



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

<b>(51) International Patent Classification <sup>5</sup> :</b>  <b>A61K 7/08</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/18737</b>  <b>(43) International Publication Date:</b> 30 September 1993 (30.09.93)
<b>(21) International Application Number:</b> PCT/US93/02128  <b>(22) International Filing Date:</b> 9 March 1993 (09.03.93)  <b>(30) Priority data:</b> 07/852,857                      17 March 1992 (17.03.92)                      US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> COTHRAN, Philip, Earl ; 3512 Shadowridge Drive, Loveland, OH 45140 (US). COFFINDAFFER, Timothy, Woodrow ; 118 Bridle Lane, Loveland, OH 45140 (US).		<b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).  <b>(81) Designated States:</b> AU, BB, BG, BR, CA, CZ, FI, HU, JP, KP, KR, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MILD SHAMPOO COMPOSITIONS  <b>(57) Abstract</b>  <p>Disclosed are mild shampoo and shampoo premix compositions, and methods of making mild shampoo and shampoo pre-mixes that are substantially free of alkyl sulfates. The preferred shampoo premix comprises alkyl ethoxylated sulfate surfactant, a specific type of imidazolinium-type amphoteric surfactant, a crystalline suspending agent that is preferably solubilized and recrystallized in the premix composition, and a relatively low amount of water. The preferred shampoo compositions hereof comprise alkyl ethoxylated sulfate surfactant, imidazoline-type amphoteric surfactant, betaine surfactant, a recrystallized suspending agent, and water. The shampoos and shampoo premixes hereof can provide mild, good lathering, pearlescent compositions. The premix compositions hereof are particularly useful for use in mild shampoo compositions containing silicone conditioning agents and/or particulate antidandruff agents.</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.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

mild shampoo compositions

5

#### TECHNICAL FIELD

The present invention is related to shampoo premix compositions as well as finished shampoo compositions. The present invention also relates to methods of making said mild shampoo and shampoo premix compositions.

10

#### BACKGROUND OF THE INVENTION

Mild shampoo compositions which provide low irritation to the skin are highly desirable. Conventional shampoos contain high levels of harsh anionic surfactants. These surfactants can provide excellent lathering and cleaning characteristics. However, they can also penetrate the skin and destroy its integrity. This results, at the very least, in rough and/or dry skin, and can ultimately lead to red, irritated skin. Ideal shampoo compositions should provide sufficient lathering and cleaning benefits to cleanse the hair while at the same time causing little or no irritation to the skin. This is particularly essential for shampoo compositions used on babies, small children, or adults with dry or sensitive skin.

15

20

30

35

Mild shampoo compositions, in general, are well known in the art having been taught in, for example, European Patent Application 0250181, published December 23, 1987; U.S. Patent 4,578,216, Fujii et al., issued March 25, 1986; U.S. Patent 4,726,915, Verdicchio, issued February 23, 1988; U.K. Patent Specification 1,508,929, published April 26, 1978; European Patent Application 0160269, published November 6, 1985; U.S. Patent 4,435,300, Guth et al., issued March 6, 1984; U.S. Patent 4,426,310, Vernunica, issued January 17, 1984; U.S. Patent 3,950,417, Verdicchio et al., issued April 13, 1976; U.S. Patent 4,443,362, Guth et al., issued April 17, 1984; U.S. Patent 4,654,207, Preston, issued March 31, 1987; U.S. Patent 4,851,154, Grollier et al., issued July 25, 1989; U.S. Patent 4,292,212, Melby, issued September 29, 1981; and U.S. Patent 4,329,334, Su et al., issued May 11, 1982. These

- 2 -

references teach the use of a wide variety of surfactant combinations to achieve mildness. These surfactants include mild anionic surfactants, such as ethoxylated alkyl sulfates, amphoteric surfactants, nonionic surfactants, and various combinations thereof.

5 One well-known mild shampoo is Johnson's Baby Shampoo (Johnson & Johnson). This product contains relatively high levels of nonionic surfactant (PEG-80 Sorbitan Laurate) and other mild surfactants to boost its cleaning performance (betaine, ethoxy-  
10 lated alkyl sulfate, an imidazoline-derived amphoteric, and an ethoxylated alkyl carboxylate).

The formulation of such mild shampoo compositions, however, generally is an exercise in efficacy and mildness trade-offs, with the resulting composition providing either good cleaning and  
15 lathering benefits, or good mildness or skin irritation benefits, but not good cleaning and lathering in combination with mildness and low skin irritation.

Hence, it is an object of the present invention to provide a mild shampoo composition which provides good in-use characteristics such as lathering, both in terms of stability, creaminess,  
20 and abundance of lather, while at the same time providing good cleaning and skin mildness benefits. It is also preferable that the shampoo have a pleasing aesthetic appearance which is also referred to as pearlescence, in addition to providing the above  
25 characteristics.

Also desirable in state of the art shampoo compositions are conditioning benefits inherent in the shampoo compositions. Such products are sometimes termed two-in-one shampoos, meaning the  
30 compositions include both cleaning and conditioning ingredients in the same product. Such compositions are difficult to formulate because the cleaning ingredients, in general, tend to be incompatible with the conditioning ingredients. One highly successful solution to this dilemma has been to use dispersed insoluble  
35 non-volatile silicone materials together with certain suspending agents for the silicones in shampoo compositions. Such technology is taught in U.S. Patent 4,704,272, Oh et al., issued November 3,

- 3 -

1987; U.S. Patent 4,741,855, Grote et al., issued May 3, 1988; and U.S. Patent 4,788,006, Bolich et al., issued June 5, 1984. This technology can also be used, usually at relatively lower silicone levels, to provide some conditioning benefit in shampoos not explicitly marketed as 2-in-1 shampoos. Another benefit of certain of the suspending agents referred to in these patents is their ability to improve the aesthetic appearance of shampoos by adding pearlescence. However, one problem with the use of silicone materials to deliver hair conditioning from shampoo compositions is that such materials, in general, tend to suppress lathering of the composition. If silicones are used with robust high-lathering surfactants, such as most anionic surfactants, lathering may not be unduly affected. However, if such materials are used with milder, less robust lathering surfactants, lathering may well be suppressed to an unacceptable level from a consumer standpoint.

Hence, it is a further object of the present invention to provide a shampoo composition which provides excellent lathering and cleaning benefits while at the same time being mild to the skin and providing hair conditioning benefits through the use of dispersed insoluble non-volatile silicone conditioning agents.

Alkyl sulfate surfactants can provide excellent lather and cleaning but tend to be harsh to the skin and are therefore not conducive to formulating mild shampoos. Unfortunately, in the absence of such alkyl sulfates it is difficult to get the suspending agent into the shampoo in crystalline form. It is when the suspending agent is present in the shampoo in the form of a crystalline network that it is effective in suspending the silicone composition. Providing the suspending agent in crystalline form is also critical for obtaining good lathering shampoo formulations.

It is also desirable to provide antidandruff shampoos that are mild to the skin but retain good cleaning and lathering characteristics. Preferably, the shampoo will contain particulate antidandruff agents, such as zinc pyridinethione or selenium disulfide. These particulate antidandruff agents must be suspended in the shampoo to provide a stable composition. The same

- 4 -

types of suspending agents that can be used to suspend silicone have also been found to be preferred for suspending the anti-dandruff agent. Thus, the same difficulties with respect to preparing high lathering, mild shampoos with the suspending agent free of harsh alkyl sulfate surfactants are again experienced.

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

Unless otherwise indicated, all percentages are calculated by weight of the total composition and all ratios are calculated on a weight basis.

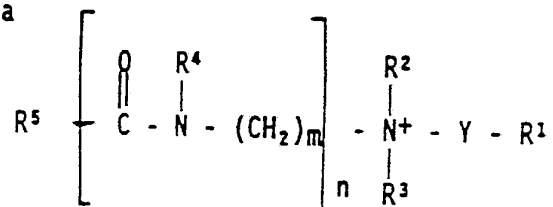
The compositions and processes herein can comprise, consist essentially of, or consist of any of the critical and optional elements and steps described in this application.

#### SUMMARY OF THE INVENTION

Mild, good lathering and cleaning shampoo compositions are provided herein comprising:

(a) from about 5% to about 20%, by weight, alkyl ethoxylated sulfate anionic surfactant ;

(b) from about 1% to about 10% of a betaine surfactant of the formula



wherein  $R_1$  is a member selected from the group consisting of COOM and  $\text{CH}-\text{CH}_2\text{SO}_3\text{M}$

|  
OH

$R_2$  is lower alkyl or hydroxyalkyl;

$R_3$  is lower alkyl or hydroxyalkyl;

$R_4$  is a member selected from the group consisting of hydrogen and lower alkyl;

$R_5$  is higher alkyl or alkenyl;

Y is lower alkyl, preferably methyl;

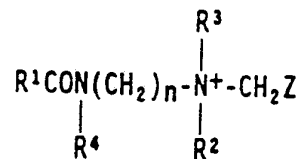
m is an integer from 2 to 7;

n is the integer 1 or 0;

M is hydrogen or a cation;

- 5 -

- (c) about 2% to about 10%, by weight, of an amphoteric surfactant having the formula



5

wherein R<sup>1</sup> is C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl, R<sup>2</sup> is hydrogen or CH<sub>2</sub>CO<sub>2</sub>M, R<sup>3</sup> is CH<sub>2</sub>CH<sub>2</sub>OH or CH<sub>2</sub>CHOCH<sub>2</sub>CH<sub>2</sub>COOM, R<sup>4</sup> is hydrogen, CH<sub>2</sub>CH<sub>2</sub>OH, or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, Z is CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, n is 2 or 3, and M is hydrogen or a cation;

10

- (d) from about 0.5% to about 5%, by weight, of a crystallized suspending agent; and

- (e) from about 60% to about 85% water

wherein said composition is substantially free of alkyl sulfate anionic surfactant, and the composition has a weight ratio of (a):(b)+(c) of about 1:1 to about 4:1, preferably about 4:3 to about 3:1, more preferably about 8:5 to about 7:3, and a weight ratio of (d):total surfactant of about 1:4 about 1:25, preferably about 1:6 to about 1:18, more preferably about 1:8 to about 1:13.

15

Also preferably, the shampoo compositions contain at least about 15%, by weight, of total surfactants, preferably at least about 16%, even more preferably at least about 17%, most preferably at least about 18%.

20

In general, the preferred shampoo compositions of the present invention will be made from a shampoo premix composition that comprise alkyl ethoxylated anionic surfactant, specific imidazolium-type amphoteric surfactant, suspending agent that has been solubilized in the premix at an elevated temperature and then crystallized to form a crystalline network by cooling the solution (hereinafter, "recrystallized suspending agent"), and about 30% to about 70% water. The shampoo premix composition is also substantially free of alkyl sulfates. These premixes can be used to make the shampoo formulations above, as well as other formulations as may be desired by the formulator.

25

30

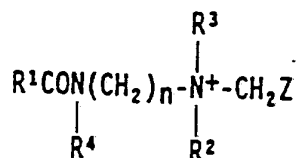
More particularly, the preferred shampoo premix compositions comprise:

35

- 6 -

- (a) at least about 10%, by weight, of alkyl ethoxylated sulfate anionic surfactant;
- (b) at least about 6%, by weight, of an amphoteric surfactant of the formula:

5



10

wherein R<sup>1</sup> is C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl, preferably C<sub>12</sub>-C<sub>16</sub>, R<sup>2</sup> is hydrogen or CH<sub>2</sub>CO<sub>2</sub>M, R<sup>3</sup> is CH<sub>2</sub>CH<sub>2</sub>OH or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, R<sup>4</sup> is hydrogen, CH<sub>2</sub>CH<sub>2</sub>OH, or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, Z is CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, n is 2 or 3, preferably 2, and M is hydrogen or a cation;

15

- (c) from about 2% to about 15%, by weight, of a suspending agent recrystallized in said premix composition; and
- (d) from about 30% to about 70% water;

20

wherein said premix has a weight ratio of (a):(b) of about 2:3 to about 3:1, a weight ratio of (c) to total surfactant present of from about 1:1 to about 1:6, and a weight ratio of (c):(d) of about 1:2 to about 1:15, and said premix composition is substantially free of alkyl sulfate anionic surfactant.

25

The present invention also provides shampoo compositions comprising shampoo premixes, as described above, further comprising: additional levels of the required surfactants or optionally other surfactants, though preferably the shampoo remains substantially free of alkyl sulfate or other ingredients that are harsh to the skin; conditioning agents, such as the preferred insoluble, nonvolatile silicone; antidandruff agents, including particulate and soluble antidandruff agents; foam boosters, preferably polyquaternium 10 or other mild-to-the-skin, non-amide foam boosters; color solutions; perfumes; preservatives; or other ingredients useful in shampoo composition; or mixtures thereof.

30

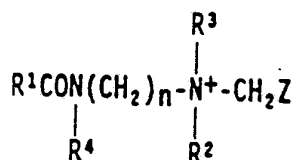
35

The present invention also provides a method for making shampoo premix compositions comprising the steps of (i) preparing a solution comprising:



- 7 -

- (a) at least about 10%, by weight, of alkyl ethoxylated sulfate anionic surfactant;
- (b) at least about 6%, by weight, of amphoteric surfactant of the formula;



wherein R<sup>1</sup> is C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl, R<sup>2</sup> is hydrogen or CH<sub>2</sub>CO<sub>2</sub>M, R<sup>3</sup> is CH<sub>2</sub>CH<sub>2</sub>OH or CH<sub>2</sub>CHOCH<sub>2</sub>CH<sub>2</sub>COOM, R<sup>4</sup> is hydrogen, CH<sub>2</sub>CH<sub>2</sub>OH, or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, Z is CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, n is 2 or 3, and M is hydrogen or a cation; and

(c) from about 30% to about 70%, by weight, water;

(ii) adding to the solution from about 2% to about 15%, by weight of the premix, of a suspending agent wherein said solution is heated and said suspending agent is provided in solubilized form; and (iii) cooling said composition to provide the solubilized suspending agent in crystalline form; wherein said premix has a weight ratio of (a):(b) of about 2:3 to about 3:1, a weight ratio of suspending agent to total surfactant present of from about 1:1 to about 1:6, and a weight ratio of suspending agent:water of about 1:2 to about 1:15, and said premix composition is prepared substantially free of alkyl sulfate anionic surfactant.

In another aspect of the invention hereof, the pH of the premix is reduced prior to providing the solubilized suspending agent in crystalline form to within about 2.0 pH, more preferably within about 1.5 pH, most preferably within about 1.0 pH, of the average pK<sub>a</sub> of the carboxylate(s) of said amphoteric surfactant.

In addition to meeting the objects of the invention described above, the shampoo and shampoo premixes hereof can also be characterized by having excellent pearlescence.

The invention, including preferred embodiments thereof, is described in more detail in the Detailed Description of the Invention, which follows.

- 8 -

## DETAILED DESCRIPTION OF THE INVENTION

The essential as well as certain preferred and optimal components of the compositions of the present invention are described below.

5 Alkyl Ethoxylated Sulfate

The shampoo composition hereof comprises at least about 5%, by weight, generally from about 5% to about 20%, preferably from about 6% to about 17%, more preferably from about 7% to about 15%, of alkyl ethoxylated sulfate anionic surfactant. The preferred  
10 shampoo premixes for making such shampoo will comprise from about 10% to about 25%, preferably about 12% to about 23%, more preferably from about 14% to about 20% of said surfactant. These types of surfactants are well known in the art. They typically have the formula  $RO(C_2H_4O)_xSO_3M$ , wherein R is alkyl or alkenyl of from  
15 about 8 to about 24 carbon atoms, x is 1 to 12, preferably, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. Useful alkyl ethoxylated sulfates are condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. Preferably, R has from  
20 about 10 to about 18 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are typically reacted with from about 1 to about 12, preferably about 2 to about 6, more  
25 preferably about about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species having, for example, an average moles of ethylene oxide per mole of alcohol also within the above limits, is sulfated and neutralized.

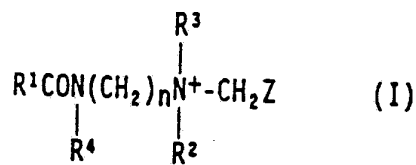
Specific examples of alkyl ethoxylated sulfates which may be  
30 used in the present invention are sodium and/or ammonium salts of coconut alkyl triethylene glycol ethoxylated sulfate, tallow alkyl triethylene glycol ethoxylated sulfate, and tallow alkyl hexaoxyethylene sulfate. Typically the alkyl ether sulfates will comprise a mixture of individual compounds, said mixture preferably  
35 having an average alkyl chain length of from about 10 to about 16

- 9 -

carbon atoms and an average degree of ethoxylation of from about 2 to about 6 moles of ethylene oxide, especially about 3. Especially preferred are narrow range alkyl ethoxylate sulfates such as those having ethoxylation levels primarily in the range of 1 to about 6, especially about 3.

#### Amphoteric Surfactant

The amphoteric surfactant will be present in the shampoo compositions hereof at levels of from about 2% to about 10%, by weight of the composition, preferably from about 2% to about 8%, more preferably about 2.5% to about 6%. The amphoteric surfactant will be used in the preferred shampoo premix compositions at a level of at least about 6%, by weight, of the premix, preferably about 8% to about 18%, more preferably about 9% to about 15%. The essential amphoteric surfactant hereof is depicted by Formula I:



wherein  $R^1$  is  $C_8 - C_{22}$  alkyl or alkenyl, preferably  $C_{12} - C_{16}$ ,  $R^2$  is hydrogen or  $\text{CH}_2\text{CO}_2\text{M}$ ,  $R^3$  is  $\text{CH}_2\text{CH}_2\text{OH}$  or  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOM}$ ,  $R^4$  is hydrogen,  $\text{CH}_2\text{CH}_2\text{OH}$ , or  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOM}$ ,  $Z$  is  $\text{CO}_2\text{M}$  or  $\text{CH}_2\text{CO}_2\text{M}$ ,  $n$  is 2 or 3, preferably 2,  $M$  is hydrogen or a cation, such as alkali metal, alkaline earth metal, or ammonium. Examples of "alkali metal" include lithium, sodium, and potassium. Examples of "alkaline earth metal" include beryllium, magnesium, calcium, strontium, and barium. This type of surfactant is sometimes classified as an imidazoline-type amphoteric surfactant, although it should be recognized that it does not necessarily have to be derived, directly or indirectly, through an imidazoline intermediate.

Suitable materials of this type are marketed under the tradename MIRANOL and are understood to comprise a complex mixture of species, and can exist in protonated and non-protonated species depending upon pH with respect to species that can have a hydrogen at  $R^2$ . All such variations and species are meant to be encompassed by Formula I.

**SUBSTITUTE SHEET**

- 10 -

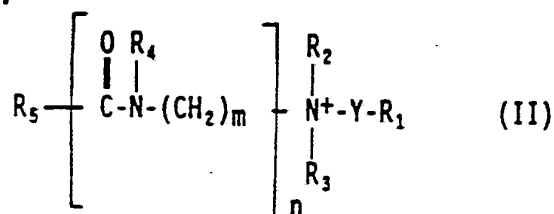
Preferred amphoteric surfactants of Formula I are monocarboxylates and dicarboxylates. Examples of these materials include cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate (alternately referred to as cocoamphodiacetate), and cocoamphoacetate.

Specific commercial products providing the amphoteric surfactant component of the present compositions include those sold under the trade names MIRANOL C2M CONC. N.P., MIRANOL C2M CONC. O.P., MIRANOL C2M SF, MIRANOL CM SPECIAL (Miranol, Inc.); ALKATERIC 2CIB (Alkaril Chemicals); AMPHOTERGE W-2 (Lonza, Inc.); MONATERIC CDX-38, MONATERIC CSH-32 (Mona Industries); REWOTERIC AM-2C (Rewo Chemical Group); and SCHERCOTERIC MS-2 (Scher Chemicals).

#### Betaine Surfactant

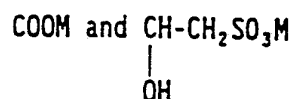
The shampoo compositions will generally comprise from about 1% to about 10%, preferably about 2% to about 8%, more preferably about 2.5% to about 6%, of a betaine surfactant.

The betaine surfactant hereof is depicted by compounds having the formula:



Wherein:

$R_1$  is a member selected from the group consisting of



$R_2$  is lower alkyl or hydroxyalkyl;

$R_3$  is lower alkyl or hydroxyalkyl;

$R_4$  is a member selected from the group consisting of hydrogen and lower alkyl;

$R_5$  is higher alkyl or alkenyl;

Y is lower alkyl, preferably methyl;

m is an integer from 2 to 7, preferably from 2 to 3;

- 11 -

n is the integer 1 or 0;

M is hydrogen or a cation, as previously described, such as an alkali metal, alkaline earth metal, or ammonium.

5 The term "lower alkyl" or "hydroxyalkyl" means straight or branch chained, saturated, aliphatic hydrocarbon radicals and substituted hydrocarbon radicals having from one to about three carbon atoms such as, for example, methyl, ethyl, propyl, iso-propyl, hydroxypropyl, hydroxyethyl, and the like. The term "higher alkyl or alkenyl" means straight or branch chained saturated (i.e., "higher alkyl") and unsaturated (i.e., "higher alkenyl") aliphatic hydrocarbon radicals having from about eight to about 20 carbon atoms such as, for example, lauryl, cetyl, stearyl, oleyl, and the like. It should be understood that the term "higher alkyl or alkenyl" includes mixtures of radicals which may contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such as hydroxyl or halogen radicals wherein the radical remains of hydrophobic character.

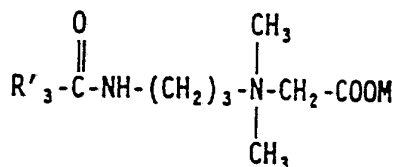
15 Examples of surfactant betaines of formula II wherein n is zero which are useful herein include the alkylbetaines such as cocodimethylcarboxymethylbetaine, lauryldimethylcarboxymethylbetaine, lauryl dimethyl-alpha-carboxyethylbetaine, cetyldimethylcarboxymethylbetaine, lauryl-bis-(2-hydroxyethyl)carboxymethylbetaine, stearyl-bis-(2-hydroxypropyl)carboxymethylbetaine, oleyldimethyl-gamma-carboxypropylbetaine, lauryl-bis-(2-hydroxypropyl)-alpha-carboxyethylbetaine, etc. The sulfobetaines may be represented by cocodimethylsulfopropylbetaine, stearyldimethylsulfopropylbetaine, lauryl-bis-(2-hydroxyethyl)sulfopropylbetaine, and the like.

20 Surfactant amido betaines and amidosulfo betaines useful in the present invention are exemplified by compounds of formula II wherein n is one but otherwise corresponding to the above examples. Examples of surfactant betaines of formula II wherein n is one which are useful herein include the amidocarboxybetaines, such as cocoamidodimethylcarboxymethylbetaine, laurylamidodi-

- 12 -

methylcarboxymethylbetaine, cetylamidodimethylcarboxymethylbetaine, laurylamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, cocoamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, etc. The amido sulfobetaines may be represented by cocoamidodimethylsulfopropylbetaine, stearylamidodimethylsulfopropylbetaine, laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

The preferred betaine in the present invention is a member selected from the group consisting of surfactant amidocarboxybetaines and amidosulfobetaines. More preferred betaines are the surfactant amidocarboxybetaines, particularly cocoamidodimethylcarboxymethylbetaines, sold by Goldschmidt Co. under the trade name Tegobetaine F, and by Hoechst-Celanese under the trade name Genagen CAB. These most preferred betaines have the formula:



wherein R'<sub>3</sub> is selected from C8 to C18 alkyl radicals and M is as defined above. In general, the preferred betaines hereof will have low levels of residual amide and sodium monochloroacetate.

#### Suspending Agent

Suspending agents useful in the present compositions include those which can exist in the compositions hereof in crystalline form. Other suspending agents useful for suspending nonvolatile, insoluble silicone fluids and/or particulate matter (such as particulate antidandruff agents) can also be used. Preferred crystalline suspending agents are acyl derivatives and amine oxides especially acyl derivatives, which can be solublized in the shampoo premix solution and then be recrystallized upon cooling. These materials will comprise long chain (e.g., C<sub>8</sub>-C<sub>22</sub> preferably C<sub>16</sub>-C<sub>22</sub>) aliphatic groups, i.e., long chain acyl derivative materials and long chain amine oxides, as well as mixtures of such materials. This suspending agent is present in the shampoo compositions hereof at a level of about 0.5% to about 5%, preferably about 1% to about 4%, most preferably about 1% to about 3%,

- 13 -

and in the shampoo premixes hereof at a level of from about 2% to about 15%, by weight, preferably from about 4% to about 12%, more preferably from about 5% to about 9%.

5 In addition to providing a network to support insoluble materials, the suspending agents hereof can also impart pearlescence to the compositions. Whereas it is preferred to include insoluble materials, such as silicone conditioning agents and particulate matter (e.g., antidandruff agents) into the compositions, it is also contemplated that this invention to  
10 compositions containing the suspending agents hereof without also containing insoluble materials that need suspending. Such compositions can still benefit by combining mildness and good cleaning and lathering in combination with improved aesthetic appearance, i.e., pearlescence.

15 Examples of suitable suspending agents are described in U.S. Patent 4,741,855, Grote and Russell, issued May 3, 1988, incorporated herein by reference. Suitable suspending agents for use herein include ethylene glycol esters of fatty acids preferably having from about 14 to about 22 carbon atoms, more preferably  
20 16-22 carbon atoms. More preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suspending agents found useful include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon  
25 atoms, more preferably about 16 to 18 carbon atoms. Preferred alkanol amides are stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain fatty acids (e.g., stearyl stearate, cetyl  
30 palmitate); glyceryl esters (e.g., glyceryl distearate) and long chain esters of long chain alkanol amides (e.g., stearamide diethanolamide distearate, stearamide monoethanolamide stearate). Ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids,  
35 in addition to the preferred materials listed above, may be used as suspending agents.

- 14 -

Suspending agents also include long chain amine oxides such as alkyl (C<sub>16</sub>-C<sub>22</sub>) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide. If the compositions contain an amine oxide or a long chain acyl derivative which is a surfactant, the suspending function could also be provided by such amine oxide or acyl derivative, provided at least a portion of them are present in crystalline form, and additional suspending agent may not be needed.

Other long chain acyl derivatives that can be used include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na and K salts), particularly N,N-di(hydrogenated) C<sub>16</sub>, C<sub>18</sub> and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

The suspending agent serves to assist in suspending the silicone material, particulate antidandruff agent, or other particulate matter in shampoo compositions hereof, and may give pearlescence to the product.

The suspending agent can be incorporated into the shampoo premixes hereof by solubilizing it into a solution containing the above described ingredients at a temperature above the melting point of the suspending agent in the surfactant premix. The suspending agent is then recrystallized, typically by cooling the solution to a temperature sufficient to induce crystallization. In order to facilitate this, it is preferred that the pH of the solution be below about 7. In a particularly preferred aspect of the invention hereof, the pH is reduced prior to providing the suspending agent in crystalline form to within about 2.0 pH, more preferably within about 1.5 pH, most preferably within about 1.0 pH of the average pK<sub>a</sub> of the carboxylate(s) of said amphoteric surfactant. In general, the pH is adjusted in the preferred embodiments, such as for cocoamphoacetate and cocoamphodiacetate, to levels of from below 7.0 to about 4.0, more preferably from about 4.5 to about 6.5. The pH of the solution, unadjusted, will normally be higher than that, and can be reduced by addition of



- 15 -

acids according to known techniques for pH adjustment. Suitable pH adjustors include hydrochloric acid, citric acid, sulfuric acid, etc., preferably hydrochloric acid and citric acid.

Water

5 The shampoo composition hereof will also comprise water. Generally, the composition will contain from about 50% to about 90% water, preferably about 60% to about 85% water, more preferably from about 65% to about 80%.

10 The shampoo premixes preferably used herein in making the shampoo composition will contain water at a level of from about 30% to about 70%, by weight, of the premix, preferably from about 45% to about 65%.

15 The shampoo premix compositions hereof are further characterized by a weight ratio of alkyl ethoxylate sulfate to the amphoteric surfactant of formula (I) of about 2:3 to about 3:1, preferably about 1:1 to about 5:2, by a weight ratio of suspending agent to total surfactant of about 1:1 to about 1:6, preferably about 2:3 to about 1:5, and by a weight ratio of suspending agent to water of about 1:2 to about 1:15, preferably about 1:4 to about 20 1:12, more preferably about 1:6 to about 1:12.

25 The shampoo and premixes hereof are substantially free of alkyl sulfate surfactants. It is recognized that there will generally be some alkyl sulfate present as a result of it being present in commercially available alkyl ethoxylated sulfate raw materials. For example, commercially available alkyl (3) ethoxylated sulfate typically contains about 20% by weight alkyl sulfate; commercially available alkyl (2) ethoxylated sulfate, about 25% to about 40% alkyl sulfate. For purposes hereof, to be 30 substantially free of alkyl sulfate the compositions hereof should have an alkyl sulfate:alkyl ethoxylated sulfate weight ratio of no more than about 0.35 (preferably no more than about 0.30, more preferably no more than about 0.25 for average ethoxylate levels of 2.5 and higher. For alkyl ethoxylated sulfate with an average ethoxylate level of less than 2.5, the ratio should be no more 35 than about 0.40, preferably no more than about 0.35, more prefer-

- 16 -

ably no more than about 0.30, most preferably no more than about 0.25. It is preferred that no additional amount of alkyl sulfate be added other than that which occurs inherently with the alkyl ethoxylated sulfate. It is also preferred that shampoo compositions made from the premixes hereof also be substantially free of alkyl sulfate, as defined above. The use of narrow range ethoxylates to lower the alkyl sulfate: alkyl ethoxylated sulfate weight ratio is preferred. "Narrow range ethoxylate" refers to alkyl ethoxylated sulfate surfactants that have been processed to reduce alkyl sulfates and optionally alkyl ethoxylated sulfates outside of the desired range of ethoxylation. The use of narrow range ethoxylates can be used to lower the alkyl sulfate:alkyl ethoxylated sulfate weight ratio to the preferred levels hereof, including to levels as low as about 0.2 or even about 0.1, and less.

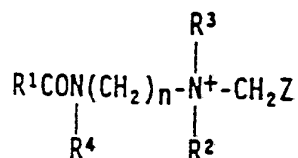
It is also preferred that no other ingredients that are harsh to the skin or cause undue eye irritation, such as amide foam boosters (e.g., cocomoethanolamide, CMEA), be added to the premix or shampoo compositions hereof.

#### Method of Making Shampoo Premix

The preferred shampoo premixes can be made according to a process comprising the steps of:

(i) preparing a solution comprising:

- (a) at least about 10%, by weight, of alkyl ethoxylated sulfate anionic surfactant;
- (b) at least about 6% by weight, of amphoteric surfactant of the formula;



wherein  $\text{R}^1$  is  $\text{C}_8$ - $\text{C}_{22}$  alkyl or alkenyl,  $\text{R}^2$  is hydrogen or  $\text{CH}_2\text{CO}_2\text{M}$ ,  $\text{R}^3$  is  $\text{CH}_2\text{CH}_2\text{OH}$  or  $\text{CH}_2\text{CHOCH}_2\text{CH}_2\text{COOM}$ ,  $\text{R}^4$  is hydrogen,  $\text{CH}_2\text{CH}_2\text{OH}$ , or  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOM}$ ,  $\text{Z}$  is  $\text{CO}_2\text{M}$  or  $\text{CH}_2\text{CO}_2\text{M}$ ,  $n$  is 2 or 3, and  $\text{M}$  is hydrogen or a cation as defined above; and

- 17 -

(c) from about 30% to about 70%, by weight, water;  
(ii) adding to the solution from about 2% to about 15%, by weight of the premix, of a suspending agent wherein said solution is heated and said suspending agent is provided in solubilized form; and cooling said composition to provide the solubilized suspending agent in crystalline form;  
5 wherein said premix has a weight ratio of (a):(b) of about 2:3 to about 3:1, a weight ratio of suspending agent to total surfactant present of from about 1:1 to about 1:6, and a weight ratio of  
10 suspending agent to water of about 1:2 to about 1:15, and said premix composition is prepared substantially free of alkyl sulfate anionic surfactant. Preferred ratios are the same as those listed above for the premix composition.

Typically, the solution will be heated to from about 60°C to  
15 about 85°C, preferably about 65°C to about 80°C, to solubilize suspending agent which has been added in crystalline form. Alternately, the solution can be first heated to a sufficient temperature for the suspending agent to remain or become solubi-  
20 lized, and then the suspending agent can be added to it in either solubilized or crystalline form. As used herein "solubilized" suspending agent, suspending agent in "solubilized form", and "solubilizing" the suspending agent shall include solubilization, emulsification, and/or melting of the suspending agent. The  
25 temperature required will vary according to the particular surfac- tants and levels chosen, as well as the level of and selection of particular suspending agent. These factors will also affect the temperature to which the premix must be cooled to induce crystal-  
30 lization. For example, higher levels of alkyl ethoxylated sulfate and lower levels of imidazolinium will generally require lower crystallization temperature. Typically, the composition will be cooled to between about 15°C and about 60°C, preferably between about 20°C and about 55°C, more preferably between about 20°C to about 45°C.

The pH of the solution (prior to recrystallizing the sus-  
35 pending agent) in preferred embodiments is below about 7, preferably from about 4 to about 7. The pH of the solution, unadjusted, will normally be higher than that, and can be reduced by addition

**SUBSTITUTE SHEET**

- 18 -

of acids according to know techniques for pH adjustment. Suitable  
pH adjustors include hydrochloric acid, citric acid, sulfuric  
acid, etc., preferably hydrochloric acid and citric acid. In a  
particularly preferred aspect of the invention hereof, the pH is  
5 reduced prior to providing the suspending agent in crystalline  
form to within about 2.0 pH, more preferably within about 1.5 pH,  
most preferably within about 1.0 pH of the average  $pK_a$  of the  
carboxylate(s) of said amphoteric surfactant. In general, the pH  
is adjusted in the preferred embodiments, such as for cocoampho-  
10 acetate and cocoamphodiacetate to levels of from below 7.0 to  
about 4.0, more preferably from about 4.5 to about 6.5.

The shampoo premix compositions hereof can be utilized  
directly for cleaning purposes. Preferably it is formulated into  
shampoo compositions, as described herein, said shampoos optional-  
15 ly containing additional surfactants of the type included in the  
premix, other surfactants, and other ingredients useful in the  
formulation of shampoos. The premixes hereof can also be used to  
make other shampoo formulations. Preferably, the ingredients  
added do not cause significant harshness to the skin. Preferred  
20 shampoo compositions have low or essentially zero levels (prefer-  
ably less than about 5%, more preferably less than about 3%, even  
more preferably less than 2%) of alkyl sulfates. The compositions  
hereof also preferably have low or essentially zero levels of  
other harsh-to-the-skin surfactants. Preferably said harsh  
25 ingredients present come from the natural distribution produced in  
the ethoxylation process) and are not added separately, although  
they may be so long as they are present within the above-defined  
limits. further, the shampoo compositions hereof and shampoo  
premixes preferably have low or essentially zero level of amide  
30 foam boosters (preferably less than about 0.5%, more preferably  
0%).

#### Additional Ingredients

In preferred formulations, the present invention provides a  
shampoo comprising shampoo premix and insoluble, nonionic silicone  
35 conditioning agent, a mild-to-the-skin foam booster, an anti-

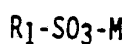
- 19 -

dandruff agent, or a combination thereof. Exemplary additional composition ingredients are described below.

Additional ingredients that can be used include other an-  
5 ionic, nonionic, and amphoteric surfactants, as well as zwitter-  
ionic and cationic surfactants and additional amounts of the  
surfactants described above.

#### Anionic Surfactants

A suitable class of anionic surfactants are the water-  
soluble, organic salts of the general formula:



10 wherein  $R_1$  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 12 to about 18, carbon  
atoms; and M is a cation. Important examples are the salts of an  
15 organic sulfuric acid reaction product of a hydrocarbon of the  
methane series, including iso-, neo-, and n-paraffins, having  
about 8 to about 24 carbon atoms, preferably about 12 to about 18  
carbon atoms and a sulfonating agent, e.g.,  $SO_3$ ,  $H_2SO_4$ , oleum,  
obtained according to known sulfonation methods, including bleach-  
20 ing and hydrolysis. Preferred are alkali metal and ammonium  
sulfonated C<sub>12-18</sub> paraffins.

Additional examples of anionic surfactants which come within  
the terms of the present invention are the reaction products of  
fatty acids esterified with isethionic acid and neutralized with  
25 sodium hydroxide where, for example, the fatty acids are derived  
from coconut oil; sodium or potassium salts of fatty acid amides  
of methyl tauride in which the fatty acids, for example, are  
derived from coconut oil. Other anionic synthetic surfactants of  
this variety are set forth in U.S. Patents 2,486,921; 2,486,922;  
30 and 2,396,278.

Still other anionic surfactants include the class designated  
as succinamates. This class includes such surface active agents  
as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-  
dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of  
35 sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic  
acid; dioctyl esters of sodium sulfosuccinic acid.

- 20 -

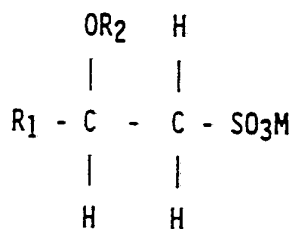
Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of  $\alpha$ -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO<sub>2</sub>, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO<sub>2</sub>, etc., when used in the gaseous form.

The  $\alpha$ -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific  $\alpha$ -olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880, Pflaumer and Kessler, issued July 25, 1967, incorporated herein by reference.

Another class of anionic surfactants are the  $\beta$ -alkyloxy alkane sulfonates. These compounds have the following formula:



- 21 -

where R<sub>1</sub> is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R<sub>2</sub> is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

5 Specific examples of  $\beta$ -alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein include: potassium- $\beta$ -methoxydecanesulfonate, sodium 2-methoxy-tridecanesulfonate, potassium 2-ethoxytetradecylsulfonate, sodium 2-isopropoxyhexadecylsulfonate, lithium 2-t-butoxytetradecyl-sulfonate, sodium  $\beta$ -methoxyoctadecylsulfonate, and ammonium  $\beta$ -n-propoxydodecyl-sulfonate.

10 Many additional synthetic anionic surfactants are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference. Soaps, of course, also fall within the scope of anionic detergent surfactants that can be used.

#### 20 Nonionic Surfactants

Nonionic surfactants in addition to the PEG glyceryl fatty esters can be used as detergent surfactants. They are preferably used in combination with an anionic, amphoteric, or zwitterionic surfactant, or mixtures thereof. Nonionic surfactants include those broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of classes of nonionic surfactants are:

30 1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms, preferably from about 6 to about 12, in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles

35

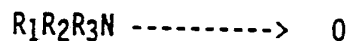
- 22 -

of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of about 2,500 to about 3,000, are satisfactory.

3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

4. Long chain tertiary amine oxides corresponding to the following general formula:



wherein  $R_1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R_2$  and  $R_3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyl dimethylamine



oxide, 3-dodecoxy-2-hydroxypropyl di(3-hydroxypropyl) amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are:

10 dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide. 3,6,9,-trioxaoctacyldimethylphosphine oxide, cetyldimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyl di(2-hydroxyethyl) phosphine oxide, stearyldimethylphosphine oxide, cetylethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldi(hydroxymethyl)phosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9,-trioxaoctacyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

35

- 24 -

7. Other nonionic surfactants can also be used in the compositions hereof. Polysorbates, e.g., sucrose esters of fatty acids. Such materials are described in U.S. Patent 3,480,616, e.g., sucrose cocoate (a mixture of sucrose esters of a coconut acid, consisting primarily of monoesters, and sold under the tradenames GRILLOTEN LSE 87K from RITA, and CRODESTA SL-40 from Croda).

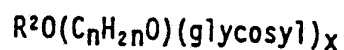
Alkyl polysaccharide nonionic surfactants are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group. The polysaccharide can contain from about 1.0 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6-positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkylene moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-

- 25 -

tri-, tetra-, penta-, and hexaglycosides, galactosides, lacto-  
sides, glucoses, fructosides, fructoses and/or galactoses.  
Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and  
pentaglycosides and tallow alkyl, tetra-, penta-, and hexaglyco-  
sides.

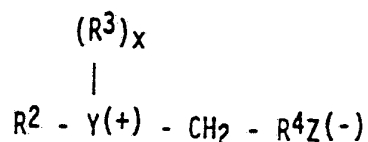
The preferred alkyl polysaccharides are alkylpolyglycosides  
of the formula



wherein  $R^2$  is selected from the group consisting of alkyl, alkyl-  
phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in  
which alkyl groups contain from about 10 to about 18, preferably  
from about 12 to about 14, carbon atoms;  $n$  is 2 or 3, preferably  
2;  $t$  is from 0 to about 10, preferably 0; and  $x$  is from 1.3 to  
about 10, preferably from 1.3 to about 3, most preferably from  
about 1.3 to about 2.7. The glycosyl is preferably derived from  
glucose. To prepare these compounds, the alcohol or alkylpoly-  
ethoxy alcohol is formed first and then reacted with glucose, or a  
source of glucose, to form the glucoside (attachment at the  
1-position). The additional glycosyl units can then be attached  
between their 1-position and the preceding glycosyl units 2-, 3-,  
4- and/or 6-position, preferably predominantly the 2-position.

#### Zwitterionic and Amphoteric Surfactants

Zwitterionic surfactants are exemplified by those which can  
be broadly described as derivatives of aliphatic quaternary  
ammonium, phosphonium, and sulfonium compounds, in which the  
aliphatic radicals can be straight or branched chain, and wherein  
one of the aliphatic substituents contains from about 8 to about  
18 carbon atoms and one contains an anionic group, e.g., carboxy,  
sulfonate, sulfate, phosphate, or phosphonate. A general formula  
for these compounds is:



wherein  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of  
from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene

- 26 -

oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R<sup>3</sup> is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R<sup>4</sup> is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of such surfactants include:

- 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradecoxylphosphonio]-2-hydroxypropane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

Examples of amphoteric 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 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylamino-

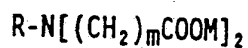
propane sulfonate, sodium lauryl sarcosinate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

Other amphoteric surfactants include sultaines and amidosultaines. Sultaines and amidosultaines can advantageously be utilized as foam enhancing surfactants that are mild to the eye in partial replacement of anionic surfactants. Sultaines, including amidosultaines, include for example, cocodimethylpropylsultaine, stearyldimethylpropylsultaine, lauryl-bis-(2-hydroxyethyl) propylsultaine and the like; and the amidosultaines such as cocoamidodimethylpropylsultaine, stearylamidodimethylpropylsultaine, laurylamidobis-(2-hydroxyethyl) propylsultaine, and the like. Preferred are amidohydroxysultaines such as the C<sub>12</sub>-C<sub>18</sub> hydrocarbyl amidopropyl hydroxysultaines, especially C<sub>12</sub>-C<sub>14</sub> hydrocarbyl amido propyl hydroxysultaines, e.g., laurylamidopropyl hydroxysultaine and cocamidopropyl hydroxysultaine. Other sultaines are disclosed in U.S. Patent 3,950,417, issued April 13, 1976, incorporated herein by reference.

Another specific class of amphoteric surfactants is defined by the aminoalkanoates of the formula:



the iminodialkanoates of the formula:



and mixtures thereof; wherein n and m are numbers from 1 to 4, R is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl, and M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium.

Examples of amphoteric surfactants falling within the aminoalkanoate formula include n-alkylamino-propionates and

- 28 -

n-alkyliminodipropionates. Such materials are sold under the tradename DERIPHAT by Henkel and MIRATAINE by Miranol, Inc. Specific examples include N-lauryl-beta-amino propionic acid or salts thereof, and N-lauryl-beta-imino-dipropionic acid (DERIPHAT 160C) or salts thereof, and mixtures thereof.

Conditioning Agent

A preferred optional component hereof is a conditioning agent suitable for conditioning hair or skin. Especially preferred are silicone conditioning agents, particularly nonvolatile, insoluble silicone conditioning agents. The shampoo compositions, in particular, will preferably comprise from about 0.01% to about 10%, by weight, of such silicone conditioning agent, more preferably from about 0.01% to about 5%, even more preferably from about 0.05% to about 3%, and most preferably from about 0.1% to about 2.5%. The silicone conditioning agent comprises a nonvolatile, insoluble silicone fluid. The silicone conditioning agent for use herein in shampoo compositions will preferably have average viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000 centistokes, even more preferably from about 100,000 to about 1,500,000 centistokes. Lower viscosity nonvolatile silicone conditioning agents, however, can also be used. Viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

As used hereinafter, the term "insoluble" in reference to the silicone conditioning agent shall mean that the silicone material is not soluble in water. The term "nonvolatile" in reference to the silicone conditioning agent as used herein shall be interpreted according to the meaning well understood to those skilled in the art, i.e., the silicone fluid exhibits very low or no significant vapor pressure at ambient conditions. The term "silicone fluid" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25°C. Generally, the viscosity of the fluid will be between about 5 and 1,000,000 centistokes at 25°C, preferably between about 10 and about 100,000

- 29 -

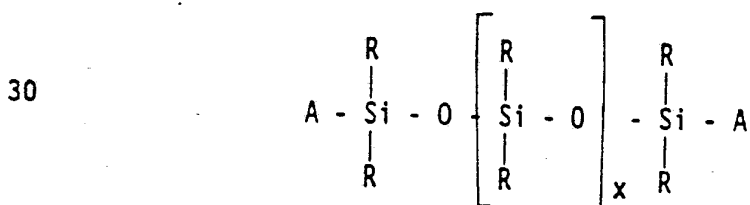
centistokes. The silicone conditioning agent hereof can also comprise silicone gums, which are also nonvolatile and insoluble, Silicone gums are later described. The term "silicone", as used herein, shall be synonymous with the term "polysiloxane".

5 Suitable nonvolatile silicone fluids for use in hair conditioning agents include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymer and mixtures thereof. However, other silicone fluids having hair conditioning properties may be used. The nonvolatile polyalkyl siloxane fluids  
10 that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company as a Viscasil series and from Dow Corning as the Dow Corning 200 series. Preferably, the viscosity ranges from about 10 centistokes to about 100,000 centistokes at 25°C.

15 The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

20 The polyether siloxane copolymer that may be used includes, for example, a polypropylene oxide modified dimethylpolysiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide level must be sufficiently low to  
25 prevent solubility in water and the composition hereof.

Silicone fluids hereof also include polyalkyl or polyaryl siloxanes with the following structure:



wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000 may be used. "A" represents groups which block the  
35 ends of the silicone chains.

- 30 -

The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition, are chemically stable under normal use and storage conditions, and are capable of being deposited on and of conditioning hair.

Suitable A groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicone atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred.

References disclosing suitable silicone fluids include U.S. Patent 2,826,551, Geen; U.S. Patent 3,964,500, Drakoff, issued June 22, 1976; U.S. Patent 4,364,837, Pader; and British Patent 849,433, Woolston. All of these patents are incorporated herein by reference. Also incorporated herein by reference is *Silicon Compounds* distributed by Petrarch Systems, Inc., 1984. This reference provides an extensive (though not exclusive) listing of suitable silicone fluids.

Another silicone material that can be especially useful in the silicone conditioning agents is insoluble silicone gum. The term "silicone gum", as used herein, means polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described by Petrarch and others including U.S. Patent 4,152,416, Spitzer et al., issued May 1, 1979, and Noll, Walter, *Chemistry and Technology of Silicones*, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference. The "silicone gums" will



- 31 -

typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

5 Preferably the silicone hair conditioning agent comprises a mixture of a polydimethylsiloxane gum, having a viscosity, at 25°C, greater than about 1,000,000 centistokes and polydimethylsiloxane fluid having a viscosity, at 25°C, of from about 10 centipoise to about 100,000 centistokes, wherein the ratio of gum to fluid is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40.

Cationic silicone fluids and gums may be used, although nonionic silicone fluids and gums are preferred.

15 Antidandruff Agent

The shampoo compositions also contain one or more antidandruff agents. Soluble antidandruff agents as well as particulate antidandruff agents can be used. Especially preferred are particulate antidandruff agents, particularly pyridinethione salts and selenium sulfide.

20 Selenium sulfide is a staple item of commerce. Selenium sulfide is generally regarded as a compound having one mole of selenium and two moles of sulfur. However, it may take the form of a cyclic structure,  $Se_xS_y$ , wherein  $x + y = 8$ .

25 U.S. Patent 2,694,668, Baldwin et al., issued November 16, 1954; U.S. Patent 3,152,046, Kapral, issued October 6, 1984; U.S. Patent 4,089,945, Brinkman, issued May 16, 1978; and U.S. Patent 4,885,107, Wetzel, issued December 12, 1989, all incorporated herein by reference, disclose selenium disulfide as an active ingredient in antidandruff shampoo compositions.

30 Selenium sulfide as provided by suppliers can be used in the present compositions provided the particle size of the selenium sulfide particles, on an average, is less than about  $15\mu$ , preferably less than about  $10\mu$ . These measurements are made using a forward laser light scattering device (e.g., a Malvern 3600 instrument).

- 32 -

If used, selenium sulfide is typically present in the shampoo compositions of this invention at a level of from about 0.1% to about 5.0%, preferably from about .6% to about 2.5%.

Preferred pyridinethione antidandruff agents are  
5 1-hydroxy-2-pyridinethione salts. These types of antidandruff agents are well known in the art. Particularly preferred are those 1-hydroxy-2-pyridinethione salts in platelet particle form, wherein the particles have an average size of from about 1 micron to about 20 microns, preferably from about 2 microns to about 8  
10 microns. The active is generally used at a level of from about 0.1% to about 4%, preferably about 0.5% to about 2%, of the shampoo composition. 1-hydroxy-2-pyridinethione salts are disclosed for use in antidandruff shampoos in U.S. Patent 2,809,971, Bernstein, issued October 15, 1957; U.S. Patent 3,236,733, Karsten et al., issued February 22, 1966; U.S. Patent 3,753,196, Parran,  
15 issued August 21, 1973; U.S. Patent 3,761,418, Parran, issued September 25, 1973; U.S. Patent 4,345,080, Bolich, issued August 17, 1982; U.S. Patent 4,323,683, Bolich et al., issued April 6, 1982; U.S. Patent 4,379,753, Bolich, issued April 12, 1983; and  
20 U.S. Patent 4,470,982, Winkler, issued September 11, 1984; all incorporated herein by reference. The pyridinethione salts preferred herein can generally be defined as water-insoluble salts of 1-hydroxy-2-pyridinethione.

Preferred salts are formed from metals such as zinc, tin,  
25 cadmium, magnesium, aluminium and zirconium. The most preferred metal herein is zinc which forms 2-zinc pyrithione or ZPT. Other cations such as sodium are also suitable.

In addition the shampoo composition disclosed herein may include other known antidandruff actives. Such antidandruff  
30 actives can include, for example, pyridone salts, coal tar, etc.

Hydroxypyridone salts are disclosed in *Cosmetics and Drug Preservation, Principles and Practice*, p 742 (edited by J. Kabura, 1984), incorporated herein by reference. Hydroxypyridone salts used herein include those generally described as 1-hydroxy-4-  
35 methyl-(1H)-pyridones having an aliphatic or aromatic moiety (R)

- 33 -

at the 6 position thereof, wherein R has a factor of at least 1:3, preferably from 2 to 6, more preferably from 3 to 5.5. The factor is a measure of the lipophilicity/ hydrophilicity of the substituent and is defined in detail in the paper by W. Dittmar, E. Druckrey and H. Urbach, *J. Med. Chem.* 17(7), 753-6 (1974) and references cited therein; all of which are incorporated herein by reference.

In structural terms, preferred R substituents are selected from linear and branched C<sub>3</sub>-C<sub>11</sub>, preferably C<sub>6</sub>-C<sub>11</sub>, alkyl and alkenyl groups, C<sub>5</sub>-C<sub>8</sub> cycloalkyl groups, and C<sub>5</sub>-C<sub>8</sub> aryl groups. The cyclic moieties, discussed above, can also be substituted with one or more alkyl or alkenyl groups up to C<sub>4</sub>. The R groups can further be substituted with halogen atoms. Of the above, preferred R moieties are cyclohexyl and 2,4,4-trimethyl pentyl, the latter being highly preferred.

The above mentioned compounds can be used both in the free form and as salts, for example, salts with organic bases or inorganic cations. Low molecular weight alkanolamines are especially preferred organic bases. The preferred hydroxypyridone salt for use herein is monoethanolamine salt known as piroctone olamine or Octopirox; see *Cosmetic and Drug Preservation, supra*.

Piroctone olamine is described for use in deodorant compositions in Japanese Patent Application Sho 57-104,313, published Decembr 23, 1983; Japanese Patent Application Sho 58-127,893, published February 5, 1985 (both to Lion) and U.S. Patent Application Serial No. 314,627, Melanson and Sturm, filed February 23, 1989. Japanese Patent Application Sho 57-080,644 (Lion), published November 18, 1983, discloses the use of a broad group of hydroxypyridone compounds for dandruff control. All above cited references are incorporated herein by reference.

#### Optional Components

The compositions herein can contain a variety of non-essential optional components. Such optional ingredients include, for example, preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; cationic conditioning

- 34 -

agents, including both cationic conditioning surfactant and cationic conditioning polymers; fatty alcohols; block polymers of ethylene oxide and propylene oxide such as Pluronic F88 offered by BASF Wyandotte; sodium chloride; sodium sulfate; ammonium xylene sulfonate; propylene glycol; polyvinyl alcohol; ethyl alcohol; foam boosters such as Polyquaternium-10 (an industry term designated by The Cosmetic, Toiletry and Fragrance Association (CTFA) for the polymeric quaternary ammonium salt of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide), commercially available from Union Carbide Corp. (Danbury, Connecticut, USA) under their UCARE POLYMER JR series of materials, e.g., UCARE POLYMER JR-30M, JR-125 and JR-400, such foam boosters being a preferred ingredient for use in the shampoos herein; additional pH adjusting agents for the final shampoo composition such as citric acid, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate, etc.; perfumes; dyes; and sequestering agents such as disodium ethylenediamine tetraacetate. These optional ingredients are typically used at levels of from about 0.01% to about 10% of the composition. This list of optional ingredients is not meant to be inclusive, and other optional components can be utilized.

Pediculicides can also be included in the compositions hereof to provide control of lice infestations. Suitable pediculicides are well known in the art and include, for example, pyrethrins such as those disclosed in U.S. Patent 4,668,666, Allan, incorporated herein by reference.

#### Optional Thickeners and Suspending Agents

Another type of suspending agent that can be used is carboxyvinyl polymer. Preferred polymers are copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, Brown, issued July 2, 1957, incorporated herein by reference. These polymers are provided by B. F. Goodrich Company as, for example, Carbopol 934, 940, 941, and 956.

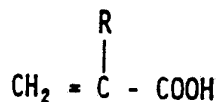
A carboxyvinyl polymer is an interpolymer of a monomeric mixture comprising a monomeric olefinically unsaturated carboxylic acid, and from about 0.1% to about 10% by weight of the total

- 35 -

monomers of a polyether of a polyhydric alcohol, which polyhydric alcohol contains at least four carbon atoms to which are attached at least three hydroxyl groups, the polyether containing more than one alkenyl group per molecule. Other monoolefinic monomeric materials may be present in the monomeric mixture if desired, even in predominant proportion. Carboxyvinyl polymers are substantially insoluble in liquid, volatile organic hydrocarbons and are dimensionally stable on exposure to air.

Preferred polyhydric alcohols used to produce carboxyvinyl polymers include polyols selected from the class consisting of oligosaccharides, reduced derivatives thereof in which the carbonyl group is converted to an alcohol group, and pentaerythritol; more preferred are oligosaccharides, most preferred is sucrose. It is preferred that the hydroxyl groups of the polyol which are modified be etherified with allyl groups, the polyol having at least two allyl ether groups per polyol molecule. When the polyol is sucrose, it is preferred that the sucrose have at least about five allyl ether groups per sucrose molecule. It is preferred that the polyether of the polyol comprise from about 0.1% to about 4% of the total monomers, more preferably from about 0.2% to about 2.5%.

Preferred monomeric olefinically unsaturated carboxylic acids for use in producing carboxyvinyl polymers used herein include monomeric, polymerizable, alpha-beta monoolefinically unsaturated lower aliphatic carboxylic acids; more preferred are monomeric monoolefinic acrylic acids of the structure



where R is a substituent selected from the group consisting of hydrogen and lower alkyl groups; most preferred is acrylic acid.

Preferred carboxyvinyl polymers used in formulations of the present invention have a molecular weight of at least about 750,000; more preferred are carboxyvinyl polymers having a molecular weight of at least about 1,250,000; most preferred are carboxyvinyl polymers having a molecular weight of at least about 3,000,000.

- 36 -

Other materials can also be used as suspension agents, including those that can impart a gel-like viscosity to the composition, such as water soluble or colloiddally water soluble polymers like cellulose ethers (e.g., hydroxyethyl cellulose), guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other thickeners, viscosity modifiers, gelling agents, etc. Mixtures of these materials can also be used.

Such optional suspending agent thickeners, and viscosity modifiers, etc., in general, are used at a level of from about 0.1% to about 10%, most commonly from about 0.3% to about 5.0% by weight of the total composition.

Another type of suspending agent that can be used is xanthan gum. Shampoo compositions utilizing xanthan gum as a suspending agent for the silicone hair conditioning component are described in U.S. Patent 4,788,006, Bolich and Williams, issued November 29, 1988, incorporated herein by reference. Xanthan gum is bio-synthetic gum material that is commercially available. It is a heteropolysaccharide with a molecular weight of greater than 1 million. It is believed to contain D-glucose, D-mannose and D-glucuronate in the molar ratio of 2.8:2.0:2.0. The polysaccharide is partially acetylated with 4.7% acetyl. This information and other is found in Whistler, Roy L. Editor *Industrial Gums - Polysaccharides and Their Derivatives* New York: Academic Press, 1973. Kelco, a Division of Merck & Co., Inc. offers xanthan gum as Keltrol®. The gum, when used as the silicone hair conditioning component suspending agent, will typically be present in pourable, liquid formulations at a level of from about 0.3% to about 3%, preferably from about 0.4% to about 1.2%, in the compositions of the present invention.

The pH of the compositions for direct use for cleaning applications is not generally critical and may be in the range of from 2 to about 10, preferably from about 3 to about 9, more preferably from about 4 to about 8, most preferably from about 6 to about 8.

- 37 -

METHOD OF USE

The present compositions are used in a conventional manner for cleaning hair. An effective amount of the composition for cleaning hair, typically, from about 1 g to about 20 g of the composition, is applied to hair that has preferably been wetted, generally with water, and then rinsed out. Application to the hair typically includes working the composition through the hair such that most or all of the hair is contacted with the composition.

EXAMPLES

The following Examples further describe and demonstrate the preferred 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 its spirit and scope.

EXAMPLES I-XX

The following examples exemplify shampoo compositions of the present invention.

Table I

<u>Component</u> (ppm or %, by weight, of composition)	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>
Sodium Laureth-3 Sulfate (%) <sup>7</sup>	10.00	14.00	13.60	13.60	13.00
Cocoamphodiacetate (%) <sup>3</sup>	3.50	3.50	3.40	3.40	3.50
CAPB <sup>5</sup>	2.00	2.00	3.40	3.40	3.50
LIDP <sup>6</sup>	3.50	3.50	-	-	-
Polyquaternium 10 (%) <sup>1</sup>	0.05	0.05	0.05	0.05	0.05
Ethylene Glycol Distearate (%)	2.00	2.00	2.00	2.00	2.00
Dimethicone (%) <sup>2</sup>	1.00	1.00	1.00	1.40	1.00
Perfume Solution (%)	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin (%)	0.20	0.20	0.20	0.20	0.20
Citric Acid (%)	-	0.34	0.34	0.34	0.34
Cetyl Alcohol (%)	0.12	0.06	0.06	0.10	0.06

- 38 -

	Stearyl Alcohol (%)	0.06	0.12	0.12	0.18	0.12
	Tricetylmethylammonium chloride <sup>8</sup> (%)	-	0.57	0.57	0.57	-
	Zinc Pyridinethione (%)	-	-	-	-	1.00
5	Color Solution (ppm)	4	4	4	4	4
	Water	- - - - - q. s. to 100% - - - - -				

Table II

<u>Component</u>	<u>VI</u>	<u>VII</u>	<u>VIII</u>	<u>IX</u>	<u>X</u>
10 (ppm or %, by weight, of composition)					
Sodium Laureth-3 Sulfate (%) <sup>7</sup>	10.00	13.00	14.00	13.00	13.00
Cocoamphodiacetate (%) <sup>3</sup>	3.50	4.50	4.50	3.00	3.00
CAPB <sup>5</sup>	3.50	3.00	2.00	5.00	5.00
15 LIDP <sup>6</sup>	-	-	-	-	-
Polyquaternium 10 (%) <sup>1</sup>	0.10	-	0.09	0.03	-
Ethylene Glycol Distearate (%)	1.00	3.00	1.00	3.00	1.50
Dimethicone (%) <sup>2</sup>	0.50	2.00	0.50	1.00	-
Perfume Solution (%)	0.60	0.60	0.60	0.60	0.50
20 DMDM Hydantoin (%)	0.20	0.20	0.20	0.20	0.20
Citric Acid (%)	0.30	0.45	0.45	0.28	0.28
Cetyl Alcohol (%)	0.03	0.12	-	0.16	-
Stearyl Alcohol (%)	0.06	0.24	-	0.12	-
Tricetylmethylammonium chloride <sup>8</sup> (%)	-	0.50	0.57	-	-
Zinc Pyridinethione (%)	-	-	1.00	2.00	-
Color Solution (ppm)	20	20	20	20	20
Water	- - - - - q. s. to 100% - - - - -				

Table III

<u>Component</u>	<u>XI</u>	<u>XII</u>	<u>XIII</u>	<u>XIV</u>	<u>XV</u>
30 (ppm or %, by weight, of composition)					
Sodium Laureth-3 Sulfate (%) <sup>7</sup>	10.00	14.00	13.60	13.60	13.00
Cocoamphoacetate (%) <sup>4</sup>	3.50	3.50	3.40	3.40	3.50
35 CAPB <sup>5</sup>	2.00	2.00	3.40	3.40	3.50



	LIDP <sup>6</sup>	3.50	3.50	-	-	-
	Polyquaternium 10 (%) <sup>1</sup>	0.05	0.05	0.05	0.05	0.05
	Ethylene Glycol Distearate (%)	2.00	2.00	2.00	2.00	2.00
	Dimethicone (%) <sup>2</sup>	1.00	1.00	1.00	1.40	1.00
5	Perfume Solution (%)	0.70	0.70	0.70	0.70	0.70
	DMDM Hydantoin (%)	0.20	0.20	0.20	0.20	0.20
	Citric Acid (%)	-	0.25	0.25	0.25	0.25
	Cetyl Alcohol (%)	0.12	0.06	0.06	0.10	0.06
	Stearyl Alcohol (%)	0.06	0.12	0.12	0.18	0.12
10	Tricetylmethylammonium chloride <sup>8</sup> (%)	-	0.57	0.57	0.57	-
	Zinc Pyridinethione (%)	-	-	-	-	-
	Color Solution (ppm)	4	4	4	4	4
	Water	- - - - - q. s. to 100% - - - - -				

15

Table IV

<u>Component</u> (ppm or %, by weight, of composition)	<u>XVI</u>	<u>XVII</u>	<u>XVIII</u>	<u>XIX</u>	<u>XX</u>
20 Sodium Laureth-3 Sulfate (%) <sup>7</sup>	10.00	13.00	14.00	13.00	13.00
Cocoamphodiacetate (%) <sup>4</sup>	3.50	4.50	4.50	3.00	3.00
CAPB <sup>5</sup>	3.50	3.00	2.00	5.00	5.00
LIDP <sup>6</sup>	-	-	-	-	-
Polyquaternium 10 (%) <sup>1</sup>	0.10	-	0.09	0.03	-
25 Ethylene Glycol Distearate (%)	1.00	3.00	1.00	3.00	1.50
Dimethicone (%) <sup>2</sup>	0.50	2.00	0.50	1.00	-
Perfume Solution (%)	0.60	0.60	0.60	0.60	0.50
DMDM Hydantoin (%)	0.20	0.20	0.20	0.20	0.20
Citric Acid (%)	0.20	0.30	0.30	0.20	0.20
30 Cetyl Alcohol (%)	0.03	0.12	-	0.16	-
Stearyl Alcohol (%)	0.06	0.24	-	0.12	-
Tricetylmethylammonium chloride <sup>8</sup> (%)	-	0.50	0.57	-	-
Zinc Pyridinethione (%)	-	-	1.00	2.00	-

35

- 40 -

Color Solution (ppm)	20	20	20	20	20
Water	- - - - - q. s. to 100% - - - - -				

- 1 UCARE Polymer JR-30M, commercially available from Union Carbide Corporation.
- 5 2 A 50/50 blend of SE-76 silicone gum available from GE Silicones and a silicone fluid having a viscosity of about 350 centistokes.
- 3 Available under the tradename MIRANOL C-2M from Miranol, Inc. in a 38% active solution.
- 10 4 Available under the tradename MIRANOL CM CONC from Miranol, Inc. in a 37% active solution.
- 5 Available under the tradename GENAGEN CAB from Hoechst Celanese as a 30% active solution.
- 6 Available under the tradename DERIPHAT from Henkel Corp. as a 30% active solution.
- 15 7 Available commercially as a 28.5% active solution.
- 8 "TCMAC" Available commercially from Akzo-Chemie as ARQUAD-316 as a 90% suspension.

20 The compositions are prepared as follows. A silicone premix is first prepared by adding a small portion (e.g., about 0.2% by weight of the finished product) of the sodium laureth-3 sulfate to the premix tank and heating to 71°C. The cetyl and stearyl alcohols, as applicable, are added. The dimethicone is then added and mixed until an emulsion is formed.

25 For Examples I-IV and XI-XIV, about one-third of the sodium laureth-3 sulfate, the cocoamphodiacetate and/or cocoamphoacetate, the CAPB and TCMAC, as applicable, are placed in a tank. The mixture (the "main premix") is agitated and heated to 71°C. The ethylene glycol distearate is then added and allowed to melt. The  
 30 citric acid in the form of a 50% active solution is added to adjust pH. The main mix is passed through a heat exchanger where it is cooled to 32°C and collected in a finishing tank. As a result of this cooling step, the ethylene glycol distearate crystallizes to form a crystalline network in the product. The  
 35 Polyquaternium 10, if applicable, is then added as a solid or

- 41 -

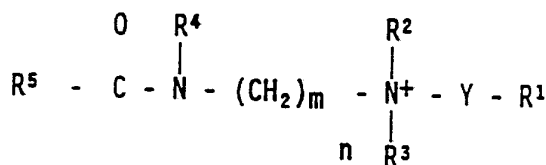
predissolved in water to the main premix. For Examples V-X and XV-XX, the CAPB is mixed into the main premix after the ethylene glycol distearate has been crystallized instead of being added at the above-indicated earlier stage. The silicone premix is collected in the same finishing tank after being cooled to about 30°C, where the main premix and the silicone premix are mixed until homogeneous. Finally, the remainder of the ingredients are added and mixed into the shampoo composition. The final pH is adjusted as desired by the addition of citric acid and/or NaOH. The final viscosity is adjusted as desired by the addition of ammonium xylene sulfonate and/or NaCl.

The compositions of the Examples can provide excellent in-use hair cleaning, lather, mildness, conditioning and dandruff control (where applicable), and pearlescence.

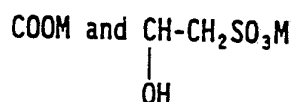
-42-

CLAIMS

1. A shampoo composition characterized in that it comprises:
- (a) from 5% to 15%, by weight, alkyl ethoxylated sulfate anionic surfactant ;
- (b) from 1% to 10% of a betaine surfactant of the formula:



wherein  $R_1$  is a member selected from the group consisting of



$R_2$  is lower alkyl or hydroxyalkyl;

$R_3$  is lower alkyl or hydroxyalkyl;

$R_4$  is a member selected from the group consisting of hydrogen and lower alkyl;

$R_5$  is higher alkyl or alkenyl;

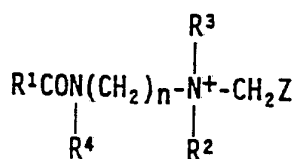
Y is lower alkyl, preferably methyl;

m is an integer from 2 to 7;

n is the integer 1 or 0;

M is hydrogen or a cation;

- (c) 2% to 10%, by weight, of an amphoteric surfactant having the formula

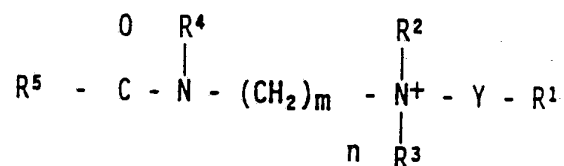


wherein  $R^1$  is  $C_8-C_{22}$  alkyl or alkenyl,  $R^2$  is hydrogen or  $CH_2CO_2M$ ,  $R^3$  is  $CH_2CH_2OH$  or  $CH_2CHOCH_2CH_2COOM$ ,  $R^4$  is hydrogen,  $CH_2CH_2OH$ , or  $CH_2CH_2OCH_2CH_2COOM$ , Z is  $CO_2M$  or  $CH_2CO_2M$ , n is 2 or 3, and M is hydrogen or a cation; and

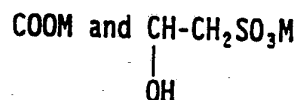
- (d) from 0.5% to 5%, by weight, of a crystalline suspending agent; and

(e) from 60% to 85% water;  
 wherein said shampoo composition is substantially free of alkyl sulfate anionic surfactant, and the weight ratio of (a):(b)+(c) is 1:1 to 4:1, and the weight ratio of (d):total surfactant is 1:4 to 1:25.

2. A shampoo composition characterized in that it comprises:
- (a) from 6% to 17%, by weight, alkyl ethoxylated sulfate anionic surfactant ;
  - (b) from 2% to 8% of a betaine surfactant of the formula:



wherein R<sub>1</sub> is a member selected from the group consisting of



R<sub>2</sub> is lower alkyl or hydroxyalkyl;

R<sub>3</sub> is lower alkyl or hydroxyalkyl;

R<sub>4</sub> is a member selected from the group consisting of hydrogen and lower alkyl;

R<sub>5</sub> is higher alkyl or alkenyl;

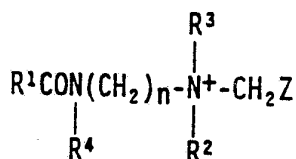
Y is lower alkyl, preferably methyl;

m is an integer from 2 to 7;

n is the integer 1 or 0;

M is hydrogen or a cation;

- (c) 2% to 8%, by weight, of an amphoteric surfactant having the formula



wherein  $R^1$  is  $C_8$ - $C_{22}$  alkyl or alkenyl,  $R^2$  is hydrogen or  $CH_2CO_2M$ ,  $R^3$  is  $CH_2CH_2OH$  or  $CH_2CHOCH_2CH_2COOM$ ,  $R^4$  is hydrogen,  $CH_2CH_2OH$ , or  $CH_2CH_2OCH_2CH_2COOM$ ,  $Z$  is  $CO_2M$  or  $CH_2CO_2M$ ,  $n$  is 2 or 3, and  $M$  is hydrogen or a cation; and

(d) from 1% to 4%, by weight, of a crystalline suspending agent; and

(e) from 65% to 80% water;

wherein said shampoo composition is substantially free of alkyl sulfate anionic surfactant, and the weight ratio of (a):(b)+(c) is 4:3 to 3:1, and the weight ratio of (d):total surfactant is 1:6 to 1:18.

3. A shampoo composition as in Claim 2 comprising:

(a) from 7% to 15%, by weight, of said alkyl ethoxylated sulfate anionic surfactant ;

(b) from 2.5% to 6% of said betaine surfactant;

(c) from 2.5% to 6%, by weight, of said amphoteric imidazolinium surfactant;

(d) from 1% to 3%, by weight, of said suspending agent; and

(e) from 65% to 80% water;

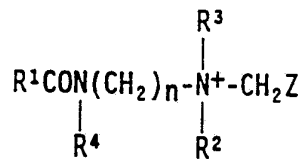
and said ratio of (a):(b)+(c) is from 8:5 to 7:3 and said ratio of (d):total surfactant is from 1:8 to 1:13.

4. A mild shampoo composition, as in Claim 1, 2, or 3, wherein said shampoo composition comprises a shampoo premix composition comprising:

(a) at least 10%, by weight, of alkyl ethoxylated sulfate anionic surfactant, preferably from 10% to 25%;

(b) at least 6%, by weight, of an amphoteric surfactant, preferably from 8% to 18% of the formula:

-45-



wherein R<sup>1</sup> is C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl, R<sup>2</sup> is hydrogen or CH<sub>2</sub>CO<sub>2</sub>M, R<sup>3</sup> is CH<sub>2</sub>CH<sub>2</sub>OH or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, R<sup>4</sup> is hydrogen, CH<sub>2</sub>CH<sub>2</sub>OH, or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, Z is CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, n is 2 or 3, and M is hydrogen or a cation;

(c) from 2% to 15%, by weight, of a recrystallized suspending agent preferably from 4% to 12%; and

(d) from 30% to 70% water, preferably from 45% to 65%;

wherein said premix has a weight ratio of (a):(b) of 2:3 to 3:1, preferably from 1:1 to 5:2, a weight ratio of (c) to total surfactant present of from 1:1 to 1:6, preferably from 2:3 to 1:3 and the weight ratio of (c):(d) of 1:2 to 1:15, preferably from 1:4 to 1:12 and said premix composition is substantially free of alkyl sulfate anionic surfactant.

5. A shampoo composition according to Claim 4, wherein said suspending agent of said premix is ethylene glycol distearate.

6. A shampoo composition according to Claim 1, 2, 3, 4, or 5, wherein said amphoteric surfactant is a monocarboxylate or a dicarboxylate, or a mixture thereof.

7. A shampoo composition as in Claim 6 wherein said amphoteric surfactant comprises cocoamphocarboxyglycinate, cocoamphoacetate, cocoamphocarboxypropionate, or cocoamphocarboxypropionic acid, or a mixture thereof, and for said betaine surfactant, R<sub>1</sub> is COOM, R<sub>2</sub> and R<sub>3</sub> are CH<sub>3</sub>, R<sub>4</sub> is H, R<sub>5</sub> is selected from C<sub>8</sub>-C<sub>18</sub> alkyls m is 2 or 3, and n is 1.

8. A shampoo composition according to Claim 1, 2, 3, 4, 5, 6, or 7, further comprising a hair conditioning agent.

9. A shampoo composition according to Claim 8 wherein said hair conditioning agent comprises insoluble, nonvolatile silicone dispersed in said composition, preferably a mixture of polydimethylsiloxane gum having a viscosity, at 25°C, greater than 1,000,000 centipoise and polydimethylsiloxane fluid having a viscosity, at 25°C, of from 10 centipoise to 100,000 centipoise, said mixture having a gum:fluid weight ratio of from 30:70 to 70:30.

10. A shampoo composition according to Claim 1, 2, 3, 4, 5, 6, 7, 8, or 9 further comprising a foam booster, preferably a quaternary ammonium salt of hydroxyethylcellulose reacted with trimethyl ammonium-substituted epoxide wherein said shampoo is also substantially free of amide-containing foam boosters.

11. A shampoo composition according to Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 further comprising a particulate anti-dandruff agent.

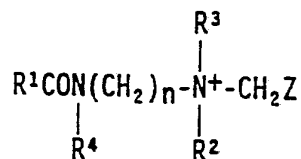
12. A shampoo composition as in Claim 4, 5, 6, 7, 8, 9, 10, or 11, wherein said suspending agent of said premix is recrystallized at pH within 1.0 pH of the average pK<sub>a</sub> of the carboxylates of said amphoteric surfactant of said premix.

13. A process for making a mild shampoo premix composition characterized in that it comprises the steps of:

(i) preparing a solution comprising:

(a) at least 10%, by weight, of alkyl ethoxylated sulfate anionic surfactant;

(b) at least 6%, by weight, of amphoteric surfactant having the formula





wherein  $R^1$  is  $C_8$ - $C_{22}$  alkyl or alkenyl,  $R^2$  is hydrogen or  $CH_2CO_2M$ ,  $R^3$  is  $CH_2CH_2OH$  or  $CH_2CHOCH_2CH_2COOM$ ,  $R^4$  is hydrogen,  $CH_2CH_2OH$ , or  $CH_2CH_2OCH_2CH_2COOM$ ,  $Z$  is  $CO_2M$  or  $CH_2CO_2M$ ,  $n$  is 2 or 3, and  $M$  is hydrogen or a cation; and  
(c) from 30% to 70%, by weight, water;

(ii) adding to the solution from 2% to 15%, by weight of the premix, of a suspending agent wherein said solution is heated and said suspending agent is provided in solubilized form; and cooling said composition to provide said suspending agent in crystalline form;

wherein: said premix has a weight ratio of (a):(b) of 2:3 to 3:1, a weight ratio of said suspending agent to total surfactant present of from 1:1 to 1:6, and a weight ratio of said suspending agent to water, of 1:2 to 1:15; and said premix composition is prepared substantially free of alkyl sulfate anionic surfactant; and the pH of said solution is reduced to within 2.0 pH of the average  $pK_a$  of the carboxylates of the amphoteric surfactant prior to providing said suspending agent in crystalline form.

14. A process according to Claim 13, wherein the pH of said solution is reduced to within 1.5 pH, preferably within 1.0pH, of the average  $pK_a$  of the carboxylates of the amphoteric surfactant prior to providing said suspending agent in crystalline form.

15. A process as in Claim 13 or 14, wherein said suspending agent is selected from the group consisting of acyl derivatives having  $C_8$ - $C_{22}$  hydrocarbyl chains and long chain amine oxides having  $C_{16}$ - $C_{22}$  hydrocarbyl chains, and mixtures thereof.

16. A process for making a shampoo composition comprising adding surfactant, foam booster, hair conditioning agent, anti-dandruff agent, water, or a mixture thereof to a premix composition prepared according to Claim 13, 14, or 15.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/02128

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A61K7/08		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	A61K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>o</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X, P	WO,A,924 882 (PROCTER & GAMBLE) 2 April 1992 see page 5, line 14 - page 24, line 36; claims 1-16; example 6 ---	1-16
X, P	WO,A,925 234 (PROCTER & GAMBLE) 2 April 1992 see the whole document ---	1-16
Y	EP,A,0 400 976 (UNILEVER) 5 December 1990 see the whole document ---	1-16
Y	EP,A,0 122 324 (MIRANOL CHEMICAL COMPANY) 24 October 1984 see page 5; examples A,B,C,D ---	1-16
-/--		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>o</sup> Special categories of cited documents :<sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
22 JUNE 1993	02.07.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	FISCHER J.P.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	AU,B,7 724 487 (NOSS ET AL.) 20 October 1987 see the whole document ---	1-16
A	EP,A,0 250 181 (HELENE CURTIS INDUSTRIES) 23 December 1987 see the whole document ---	1-16
A	FR,A,2 315 905 (S.C. JOHNSON & SON) 28 January 1977 see the whole document ---	1-16
A	US,A,4 181 634 (KENNEDY ET AL.) 1 January 1980 see examples E,F,G,H,I,13 -----	1-16

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9302128  
SA 71983

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 22/06/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-924882		None	
WO-A-925234		None	
EP-A-0400976	05-12-90	AU-B- 624514 AU-A- 5606690 JP-A- 3068509 JP-B- 4000964 US-A- 5152914	11-06-92 06-12-90 25-03-91 09-01-92 06-10-92
EP-A-0122324	24-10-84	DE-A- 3375135 JP-A- 59193855	11-02-88 02-11-84
AU-B-7724487		None	
EP-A-0250181	23-12-87	AU-B- 596187 AU-A- 7377087 JP-A- 63022900	26-04-90 17-12-87 30-01-88
FR-A-2315905	28-01-77	NL-A- 7607314	04-01-77
US-A-4181634	01-01-80	US-A- 4110263 AU-B- 518837 AU-A- 3673378 BE-A- 868215 CA-A- 1091157 CH-A- 640134 GB-A- 1594290 JP-C- 1389955 JP-A- 54007407 JP-B- 61059283 LU-A- 79829 NL-A- 7806535	29-08-78 22-10-81 06-12-79 18-12-78 09-12-80 30-12-83 30-07-81 23-07-87 20-01-79 16-12-86 07-12-78 19-12-78

EPO FORM P0479