloride, dicetyl methyl ammonium bromide, dilauryl methyl ammonium chloride, dilauryl methyl ammonium bromide, distearyl methyl ammonium chloride, distearyl methyl ammonium bromide, and mixtures thereof. Additional quaternary ammonium salts include those wherein the C<sub>12</sub> to C<sub>30</sub> alkyl carbon chain is derived from a tallow fatty acid or from a coconut fatty acid. The term "tallow" refers to an alkyl group derived from tallow fatty acids (usually hydrogenated tallow fatty acids), which generally have mixtures of alkyl chains in the C<sub>16</sub> to C<sub>18</sub> range. The term "coconut" refers to an alkyl group derived from a coconut fatty acid, which generally have mixtures of alkyl chains in the C<sub>12</sub> to C<sub>14</sub> range. Examples of quaternary ammonium salts derived from these tallow and coconut sources include ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, di(hydrogenated tallow) dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl)dimethyl ammonium chloride, di(coconutalkyl)dimethyl ammonium bromide, tallow ammonium chloride, coconut ammonium chloride, stearamidopropyl PG-dimonium chloride phosphate, stearamidopropyl ethyldimonium ethosulfate, stearamidopropyl dimethyl (myristyl acetate) ammonium chloride, stearamidopropyl dimethyl cetearyl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof. An example of a quaternary ammonium compound having an alkyl group with an ester linkage is ditallowyl oxyethyl dimethyl ammonium chloride.

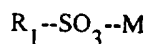
More preferred cationic surfactants are those selected from the group consisting of behenamidopropyl PG dimonium chloride, dilauryl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dimyristyl dimethyl ammonium chloride, dipalmityl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, stearamidopropyl PG-dimonium chloride phosphate, stearamidopropyl ethyldiammonium ethosulfate, stearamidopropyl dimethyl (myristyl acetate) ammonium chloride, stearamidopropyl dimethyl cetearyl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof.

Most preferred cationic surfactants are those selected from the group consisting of behenamidopropyl PG dimonium chloride, dilauryl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dimyristyl dimethyl ammonium chloride, dipalmityl dimethyl ammonium chloride, and mixtures thereof.

A wide variety of anionic surfactants are also useful herein. See, e.g., U.S. Patent No. 3,929,678, to Laughlin et al., issued December 30, 1975, which is incorporated herein by reference in its entirety. Nonlimiting examples of anionic surfactants include the alkoyl isethionates, and the

alkyl and alkyl ether sulfates. The alkoyl isethionates typically have the formula  $\text{RCO-OCH}_2\text{CH}_2\text{SO}_3\text{M}$  wherein R is alkyl or alkenyl of from about 10 to about 30 carbon atoms, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. Nonlimiting examples of these isethionates include those alkoyl isethionates selected from the group consisting of ammonium cocoyl isethionate, sodium cocoyl isethionate, sodium lauroyl isethionate, sodium stearyl isethionate, and mixtures thereof.

The alkyl and alkyl ether sulfates typically have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 10 to about 30 carbon atoms, x is from about 1 to about 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein  $\text{R}_1$  is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 16, carbon atoms; and M is a cation. Still other anionic synthetic surfactants include the class designated as succinamates, olefin sulfonates having about 12 to about 24 carbon atoms, and b-alkyloxy alkane sulfonates. Examples of these materials are sodium lauryl sulfate and ammonium lauryl sulfate.

Other anionic materials useful herein are soaps (i.e. alkali metal salts, e.g., sodium or potassium salts) of fatty acids, typically having from about 8 to about 24 carbon atoms, preferably from about 10 to about 20 carbon atoms. The fatty acids used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., palm oil, coconut oil, soybean oil, castor oil, tallow, lard, etc.) The fatty acids can also be synthetically prepared. Soaps are described in more detail in U.S. Patent No. 4,557,853, cited above.

Amphoteric and zwitterionic surfactants are also useful herein. Examples of amphoteric and zwitterionic surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 22 carbon atoms (preferably  $\text{C}_8 - \text{C}_{18}$ ) and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples are alkyl imino acetates, and iminodialkanoates and aminoalkanoates of the formulas  $\text{RN}[\text{CH}_2]_m\text{CO}_2\text{M}]_2$  and  $\text{RNH}(\text{CH}_2)_m\text{CO}_2\text{M}$  wherein m is from 1 to 4, R is a  $\text{C}_8\text{-C}_{22}$  alkyl or alkenyl, and M is H, alkali metal, alkaline earth metal ammonium, or alkanolammonium. Also included are imidazolium and ammonium derivatives. Specific examples of suitable amphoteric surfactants include sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072 which is incorporated herein by reference in its entirety; N-higher alkyl aspartic acids such as those produced according to the teaching of U.S.

Patent 2,438,091 which is incorporated herein by reference in its entirety; and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378, which is incorporated herein by reference in its entirety. Other examples of useful amphoteric phosphates include phosphates, such as coamidopropyl PG-dimonium chloride phosphate (commercially available as Monaquat PTC, from Mona Corp.).

Also useful herein as amphoteric or zwitterionic surfactants are the betaines. Examples of betaines include the higher alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, cetyl dimethyl betaine (available as Lonzaine 16SP from Lonza Corp.), lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine, coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine, and amidobetaines and amidosulfobetaines (wherein the  $\text{RCONH}(\text{CH}_2)_3$  radical is attached to the nitrogen atom of the betaine), oleyl betaine (available as amphoteric Velvetex OLB-50 from Henkel), and cocamidopropyl betaine (available as Velvetex BK-35 and BA-35 from Henkel).

Other useful amphoteric and zwitterionic surfactants include the sultaines and hydroxysultaines such as cocamidopropyl hydroxysultaine (available as Mirataine CBS from Rhone-Poulenc), and the alkanoyl sarcosinates corresponding to the formula  $\text{RCON}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CO}_2\text{M}$  wherein R is alkyl or alkenyl of about 10 to about 20 carbon atoms, and M is a water-soluble cation such as ammonium, sodium, potassium and trialkanolamine (e.g., triethanolamine), a preferred example of which is sodium lauroyl sarcosinate.

#### Thickening Agent

The compositions of the present invention can also comprise from about 0.1% to about 5%, more preferably from about 0.1% to about 3%, and most preferably from about 0.25% to about 2% of a thickening agent.

Nonlimiting classes of thickening agents include those selected from the group consisting of carboxylic acid polymers, crosslinked polyacrylate polymers, polyacrylamide polymers, polysaccharides, gums, vinyl ether/maleic anhydride copolymers, crosslinked poly(N-vinylpyrrolidones), and mixtures thereof. Preferred thickening agents are those selected from the group consisting of carboxylic acid polymers, crosslinked polyacrylate polymers, polyacrylamide polymers, and mixtures thereof. More preferred thickening agents are those selected from the group consisting of crosslinked polyacrylate polymers, polyacrylamide polymers, and mixtures thereof. See, U.S. Patent No., 4,387,107, to Klein et al., issued June 7, 1983 and "Encyclopedia of Polymer and Thickeners for Cosmetics," R.Y. Lochhead and W.R. Fron, eds., Cosmetics & Toiletries, vol. 108, pp. 95-135 (May 1993), which list a variety of thickening or gelling agents, and which are all incorporated herein by reference in their entirety.

Carboxylic Acid Polymers These polymers are crosslinked compounds containing one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and is derived from a polyhydric alcohol. The preferred carboxylic acid polymers are of two general types. The first type of polymer is a crosslinked homopolymer of an acrylic acid monomer or derivative thereof (e.g., wherein the acrylic acid has substituents on the two and three carbon positions independently selected from the group consisting of C<sub>1-4</sub> alkyl, -CN, -COOH, and mixtures thereof). The second type of polymer is a crosslinked copolymer having a first monomer selected from the group consisting of an acrylic acid monomer or derivative thereof (as just described in the previous sentence), a short chain alcohol (i.e., a C<sub>1-4</sub>) acrylate ester monomer or derivative thereof (e.g., wherein the acrylic acid portion of the ester has substituents on the two and three carbon positions independently selected from the group consisting of C<sub>1-4</sub> alkyl, -CN, -COOH, and mixtures thereof), and mixtures thereof; and a second monomer which is a long chain alcohol (i.e. C<sub>8-40</sub>) acrylate ester monomer or derivative thereof (e.g., wherein the acrylic acid portion of the ester has substituents on the two and three carbon positions independently selected from the group consisting of C<sub>1-4</sub> alkyl, -CN, -COOH, and mixtures thereof). Combinations of these two types of polymers are also useful herein.

In the first type of crosslinked homopolymers, the monomers are preferably selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, and mixtures thereof, with acrylic acid being most preferred. In the second type of crosslinked copolymers the acrylic acid monomer or derivative thereof is preferably selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, and mixtures thereof, with acrylic acid, methacrylic acid, and mixtures thereof being most preferred. The short chain alcohol acrylate ester monomer or derivative thereof is preferably selected from the group consisting of C<sub>1-4</sub> alcohol acrylate esters, C<sub>1-4</sub> alcohol methacrylate esters, C<sub>1-4</sub> alcohol ethacrylate esters, and mixtures thereof, with the C<sub>1-4</sub> alcohol acrylate esters, C<sub>1-4</sub> alcohol methacrylate esters, and mixtures thereof, being most preferred. The long chain alcohol acrylate ester monomer is selected from C<sub>8-40</sub> alkyl acrylate esters, with C<sub>10-30</sub> alkyl acrylate esters being preferred.

The crosslinking agent in both of these types of polymers is a polyalkenyl polyether of a polyhydric alcohol containing more than one alkenyl ether group per molecule, wherein the parent polyhydric alcohol contains at least 3 carbon atoms and at least 3 hydroxyl groups. Preferred crosslinkers are those selected from the group consisting of allyl ethers of sucrose and allyl ethers of pentaerythritol, and mixtures thereof. These polymers useful in the present invention are more fully described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 4,509,949, to Huang et al., issued April 5, 1985; U.S. Patent No. 2,798,053, to Brown, issued July 2, 1957; which are both incorporated by reference herein in their entirety. See also, CTFA International

Cosmetic Ingredient Dictionary, fourth edition, 1991, pp. 12 and 80; which are also incorporated herein by reference in their entirety.

Examples of commercially available homopolymers of the first type useful herein include the carbomers, which are homopolymers of acrylic acid crosslinked with allyl ethers of sucrose or pentaerytritol. The carbomers are available as the Carbopol<sup>®</sup> 900 series from B.F. Goodrich. Examples of commercially available copolymers of the second type useful herein include copolymers of C<sub>10-30</sub> alkyl acrylates with one or more monomers of acrylic acid, methacrylic acid, or one of their short chain (i.e. C<sub>1-4</sub> alcohol) esters, wherein the crosslinking agent is an allyl ether of sucrose or pentaerytritol. These copolymers are known as acrylates/C10-30 alkyl acrylate crosspolymers and are commercially available as Carbopol<sup>®</sup> 1342, Pemulen TR-1, and Pemulen TR-2, from B.F. Goodrich. In other words, examples of carboxylic acid polymer thickeners useful herein are those selected from the group consisting of carbomers, acrylates/C10-C30 alkyl acrylate crosspolymers, and mixtures thereof.

Crosslinked Polyacrylate Polymers The crosslinked polyacrylate polymers useful as thickeners or gelling agents include both cationic and nonionic polymers, with the cationics being generally preferred. Examples of useful crosslinked nonionic polyacrylate polymers and crosslinked cationic polyacrylate polymers are those described in U.S. Patent 5,100,660, to Hawe et al., issued March 31, 1992; U.S. Patent 4,849,484, to Heard, issued July 18, 1989; U.S. Patent 4,835,206, to Farrar et al., issued May 30, 1989; U.S. Patent 4,628,078 to Glover et al. issued December 9, 1986; U.S. Patent 4,599,379 to Flesher et al. issued July 8, 1986; and EP 228,868, to Farrar et al., published July 15, 1987; all of which are incorporated by reference herein in their entirety.

The crosslinked polyacrylate polymers are high molecular weight materials that can be characterized by the general formula: (A)<sub>l</sub>(B)<sub>m</sub>(C)<sub>n</sub> and comprise the monomer units (A)<sub>l</sub>, (B)<sub>m</sub>, and (C)<sub>n</sub>, wherein (A) is a dialkylaminoalkyl acrylate monomer or its quaternary ammonium or acid addition salt, (B) is a dialkylaminoalkyl methacrylate monomer or its quaternary ammonium or acid addition salt, (C) is a monomer that is polymerizable with (A) or (B), for example a monomer having a carbon-carbon double bond or other such polymerizable functional group, l is an integer of 0 or greater, m is an integer of 0 or greater, n is an integer of 0 or greater, but where either l or m, or both, must be 1 or greater.

The (C) monomer can be selected from any of the commonly used monomers. Nonlimiting examples of these monomers include ethylene, propylene, butylene, isobutylene, eicosene, maleic anhydride, acrylamide, methacrylamide, maleic acid, acrolein, cyclohexene, ethyl vinyl ether, and methyl vinyl ether. In the cationic polymers of the present invention, (C) is preferably acrylamide. The alkyl portions of the (A) and (B) monomers are short chain length alkyls such as C<sub>1-8</sub>, preferably C<sub>1-5</sub>, more preferably C<sub>1-3</sub>, and most preferably C<sub>1-2</sub>. When quaternized, the polymers are preferably quaternized with short chain alkyls, i.e., C<sub>1-8</sub>, preferably C<sub>1-5</sub>, more preferably C<sub>1-3</sub>, and most preferably C<sub>1-2</sub>. The acid addition salts refer to polymers having



protonated amino groups. Acid addition salts can be performed through the use of halogen (e.g. chloride), acetic, phosphoric, nitric, citric, or other acids.

These (A)<sub>l</sub>(B)<sub>m</sub>(C)<sub>n</sub> polymers also comprise a crosslinking agent, which is most typically a material containing two or more unsaturated functional groups. The crosslinking agent is reacted with the monomer units of the polymer and is incorporated into the polymer thereby forming links or covalent bonds between two or more individual polymer chains or between two or more sections of the same polymer chain. Nonlimiting examples of suitable crosslinking agents include those selected from the group consisting of methylenebisacrylamides, diallyldialkyl ammonium halides, polyalkenyl polyethers of polyhydric alcohols, allyl acrylates, vinyloxyalkylacrylates, and polyfunctional vinylidenes. Specific examples of crosslinking agents useful herein include those selected from the group consisting of methylenebisacrylamide, ethylene glycol di-(meth)acrylate, di-(meth)acrylamide, cyanomethylacrylate, vinyloxyethylacrylate, vinyloxyethylmethacrylate, allyl pentaerythritol, trimethylolpropane diallylether, allyl sucrose, butadiene, isoprene, divinyl benzene, divinyl naphthalene, ethyl vinyl ether, methyl vinyl ether, and allyl acrylate. Other crosslinkers include formaldehyde and glyoxal. Preferred for use herein as a crosslinking agent is methylenebisacrylamide.

Widely varying amounts of the crosslinking agent can be employed depending upon the properties desired in the final polymer, e.g. viscosifying effect. Without being limited by theory, it is believed that incorporation of a crosslinking agent into these cationic polymers provides a material that is a more effective viscosifying agent without negatives such as stringiness and viscosity breakdown in the presence of electrolytes. The crosslinking agent, when present, can comprise from about 1 ppm to about 1000 ppm, preferably from about 5 ppm to about 750 ppm, more preferably from about 25 ppm to about 500 ppm, even more preferably from about 100 ppm to about 500 ppm, and most preferably from about 250 ppm to about 500 ppm of the total weight of the polymer on a weight/weight basis.

The intrinsic viscosity of the crosslinked polymer, measured in one molar sodium chloride solution at 25 °C, is generally above 6, preferably from about 8 to about 14. The molecular weight (weight average) of the crosslinked polymers hereof is high, and is believed to typically be between about 1 million and about 30 million. The specific molecular weight is not critical and lower or higher weight average molecular weights can be used as long as the polymer retains its intended viscosifying effects. Preferably, a 1.0% solution of the polymer (on an actives basis) in deionized water will have a viscosity at 25 °C of at least about 20,000 cP, preferably at least about 30,000 cP, when measured at 20 RPM by a Brookfield RVT (Brookfield Engineering Laboratories, Inc. Stoughton, MA, USA).

These cationic polymers can be made by polymerization of an aqueous solution containing from about 20% to about 60%, generally from about 25% to about 40%, by weight monomer, in the presence of an initiator (usually redox or thermal) until the polymerization terminates. The

crosslinking agent can also be added to the solution of the monomers to be polymerized, to incorporate it into the polymer. In the polymerization reactions, the temperature generally starts between about 0° and 95° C. The polymerization can be conducted by forming a reverse phase dispersion of an aqueous phase of the monomers (and also any additional crosslinking agents) into a nonaqueous liquid, e.g. mineral oil, lanolin, isododecane, oleyl alcohol, and other volatile and nonvolatile esters, ethers, and alcohols, and the like.

All percentages describing the polymer in this section of the description herein are molar, unless otherwise specified. When the polymer contains (C) monomer, the molar proportion of (C) monomer, based on the total molar amount of (A), (B), and (C), can be from 0% to about 99%. The molar proportions of (A) and (B) can each be from 0% to 100%. When acrylamide, is used as the (C) monomer, it will preferably be used at a level of from about 20% to about 99%, more preferably from about 50% to about 90%.

Where monomer (A) and (B) are both present, the ratio of monomer (A) to monomer (B) in the final polymer, on a molar basis, is preferably from about 99:5 to about 15:85, more preferably from about 80:20 to about 20:80. Alternatively, in another class of polymers, the ratio is from about 5:95 to about 50:50, preferably from about 5:95 to about 25:75.

In another alternative class of polymers, the ratio (A):(B) is from about 50:50 to about 85:15. Preferably the ratio (A):(B) is about 60:40 to about 85:15, most preferably about 75:25 to about 85:15.

Most preferred is where monomer (A) is not present and the ratio of monomer (B):monomer (C) is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40 and most preferably from about 45:55 to about 55:45.

Cationic polymers that are useful herein that are especially preferred are those conforming to the general structure (A)<sub>l</sub>(B)<sub>m</sub>(C)<sub>n</sub> wherein l is zero, (B) is methyl quaternized dimethylaminoethyl methacrylate, the ratio of (B):(C) is from about 45:55 to about 55:45, and the crosslinking agent is methylenebisacrylamide. An example of such a cationic polymer is one that is commercially available as a mineral oil dispersion (which can also include various dispersing aids such as PPG-1 trideceth-6) under the trademark Salcare<sup>®</sup> SC92 from Allied Colloids Ltd. (Norfolk, Virginia). This polymer has the proposed CTFA designation, "Polyquaternium 32 (and) Mineral Oil".

Other cationic polymers useful herein, are those not containing acrylamide or other (C) monomers, that is, n is zero. In these polymers the (A) and (B) monomer components are as described above. An especially preferred group of these non-acrylamide containing polymers is one in which l is also zero. In this instance the polymer is essentially a homopolymer of a dialkylaminoalkyl methacrylate monomer or its quaternary ammonium or acid addition salt. These dialkylaminoalkyl methacrylate polymers preferably contain a crosslinking agent as described above.

A cationic polymer, which is essentially a homopolymer, useful herein is one conforming to the general structure (A)<sub>l</sub>(B)<sub>m</sub>(C)<sub>n</sub> wherein l is zero, (B) is methyl quaternized dimethylaminoethyl

methacrylate, n is zero, and the crosslinking agent is methylenebisacrylamide. An example of such a homopolymer is commercially available as a mixture containing approximately 50% of the polymer, approximately 44% mineral oil, and approximately 6% PPG-1 trideceth-6 as a dispersing aid, from Allied Colloids Ltd, (Norfolk, VA) under the trademark Salcare® SC95. This polymer has recently been given the CTFA designation "Polyquaternium 37 (and) Mineral Oil (and) PPG-1 Trideceth-6".

Polyacrylamide Polymers Also useful herein are polyacrylamide polymers, especially non-ionic polyacrylamide polymers including substituted branched or unbranched polymers. These polymers can be formed from a variety of monomers including acrylamide and methacrylamide which are unsubstituted or substituted with one or two alkyl groups (preferably C<sub>1</sub> to C<sub>5</sub>). Preferred are acrylate amide and methacrylate amide monomers in which the amide nitrogen is unsubstituted, or substituted with one or two C<sub>1</sub> to C<sub>5</sub> alkyl groups (preferably methyl, ethyl, or propyl), for example, acrylamide,

methacrylamide, N-methacrylamide, N-methylmethacrylamide, N,N-dimethylmethacrylamide, N-isopropylacrylamide, N-isopropylmethacrylamide, and N,N-dimethylacrylamide. These polymers have a molecular weight greater than about 1,000,000 preferably greater than about 1,500,000 and range up to about 30,000,000. Most preferred among these polyacrylamide polymers is the non-ionic polymer given the CTFA designation polyacrylamide and isoparaffin and laureth-7, available under the Tradename Sepigel 305 from Seppic Corporation (Fairfield, NJ).

Other polyacrylamide polymers useful herein include multi-block copolymers of acrylamides and substituted acrylamides with acrylic acids and substituted acrylic acids. Commercially available examples of these multi-block copolymers include Hypan SR150H, SS500V, SS500W, SSSA100H, from Lipo Chemicals, Inc., (Patterson, NJ).

Polysaccharides A wide variety of polysaccharides are useful herein. By "polysaccharides" are meant gelling agents containing a backbone of repeating sugar (i.e. carbohydrate) units. Nonlimiting examples of polysaccharide gelling agents include those selected from the group consisting of cellulose, carboxymethyl hydroxyethylcellulose, cellulose acetate propionate carboxylate, hydroxyethylcellulose, hydroxyethyl ethylcellulose, hydroxypropylcellulose, hydroxypropyl methylcellulose, methyl hydroxyethylcellulose, microcrystalline cellulose, sodium cellulose sulfate, and mixtures thereof. Also useful herein are the alkyl substituted celluloses. In these polymers, the hydroxy groups of the cellulose polymer is hydroxyalkylated (preferably hydroxyethylated or hydroxypropylated) to form a hydroxyalkylated cellulose which is then further modified with a C10-C30 straight chain or branched chain alkyl group through an ether linkage. Typically these polymers are ethers of C10-C30 straight or branched chain alcohols with hydroxyalkylcelluloses. Examples of alkyl groups useful herein include those selected from the group consisting of stearyl, isostearyl, lauryl, myristyl, cetyl, isocetyl, cocoyl (i.e. alkyl groups derived from the alcohols of coconut oil), palmityl, oleyl, linoleyl, linolenyl, ricinoleyl, behenyl, and mixtures thereof.

Preferred among the alkyl hydroxyalkyl cellulose ethers is the material given the CTFA designation cetyl hydroxyethylcellulose, which is the ether of cetyl alcohol and hydroxyethylcellulose. This material is sold under the tradename Natrosol<sup>®</sup> CS Plus from Aqualon Corporation.

Other useful polysaccharides include scleroglucans comprising a linear chain of (1->3) linked glucose units with a (1->6) linked glucose every three units, a commercially available example of which is Clearogel<sup>™</sup> CS11 from Michel Mercier Products Inc. (Mountainside, NJ).

Gums Other additional thickening and gelling agents useful herein include materials which are primarily derived from natural sources. Nonlimiting examples of these gelling agent gums include materials selected from the group consisting of acacia, agar, algin, alginic acid, ammonium alginate, amylopectin, calcium alginate, calcium carrageenan, carnitine, carrageenan, dextrin, gelatin, gellan gum, guar gum, guar hydroxypropyltrimonium chloride, hectorite, hyaluronic acid, hydrated silica, hydroxypropyl chitosan, hydroxypropyl guar, karaya gum, kelp, locust bean gum, natto gum, potassium alginate, potassium carrageenan, propylene glycol alginate, sclerotium gum, sodium carboxymethyl dextran, sodium carrageenan, tragacanth gum, xanthan gum, and mixtures thereof.

Crosslinked Vinyl Ether/Maleic Anhydride Copolymers Other additional thickening and gelling agents useful herein include crosslinked copolymers of alkyl vinyl ethers and maleic anhydride. In these copolymers the vinyl ethers are represented by the formula  $R-O-CH=CH_2$  wherein R is a C1-C6 alkyl group, preferably R is methyl. Preferred crosslinking agents are C4-C20 dienes, preferably C6 to C16 dienes, and most preferably C8 to C12 dienes. A particularly preferred copolymer is one formed from methyl vinyl ether and maleic anhydride wherein the copolymer has been crosslinked with decadiene, and wherein the polymer when diluted as a 0.5% aqueous solution at pH 7 at 25°C has a viscosity of 50,000-70,000 cps when measured using a Brookfield RTV viscometer, spindle #7 at 10 rpm. This copolymer has the CTFA designation PVM/MA decadiene crosspolymer and is commercially available as Stabileze<sup>™</sup> 06 from International Specialty Products (Wayne NJ).

Crosslinked poly(N-vinylpyrrolidones) Crosslinked polyvinyl(N-pyrrolidones) useful herein as additional thickening and gelling agents and include those described in U.S. Patent No. 5,139,770, to Shih et al, issued August 18, 1992, and U.S. Patent No. 5,073,614, to Shih et al., issued December 17, 1991, both patents of which are incorporated by reference herein in their entirety. These gelling agents typically contain from about 0.25% to about 1% by weight of a crosslinking agent selected from the group consisting of divinyl ethers and diallyl ethers of terminal diols containing from about 2 to about 12 carbon atoms, divinyl ethers and diallyl ethers of polyethylene glycols containing from about 2 to about 600 units, dienes having from about 6 to about 20 carbon atoms, divinyl benzene, vinyl and allyl ethers of pentaerythritol, and the like. Typically, these gelling agents have a viscosity from about 25,000 cps to about 40,000 cps when measured as a 5% aqueous solution at 25°C using a Brookfield RVT viscometer with Spindle #6 at 10 rpm. Commercially available examples of these polymers include ACP-1120, ACP-1179, and ACP-1180, available from International Specialty Products (Wayne, NJ).

### Water

The compositions of the present invention comprise from about 25% to about 99.1%, more preferably from about 50% to about 95%, and most preferably from about 60% to about 90% water. The exact amount of water in the formulation will vary with the ranges of the required and optional components chosen.

### Optional Components

The compositions of the present invention can comprise a wide range of additional components. These additional components should be pharmaceutically acceptable. The CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, which is incorporated by reference herein in its entirety, describes a wide variety of nonlimiting cosmetic and pharmaceutical ingredients commonly used in the skin care industry, which are suitable for use in the compositions of the present invention. Nonlimiting examples of functional classes of ingredients are described at page 537 of this reference. Examples of these functional classes include: abrasives, absorbents, anti-acne agents, anticaking agents, antifoaming agents, antimicrobial agents, antioxidants, binders, biological additives, buffering agents, bulking agents, chelating agents, chemical additives, colorants, cosmetic astringents, cosmetic biocides, denaturants, drug astringents, external analgesics, film formers, fragrance components, humectants, opacifying agents, pH adjusters, preservatives, propellants, reducing agents, skin bleaching agents, skin-conditioning agents (humectants, miscellaneous, and occlusive).

Some nonlimiting examples of these additional components cited in the CTFA Cosmetic Ingredient Handbook, as well as other materials useful herein, include the following: vitamins and derivatives thereof (e.g. tocopherol, tocopherol acetate, retinoic acid, retinol, retinoids, and the like); polymers for aiding the film-forming properties and substantivity of the composition (such as a copolymer of eicosene and vinyl pyrrolidone, an example of which is available from GAF Chemical Corporation as Ganex<sup>®</sup> V-220); preservatives for maintaining the antimicrobial integrity of the compositions; other anti-acne medicaments (e.g., resorcinol, sulfur, salicylic acid, erythromycin, zinc, and the like); skin bleaching (or lightening) agents including but not limited to hydroquinone, kojic acid; antioxidants; chelators and sequestrants; skin treating agents such as alpha-hydroxy acids such as lactic acid and glycolic acid, and aesthetic components such as fragrances, pigments, colorings, essential oils, skin sensates, astringents, skin soothing agents, skin healing agents and the like, nonlimiting examples of these aesthetic components include panthenol and derivatives (e.g. ethyl panthenol), aloe vera, pantothenic acid and its derivatives, clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate, allantoin, bisabolol, dipotassium glycyrrhizinate and the like; and skin conditioning agents such as the propoxylated glycerols described in U.S. Patent No. 4,976,953, to Orr et al., issued December 11, 1990, which is incorporated by reference herein in its entirety.

### Methods For Protecting The Skin From UV Radiation

The compositions of the present invention are useful for providing protection to human skin from the harmful effects of UV radiation. To protect the skin a safe and effective amount of the composition is applied to the skin. By "safe and effective amount" is meant an amount effective for providing the benefits of the present invention, i.e. protection from the harmful effects of UV radiation, without any undue toxicity, allergic, or other unwanted side effects. By "protection" is meant that these compositions attenuate or reduce the amount of UV radiation reaching the skin's surface. Quantities of composition which are typically applied to provide protection are about, but not limited to, about 2 mg/cm<sup>2</sup>.

### EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention.

Ingredients are identified by chemical or CTFA name.

### EXAMPLES I-II

#### Photoprotective Compositions

<u>Ingredient</u>	<u>I</u>	<u>II</u>
	WT. %	WT. %
Octyl methoxycinnamate	6.0	6.0
Zinc Oxide	5.0	5.0
Isohexadecane	4.0	4.0
Glycerin	3.0	6.0
Polyquaternium 37 (and) mineral oil (and) PPG-1-trideceth-6 <sup>1</sup>	2.0	0.0
Polyacrylamide (and) C13-14 isoparaffin (and) laureth-7 <sup>2</sup>	0.0	2.25
Dimethicone (and) dimethiconol <sup>3</sup>	0.0	1.0
Cetyl palmitate	0.0	1.0
Isopropyl palmitate	0.0	1.0
Cyclomethicone (and) dimethiconol <sup>4</sup>	0.5	0.0
Stearth-21	0.9	0.45
Stearyl alcohol	0.8	1.5
Cetyl alcohol	0.8	1.5
Cyclomethicone (and) dimethicone copolyol <sup>5</sup>	0.5	0.0

Benzyl alcohol	0.5	0.5
Methyl paraben	0.25	0.25
Vitamin E acetate	0.2	0.5
Propyl paraben	0.15	0.15
Disodium EDTA	0.13	0.13
DEA Oleth-3 phosphate	0.1	0.1
Steareth-2	0.1	0.05
Water	QS 100	QS 100

- <sup>1</sup> Available as Salcare SC95 from Allied Colloids.
- <sup>2</sup> Available as Sepigel 305 from Seppic, Inc.
- <sup>3</sup> Available as Dow Corning Q2-1403 fluid from Dow Corning Corporation.
- <sup>4</sup> Available as Dow Corning Q2-1401 fluid from Dow Corning Corporation.
- <sup>5</sup> Available as Dow Corning Q2-3225C from Dow Corning Corporation.

The above compositions are prepared as follows:

The emulsion water phase is prepared by combining the glycerin, methylparaben, disodium EDTA, and water in a mixing vessel. Next, a zinc dispersion premix is prepared by combining the isohexadecane, octyl methoxycinnamate, and DEA oleth-3 phosphate in a separate vessel, and warming slightly to solubilize the DEA oleth-3 phosphate. The zinc oxide is then stirred into the mix of oils for about several minutes, and this zinc dispersion is then milled. Next, the remaining oil phase ingredients (cetyl palmitate, isopropyl palmitate, steareth-21, stearyl alcohol, cetyl alcohol, Dow Corning Q2-3225C, vitamin E acetate, propylparaben, and steareth-2) are mixed into the zinc dispersion.

Both the water phase and oil phase are then heated to 70 - 80°C, and the oil phase is slowly added to the water phase while the system is milled to form an emulsion. The emulsion is then cooled with stirring. When the system reaches about 60°C, the Salcare SC95, Sepigel 305, Dow Corning Q2-1401, and Dow Corning Q2-1403 are added, and the product is milled again to disperse the polymers and silicones (when present). The system is then further cooled with stirring. The benzyl alcohol is then added when the product reaches about 48°C, and the product is poured into appropriate containers at about 30°C.

These compositions are useful for applying to human skin to provide protection from the harmful effects of UV radiation.

## WHAT IS CLAIMED IS:

1. A photoprotective composition comprising:
  - (a) from 0.1% to 30% of a sunscreen active;
  - (b) from 0.5% to 20% of a hydrophobic, structuring agent selected from the group consisting of saturated C<sub>16</sub> to C<sub>30</sub> fatty alcohols, saturated C<sub>16</sub> to C<sub>30</sub> fatty alcohols containing from 1 to 5 moles of ethylene oxide, saturated C<sub>16</sub> to C<sub>30</sub> diols, saturated C<sub>16</sub> to C<sub>30</sub> monoglycerol ethers, saturated C<sub>16</sub> to C<sub>30</sub> hydroxy fatty acids, and mixtures thereof, having a melting point of at least 40°C;
  - (c) from 0.2 % to 10% of a hydrophilic surfactant selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, zwitterionic surfactants, amphoteric surfactants, and mixtures thereof; and
  - (d) from 0.1% to 5% of a thickening agent selected from the group consisting of carboxylic acid polymers, crosslinked polyacrylate polymers, polyacrylamide polymers, polysaccharides, gums, crosslinked vinyl ether/maleic anhydride copolymers, crosslinked poly(N-vinylpyrrolidones), and mixtures thereof, and
  - (e) from 25% to 99.1% water.
  
2. A composition according to Claim 1 wherein said sunscreen active is selected from the group consisting of 2-ethylhexyl N,N-dimethyl-*p*-aminobenzoate, 2-ethylhexyl *p*-methoxycinnamate, octocrylene, octyl salicylate, homomenthyl salicylate, *p*-aminobenzoic acid, oxybenzone, 2-phenylbenzimidazole-5-sulfonic acid, DEA *p*-methoxycinnamate, 4,4'-methoxy-*t*-butyldibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-(4-methylbenzylidene)camphor, 3-benzylidene camphor, titanium dioxide, zinc oxide, iron oxide, and mixtures thereof.
  
3. A composition according to Claim 2 wherein said thickening agent is selected from the group consisting of carboxylic acid polymers, crosslinked polyacrylate polymers, polyacrylamide polymers, and mixtures thereof; preferably wherein said thickening agent is selected from the group consisting of crosslinked polyacrylate polymers, polyacrylamide polymers, and mixtures thereof.
  
4. A composition according to Claim 3 wherein said crosslinked cationic polymer corresponds to the formula (A)<sub>l</sub>(B)<sub>m</sub>(C)<sub>n</sub> wherein (A) is a dialkylaminoalkyl acrylate monomer or its quaternary ammonium or acid addition salt, (B) is a dialkylaminoalkyl methacrylate monomer or its quaternary ammonium or acid addition salt, (C) is acrylamide, l is an integer of 0 or greater, m is an integer of 1 or greater, and n is an integer of 0 or greater, wherein said polymer contains a crosslinking agent.



5. A composition according to Claim 4 wherein said crosslinking agent is selected from the group consisting of methylene bisacrylamide, ethylene glycol di-(meth)acrylate, di-(meth)acrylamide, cyanomethylacrylate, vinyloxyethylacrylate, vinyloxyethylmethacrylate, allyl pentaerythritol, trimethylolpropane, diallylether, allyl sucrose, butadiene, isoprene, divinyl benzene, divinyl naphthalene, allyl acrylate, and mixtures thereof.
6. A composition according to Claim 5 wherein said crosslinked cationic polymer is selected from the group consisting of polyquaternium 32, polyquaternium 37, and mixtures thereof.
7. A composition according to Claim 3 wherein said polyacrylamide polymer has a molecular weight from 1,000,000 to 30,000,000.
8. A composition according to any of Claims 1-7 wherein said sunscreen active is selected from the group consisting of 2-ethylhexyl *p*-methoxycinnamate, 4,4'-methoxy-*t*-butyldibenzoylmethane, zinc oxide, and mixtures thereof; and wherein said hydrophobic structuring agent is selected from the group consisting of stearyl alcohol, cetyl alcohol, behenyl alcohol, polyethylene glycol ether of stearyl alcohol having an average of about 2 ethylene oxide units, and mixtures thereof.
9. A composition according to Claim 8 wherein said hydrophilic surfactant is a nonionic surfactant, preferably wherein said nonionic surfactant is selected from the group consisting of steareth-21, cetareth-20, cetareth-12, sucrose cocoate, steareth-100, PEG-100 stearate, and mixtures thereof.
10. A method for protecting human skin from the harmful effects of UV radiation, said method comprising applying a safe and effective amount of the composition of any of Claims 1-9 to human skin.

# INTERNATIONAL SEARCH REPORT

International Application No  
**PCT/US 97/01170**

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A61K/42

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

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

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 02176 A (PROCTER & GAMBLE) 3 February 1994 see claims 1-3,19 see page 14, line 15 - page 15, line 18 see page 15, line 32 - page 17, line 8 see page 19, line 16 - page 21, line 21 see example 1	1-6,8,9
X	--- EP 0 579 079 A (BAYER) 19 January 1994 see claims 1,6,8 see page 3, line 11-54	1-3,8-10
X	--- WO 95 22311 A (UNILEVER) 24 August 1995 see claims 1,3,5,10 see page 7, line 34 - page 8, line 20 --- -/--	1,3,4,10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

13 June 1997

Date of mailing of the international search report

27.06.97

Name and mailing address of the ISA  
 European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax (+ 31-70) 340-3016

Authorized officer

Peeters, J

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/01170

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 07903 A (RICHARDSON-VICKS) 29 April 1993 see claims 1-3,9,10 see page 17, line 11-15 ---	1,3-7,10
X	EP 0 193 387 A (PROCTER & GAMBLE) 3 September 1986 see claims 1,2,4-7 see page 4, line 5-31 see page 5, line 14-34 ---	1-5,8-10
X	WO 94 15580 A (PROCTER & GAMBLE) 21 July 1994 see claims 1,2 see page 11, line 7 - page 13, line 12 see page 14, line 11-31 see page 17, line 5-29 see page 18, line 27 - page 20, line 6 ---	1-3,8-10
X	WO 89 10738 A (SOLARCARE) 16 November 1989 see claims 1,3,4,7-9 see page 9, paragraph 1 - page 14, paragraph 1 see page 16, paragraph 2 see example 1 -----	1-3,8-10

# INTERNATIONAL SEARCH REPORT

information on patent family members

Inter national Application No  
PCT/US 97/01170

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9402176 A	03-02-94	AT 152630 T	15-05-97
		AU 4673993 A	14-02-94
		CA 2141192 A	03-02-94
		CN 1091317 A	31-08-94
		DE 69310518 D	12-06-97
		EP 0652774 A	17-05-95
		FI 950368 A	10-03-95
		JP 7509243 T	12-10-95
		NO 950291 A	27-03-95
		US 5614178 A	25-03-97
		-----	
EP 579079 A	19-01-94	DE 4223463 A	20-01-94
		AT 147967 T	15-02-97
		AU 4164493 A	20-01-94
		BR 9302884 A	16-02-94
		CA 2100405 A	17-01-94
		DE 59305208 D	06-03-97
		ES 2099322 T	16-05-97
		HU 64687 A	28-02-94
		JP 6157265 A	03-06-94
		ZA 9305104 A	04-02-94
		-----	
WO 9522311 A	24-08-95	AU 1809795 A	04-09-95
		CA 2180942 A	24-08-95
		EP 0744935 A	04-12-96
		JP 9501951 T	25-02-97
		US 5543074 A	06-08-96
-----			
WO 9307903 A	29-04-93	AU 675212 B	30-01-97
		AU 2863992 A	21-05-93
		BR 9206631 A	24-10-95
		CA 2117265 A	29-04-93
		CN 1072602 A	02-06-93
		CZ 9400901 A	13-07-94
		EP 0608322 A	03-08-94
		FI 941770 A	15-04-94
		HU 67046 A	30-01-95
		JP 7500594 T	19-01-95
		NO 941317 A	16-06-94
		NZ 244743 A	26-09-95

# INTERNATIONAL SEARCH REPORT

information on patent family members

Int:      onal Application No  
PCT/US 97/01170

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9307903 A		PT 100964 A	30-11-93
EP 193387 A	03-09-86	US 4663157 A	05-05-87
		AU 577755 B	29-09-88
		AU 5414986 A	04-09-86
		CA 1267095 A	27-03-90
		GB 2172503 A,B	24-09-86
		HK 48192 A	10-07-92
		JP 61267508 A	27-11-86
WO 9415580 A	21-07-94	AU 5993894 A	15-08-94
		CA 2153324 A	21-07-94
		CN 1118987 A	20-03-96
		EP 0678015 A	25-10-95
		JP 8505624 T	18-06-96
WO 8910738 A	16-11-89	AU 3744689 A	29-11-89
		US 5017365 A	21-05-91