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(54) Title: ANTIBACTERIAL MILD LIQUID SKIN CLEANSER

#### (57) Abstract

A liquid skin cleanser composition with improved mildness and degerming characteristics, comprising: (A) 0.5-5.75 weight percent of a mild ethoxylated surfactant; (B) 1-40 weight percent of a cosurfactant selected from the group consisting of nonethoxylated anionic, nonionic, zwitterionic, and amphoteric surfactants and mixtures thereof; (C) 0.01-4 weight percent of antibacterial agent; (D) 0.05-5 weight percent of water-soluble cationic polymer; and (E) 35-97 weight percent water.

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#### ANTIBACTERIAL MILD LIQUID SKIN CLEANSER

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#### BACKGROUND OF THE INVENTION

This invention relates to mild liquid skin cleansers. More particularly, this invention relates to antibacterial liquid skin cleansers.

The cleaning of skin with surface-active cleaning preparations has become a focus of great interest. Many people wash and scrub their skin with various surface active preparations several times a day. Liquid cleansers are highly preferred, especially for handwashing because of convenience and non-messiness. Antibacterial personal cleansers are preferred because they kill germs. Mild personal cleansers are desired to minimize skin irritation, dryness, etc. A personal cleansing product having all three of these preferred characteristics would be very desirable.

Skin cleansers should cleanse the skin gently, causing little or no irritation, without drying the skin after frequent routine Certain synthetic surfactants are particularly mild. However, a major drawback of mild liquid synthetic surfactant systems when formulated for skin cleansing is poor lather performance. Compared to the highest bar soap standards (bars which are rich in coconut soap and superfatted), these prior art liquid surfactant formulations have either poor lather or poor skin mildness performance. As may be expected, the lather performance is a function of the choice of surfactant and its concentration. The conceivable number of liquid surfactant compositions formulated with or without skin feel agents are numerous. Rheological and phase properties exhibited by prototypes vary widely (i.e., thin liquids, gels, thick pastes, solutions, emulsions). phase stability of prototypes is for the most part acceptable over short time periods, but only a small fraction of them will maintain their original properties and acceptability over an extended period of time. See, e.g., U.S. Pat. Nos.: 4,338,211.

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Stiros, issued July 6, 1982; 4,310,433, Stiros, issued Jan. 12, 1982; and 4,842,850, Vu, issued June 27, 1989, all of said patents being incorporated herein by reference.

Optimization of lather as a single variable is a fairly straightforward process. The use of known high sudsing anionic surfactants with lather boosters yields acceptable lather volume. Unfortunately, highest sudsing anionic surfactants are, generally, also highest in skin irritation and are worst in clinical mildness. Surfactants that are among the mildest with minimal skin irritation, such as ammonium lauryl ether (12 EO) sulfate (NH4AE12S) are extremely poor in lather. These two facts alone make the surfactant selection and the lather boosting optimization process a delicate balancing act. See, e.g., U.S. Pat. No. 4,338,211, supra, incorporated herein by reference.

The introduction of an antibacterial into the equation results in additional problems for mildness, lather, and antibacterial efficacy. It is reported in trade literature that certain mild ethoxylated nonionic surfactants, e.g., Tween® 80 (ICI Americas, Inc.) and lecithin have deactivating effects on the degerming of a preferred antibacterial, Triclosan (Irgasan® DP 300 is also referred to herein as "TCS"), Ciba-Geigy Irgasan® DP 300 Trade Bulletin, 1988.

The use of antibacterials in liquid shampoo and other personal cleansing products, per se, is known and at least two are commercially available under the trade names of LIQUID DIAL® Antibacterial Soap, and SOFTSOAP® Antibacterial Moisturizing Soap. The antibacterial liquid cleansing products on the current market are relatively harsh. So a mildness improvement over such products would be highly desirable, especially without compromising degerming efficacy. Special antibacterial liquid cleansers are disclosed in U.S. Pat. Nos.: 4,847,072, Bissett and Bush, issued July 11, 1989; 4,939,284, Degenhardt, issued July 3, 1990; and 4,820,698, Degenhardt, issued April 11, 1989, said patents being incorporated herein by reference.

In short, there are rather stringent requirements for skin cleansers which limit the choice of surface-active agents and antibacterials, and as a result the degerming final formulations

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represent some degree of compromise. Mildness is often obtained at the expense of effective degerming or effective cleansing and lathering which may be sacrificed for either mildness, product stability, or both.

The present invention offers a valuable combination of desirable properties to liquid skin-cleaning formulations.

Therefore, one object of this invention is the development of liquid skin cleaning compositions which exhibit improved mildness, good cleaning and lathering, and good degerming properties.

Another object of the present invention is the development of low cost liquid skin cleansers.

Other objects will become apparent from the detailed description below.

#### SUMMARY OF THE INVENTION

A liquid skin cleanser composition with improved mildness and degerming characteristics, comprising:

- (A) 0.5-5.75 weight percent of mild ethoxylated surfactant;
- (B) 1-40 weight percent of cosurfactant selected from the group consisting of non-ethoxylated anionic, nonionic, zwitterionic, and amphoteric surfactants and mixtures thereof, said cosurfactant comprising harsh surfactant at a level to give a ratio of harsh cosurfactant to mild ethoxylated surfactant of from about 20:1 to 1:5.8;
- (C) 0.01-4 weight percent of antibacterial agent, preferably selected from the group of halogenated aromatic antibacterial agents and octopirox, and mixtures thereof;
- (D) 0.05-5 weight percent of water-soluble cationic polymer; and
- (E) 35-97 weight percent water.

#### DETAILED DESCRIPTION OF THE INVENTION

This invention relates to mild ethoxylated surfactant liquid skin cleaning compositions with optimum degerming and preferably optimum lather performance. Cosurfactant, preferably one with good suds boosting power, typically a harsh surfactant, is used with said mild ethoxylated surfactant to provide improved lather.

Antibacterial agents are compatible with cosurfactant, e.g., alkyl sulfates, but are not so compatible with mild ethoxylated

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surfactants. This invention, however, further enhances combination of the two types of surfactants with antibacterial.

A liquid skin cleanser composition with improved mildness and degerming characteristics, comprising:

- (A) 0.5-5.75% of mild, ethoxylated surfactant selected from the group consisting of anionic; nonionics, and mixtures thereof, preferably anionic alkyl ethoxy sulfate having from 1 to 20 ethoxy groups;
  - (B) 1-40% of an antibacterial compatible cosurfactant selected from the group consisting of non-ethoxylated anionic, nonionic, zwitterionic, and amphoteric surfactants, and mixtures thereof; preferably good cleaning anionics, especially the alkyl sulfates;
    - (C) 0.01-4% of antibacterial agent, preferably selected from the group of halogenated aromatic antibacterial agents and octopirox, and mixtures thereof, and more preferably Triclosan (TCS);
    - (D) 0.05-5% of water-soluble cationic polymer, preferably cationic guar gum; and
- (E) 35-97%, preferably 50-95%, more preferably 75-90%, water.

The total level of (A) and (B) is at least about 4% and sufficient to keep the composition stable.

A more detailed description of the levels and ranges of the components of the present invention are provided in Tables 1 and 2 below.

The ranges and levels set out herein, especially in Tables 1 and 2, are approximations and should be given liberal interpretations. The levels and ranges will vary depending on the selection of the particular ingredient.

TABLE 1
LEVELS AND RATIOS

		_			
		Cosur-		Anti-	Cationic
		<u>factant</u>	MES**	<u>bacterial</u>	Polymer
5	Full Ranges	1-40%	0.5-5.8%	0.05-4%	0.05-5%
	Preferred Ranges	4-20%	2-5%	0.1-2%	0.1-2%
	More Preferred	5-10%	3-4.5%	0.2-1%	0.2-1%
	<u>Cosurfactant</u>				
10	Full Ratios	N/A	80:1-1:6	800:1-1:4	800:1-1:5
	Preferred Ratios	N/A	40:1-1:2	200:1-3:1	200:1-3:1
	More Preferred	N/A	2.1:1	50:1-10:1	50:1-10:1
		.,, ,,	2	30.1 10.1	30.1-10.1
	MES**				
15	Full Ratios	*	N/A	116:1-1:8	116:1-1:10
	Preferred Ratios	*	N/A	50:1-3:1	50:1-3:1
	More Preferred	*	N/A	25:1-5:1	25:1-5:1
	<u>Triclosan</u>				
20	Full Ratios	*	*	N/A	80:1-1:100
	Preferred Ratios	*	*	N/A	10:1-1:10
٠	More Preferred	*	*	N/A	3:1-1:3
	*Shown el	sewhere i	n the Table.		
	**Mild eth	oxylated	surfactants.		
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	Some preferred co	surfactan	t blends are	:	
			Full	Preferred	More
			<u>Range</u>	<u>Range</u>	Preferred
	Alkyl Sulfates or	Alkyl			
30	Olefin Sulfonate	es, or			
	Alkyl Glucose Ar	nides	1-20%	3-10%	4-8
	Lauramide or Cocar	nide DEA(	?) 1-10%	0.5-5%	1-2%
	Cocoamidopropyl Be	etaine	1-10%	0.5-5%	<u>1 - 2%</u>
	1	otals	3-40%	4-20%	6-12%

TABLE 2

MORE PREFERRED LEVELS AND RATIOS

		Alkyl			
		<u>Sulfate</u>	<u>AE<sub>n</sub>S</u>	<u>Triclosan</u>	<u>Polymer</u>
5	Full Ranges	1-20%	0.5-5.8%	0.05-4%	0.05-5%
	Preferred Ranges	3-10%	2-5%	0.10-2%	0.1-2%
	More Preferred	5-7%	2-5%	0.1-0.8%	0.2-1%
	Alkyl Sulfate				
10	Full Ratios	N/A	20:1-1:5.8	400:1-1:4	400:1-1:5
	Preferred Ratios	N/A	5:1-1:2	100:1-3:1	100:1-3:1
	More Preferreds	N/A	2:1-1:1	50:1-5:1	50:1-5:1
	<u>AE<sub>n</sub>S</u>				
15	Full Ratios	*	N/A	115:1-1:8	115:1-1:10
	Preferred Ratios	*	N/A	50:1-3:1	50:1-3:1
	More Preferreds	*	N/A	25:1-5:1	25:1-5:1
	<u>Triclosan</u>				
20	Full Ratios	*	*	N/A	80:1-1:100
	Preferred Ratios	*	*	N/A	10:1-1:10
	More Preferred	*	*	N/A	3.1-1:3

\*Shown elsewhere in the Table.

25 The Ethoxylated Surfactants

An essential ingredient is an ethoxylated (or propoxylated) surfactant which is mild to the skin. Propoxylated surfactants are essentially equivalents to ethoxylated surfactants as defined herein. The preferred mild, ethoxylated (propoxylated) surfactants have Relative Barrier Destruction Index Values (mildness) of about 50 or less, as defined hereinbelow. The mild ethoxylated surfactant, ammonium laureth-3-carboxylate (AE3C-NH4OH at pH 6.5), has an "Index Value" of about 50. A "harsh" surfactant is any surfactant or cosurfactant with an Index Value of more than 50.

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The ethoxylated mild surfactant is used conveniently to improve mildness of the liquid composition. For this purpose the level can be from about 0.5% to about 5.8%, preferably from about 2% to about 5%. At the higher levels, however, the ethoxylated mild surfactant diminishes antibacterial effectiveness of the composition.

Some examples of the preferred surfactants are alkali metal and ammonium salts of the sulfuric acid esters of the reaction product of 1 mole of a C8-C22 alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 20, preferably 1 to 13, more preferably 2 to 6, moles of ethylene oxide (ethoxy groups). Diethanol amines are not ethoxylated surfactants. The CTFA names of some preferred ethoxylated surfactants are:

#### **Anionics**

Ammonium Laureth Sulfate, CAS #32612-48-9 (generic)

Pareth-15-7 Carboxylic Acid

TEA-Oleamido PEG-n Sulfosuccinate, TEA = Triethanol Amine

PPG-5-Ceteth-10 Phosphate, RD #977061-68-9

#### **Nonionics**

20 Polysorbate 80

Pareth-15-5

PPG-8-Ceteth-10 CAS #9087-53-0 (generic)

PEG-5M

PEG-8 Stearate, CAS #9004-99-3 (generic)

The in vitro skin barrier penetration test (mildness), performed similar to the procedure described in U.S. Pat. No. 4,812,253, Small et al., issued Mar. 14, 1989, said patent being incorporated herein by reference, can be used to assess the relative irritancy of surfactants. The essential, mild ethoxy-lated surfactant is preferably selected to have a mildness Index Value at or below 50.

Frequently, a surfactant which tends to improve cleaning also tends to have negatives, particularly in terms of product mildness. Referring to the Relative Barrier Destruction Chart No. 1 the "Barrier Destruction Index Values" for: ALS = 100; water = 0.

Relative Rarrier

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#### Relative Barrier Destruction Chart No. 1

		Relative Dallier
	<u>Surfactant</u> <u>D</u>	estruction Index Values
	Ammonium Lauryl Sulfate (ALS)	100
5	Ammonium Laureth-3 Carboxylate (pH = 6	.5) 50
	Ammonium Laureth-3 Sulfate (AE3S)	30
	Sodium Lauroyl Sarcosinate	25
	Disodium Cocoyl Monoethanol Amine	
	Sulfosuccinate	25
10	Sodium Nonoxynol-4 Sulfate <sup>1</sup>	10
	Octyl Glycerol Ether Sulfate	10
	Lauryl Polyglucose <sup>2</sup>	10
	Water	0
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<sup>15 1</sup> Alipal HF-433

#### Cosurfactant

Another essential component of the liquid skin cleanser composition herein is one or more non-ethoxylated "cosurfactant" which is preferably selected for its cleaning, lathering, cost or antibacterial compatibility. So the selection of the cosurfactant and the term "cosurfactant" should be given a broad interpretation. Preferred are the higher lathering surfactants which are known in the art, or can be tested. The rule, as far as lather or cleaning are concerned, is that the cosurfactant should add to the lather or cleaning power of the liquid cleanser. The cosurfactant can also be selected for its mildness, as well as its cleaning or lather boosting properties. However, such cosurfactants are typically harsh (e.g., Index Value >50). The compositions that provide the best balance of properties have a ratio of harsh cosurfactant to mild ethoxylated surfactant of from about 20:1 to about 1:5.8, preferably from about 5:1 to about 1:2, more preferably from about 2:1 to about 1:1. Some preferred cosurfactant blends are set out after Table 1.

The term "cosurfactant" as used herein is intended to denote any non-ethoxylated surfactant used in the liquid compositions of

<sup>2</sup> Henkel APG 550 (1.7)

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the present invention. The cosurfactant includes all non-ethoxy-lated surface active agents, especially those which lather and clean well and which are compatible with the antibacterial, i.e., more compatible than the ethoxylated surfactant. The preferred cosurfactants of this invention are the alkali metal (e.g., sodium or potassium) and ammonium, alkyl sulfates derived by sulfation of C8-C22 alcohols, either synthetically derived or produced by reduction of glycerides, or other esters, of tallow or coconut oil fatty acid combined with similarly derived alkyl betaines (zwitterionics) and alkyl amides (nonionics).

The preferred cosurfactant referred to herein is alkyl sulfate (AS). The preferred ethoxylated surfactant is alkyl ether sulfate (AE $_{n}$ S). The U.S. patents incorporated herein by reference contain an extensive and detailed list of both ethoxylated surfactants and cosurfactants.

#### Antibacterial Agent

The antibacterial agent can be present at a level of from about 0.01% to about 4%, typically from about 0.1% to about 2%, and preferably from about 0.5% to about 1%. The level is selected to provide the desired level of antibacterial activity and can be modified as desired. The preferred antibacterial agent is 2-hydroxy-4,2',4'-trichlorodiphenylether (TCS). Other halogenated antibacterial agents are set out below. Many antibacterial agents, known to those skilled in the art and disclosed in, e.g., U.S. Pat. Nos. 3,835,057 and 4,714,563, both incorporated hereinbefore by reference, may be used.

Suitable antibacterial agents include:

- 2-hydroxy-4,2',4'-trichlorodiphenylether (TCS);
- 2,6-dimethyl-4-hydroxychlorobenzene (PCMX);
- 30 3,4,4'-trichlorocarbanilide (TCC);
  - 3-trifluoromethyl-4,4'-dichlorocarbanilide (TFC);
  - 2,2'-dihydroxy-3,3',5,5',6,6'-hexachlorodiphenylmethane;
  - 2,2'-dihydroxy-3,3',5,5'-tetrachlorodiphenylmethane;
  - 2,2'-dihydroxy-3,3',dibromo-5,5'-dichlorodiphenylmethane;
- 2-hydroxy-4,4'-dichlorodiphenylether;
  - 2-hydroxy-3,5',4-tribromodiphenylether; and

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1-hydroxyl-4-methyl-6-(2,4,4-trimethylpentyl)-2(1H)-pyridinone (Octopirox).

#### The Water-Soluble Cationic Polymer

The inclusion of an effective amount of a water-soluble cationic polymer to any liquid antibacterial composition should improve mildness, including systems which do not contain ethoxy-lated surfactant. The water-soluble cationic polymeric skin conditioning agent essential in the present invention is selected from the group consisting of:

- 10 (I) cationic polysaccharides;
  - (II) cationic copolymers of saccharides and synthetic cationic monomers, and
  - (III) synthetic polymers selected from the group consisting of:
- 15 (A) cationic polyakylene imines,
  - (B) cationic ethoxy polyalkylene imines, and
  - (C) cationic poly(N-(-3-(dimethylammonio)propyl)-N'-[3-(ethyleneoxyethylene dimethylammonio)propyl)urea dichloride).

The amount of hydrated cationic polymeric skin conditioners found useful in the composition of the present invention is from about 0.05% to about 5%, preferably from about 0.1% to about 2%, by weight of active polymer. The liquid cleaning compositions containing these relatively small amounts of polymer deliver significantly improved clinical mildness relative to a composition without the polymer. The resultant mildness is unexpectedly and surprisingly superior to that of the synthetic surfactant-based liquid antibacterial skin cleansing products currently on the market.

The cationic polymers can also provide a desirable silky, soft, smooth in-use feeling.

The cationic polymers can be employed to achieve the mildness benefit while maintaining the highly acceptable and desirable in-use liquid cleansing product characteristics of good lather character, lather volume, cleaning, rinsing, skin feel, odor. degerming, etc. This is unexpected since cationic polymers, particularly when used at the higher levels typically necessary

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for a mildness improvement and when used without the hydration specified by the present invention, have a significant negative impact on in-use characteristics. For example, they can suppress lather volume and alter its character, result in poor rinsing, and have a negative impact on odor.

(I)

The cationic polysaccharide class encompasses those polymers based on 5 or 6 carbon sugars and derivatives which have been made cationic by engraphing of cationic moieties on the polysaccharide backbone. They may be composed of one type of sugar or of more than one type, i.e. copolymers of the above derivatives and cationic materials. The monomers may be in straight chain or branched chain geometric arrangements. Cationic polysaccharide polymers include the following: cationic celluloses and hydroxyethylcelluloses; cationic starches and hydroxyalkyl starches; cationic polymers based on arabinose monomers such as those which could be derived from arabinose vegetable gums; cationic polymers derived from xylose polymers found in materials such as wood, straw, cottonseed hulls, and corn cobs; cationic polymers derived from fucose polymers found as a component of cell walls in seaweed; cationic polymers derived from fructose polymers such as Inulin found in certain plants; cationic polymers based on acidcontaining sugars such as galacturonic acid and glucuronic acid; cationic polymers based on amine sugars such as galactosamine and glucosamine; cationic polymers based on 5 and 6 membered ring polyalcohols; cationic polymers based on galactose monomers which occur in plant gums and mucilages; cationic polymers based on mannose monomers such as those found in plants, yeasts, and red algae; cationic polymers based on the galactomannan copolymer known as guar gum obtained from the endosperm of the guar bean.

Specific examples of members of the cationic polysaccaride class include the cationic hydroxyethyl cellulose JR 400 made by Union Carbide Corporation; the cationic starches Stalok® 100, 200, 300 and 400 made by Staley, Inc.; the cationic galactomannans based on guar gum of the Galactasol 800 series by Henkel, Inc., the Jaguar Series by Rhône-Poulenc (for example, Jaguar C-14-S and C162).

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(II)

The cationic copolymers of saccharides and synthetic cationic monomers useful in the present invention encompass those containing the following saccharides: glucose, galactose, mannose, arabinose, xylose, fucose, fructose, glucosamine, galactosamine, glucuronic acid, galacturonic acid, and 5 or 6 membered ring polyalcohols. Also included are hydroxymethyl, hydroxyethyl and hydroxypropyl derivatives of the above sugars. When saccharides are bonded to each other in the copolymers, they may be bonded via any of several arrangements, such as  $1,4-\alpha$ ;  $1,4,-\beta$ ;  $1,3-\alpha$ ;  $1,3-\beta$ and 1,6 linkages. The synthetic cationic monomers for use in these copolymers can include dimethyldiallylammonium chloride, dimethylaminoethylmethyacrylate, diethyldiallylammonium chloride, N,N-dially1,N-N-dialkyl ammonium halides, and the like. A preferred cationic polymer is Merquat 550 prepared with dimethyldiallylammonium chloride and acrylamide monomers.

Examples of members of the class of copolymers of saccharides and synthetic cationic monomers include those composed of cellulose derivatives (e.g., hydroxyethyl cellulose) and N,N-diallyl,N-N-dialkyl ammonium chloride available from National Starch Corporation under the trade name Celquat.

(III)

The cationic synthetic polymers useful in the present invention are cationic polyalkylene imines, ethoxypolyalklene imines, and poly[N-[-3-(dimethylammonio)propyl]-N'-[3-(ethylene-oxyethylene dimethylammonio)propyl]urea dichloride] the latter of which is available from Miranol Chemical Company, Inc. under the trademark of Miranol A-15, CAS Reg. No. 68555-36-2.

Preferred cationic polymeric skin conditioning agents of the present invention are those cationic polysaccharides of the cationic guar gum class with molecular weights of 1,000 to 3,000,000. More prefered molecular weights are from 2,500 to 350,000. These polymers have a polysaccharide backbone comprised of galactomannan units and a degree of cationic substitution ranging from about 0.04 per anhydroglucose unit to about 0.80 per anhydroglucose unit with the substituent cationic group being the adduct of 2,3-epoxypropyltrimethyl ammonium chloride to the

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natural polysaccharide backbone. Examples are Jaguar C-376-FA, C-14-S, C-15, C-17, C162, and ADMQ guar sold by Rhône-Poulenc. Some preferred cationic guar gums have 1-2% aqueous solution viscosity of from about 125 cps to about 3500  $\pm$  500 cps at 25°C, where said aqueous solution has a pH of about 9-11.

The cationic guar gum polymers useful in the present invention have been found to be more effective skin conditioners than those cationic polymers based on hydroxyethyl cellulose (e.g., JR-400 commercially available from Union Carbide Corporation). Also useful in the present invention are cationic polymers referred to in U.S. Pat. No. 3,761,418, to Parran, Jr., supra, in UK Patent Application GB 2094307A, and in commonly assigned U.S. Pat. Application Ser. No. 07/374,315, Bartolo and Wong, filed June 30, 1989, said patent and said patent applications incorporated herein by reference.

Solutions of cationic polymers Jaguar C-14-S and JR-400 which contain an anionic surfactant (sodium laurate) are evaluated. Skin condition is measured via visual evaluations of dryness and redness and via instrumental assessment of skin condition (trans epidermal water loss, skin conductivity, and sonic transmission, as set out in "Effects of Bar Soap Constituents on Product Mildness," by Dahlgren, Lukacovic, Michaels, and Visscher, in Proceedings of the Second World Conference on Detergents, Montreux, Switzerland, A.R. Baldwin, Ed. (American Oil Chemists Society, 1987), pp. 127-134). Results indicate the cationic guar gum is about twice as effective as JR-400. Thus, cationic guar gum is a more efficient skin conditioner than a hydroxyethylcellulose-based cationic polymer and is the most preferred type of cationic polymer for use in the present invention.

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#### Aqueous Carrier

The skin cleansers herein are preferably in the form of liquids or creams in which water is the principal diluent. The level of water in the compositions is typically from about 60% to about 93% by weight, preferably from about 75% to about 90%. Purified water is preferred.

#### pH Adjustment Agent

The in use pH of the liquid skin cleanser compositions herein should lie in the range of about 4 to about 10, preferably in the range of about 5 to about 8, more preferably in the range of about 6 to about 7. The pH is kept in the acidic range to maintain the stability of the antibacterial TCS and the cationic guar. Suitable pH adjustment agents include HCl, citric acid, phosphoric acid, succinic acid and a sodium citrate/citric acid combination, among many others.

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#### Optional Components

The skin cleansers herein can contain a variety of nonessential, optional ingredients suitable for improving such compositions in a variety of ways. Such conventional, optional ingredients are well known to those skilled in the art, e.g., preservatives such as HMDM Hydantoin, benzyl alcohol, methyl paraben, propyl paraben, 3-isothiazolines (Kathon CG sold by Rohm and Haas), imidazolidinyl urea, methylchloroisothiazolinone, and methylisothiazolinone can be used in amounts of from 1 to 5,000 ppm; thickeners and viscosity modifiers such as sodium sulfate, polyethylene glycols, sodium chloride, ammonium chloride, carboxymethylcellulose, methylcellulose, polyvinyl alcohol, and ethyl alcohol; suspending agents such as magnesium/aluminum silicate; perfumes, dyes; opacifiers such as ethylene glycol distearate, glycol monostearate, styrene acrylate copolymer, mica, behenic acid, and calcium stearate; sequestering agents such as disodium ethlyenediamine tetraacetate; emollients, moisturizers and various other skin treating ingredients such as glycerin; buffers and builders such as citrates and phosphates. If present, such agents individually generally comprise from about 0.01% to about 5% by weight of the composition.

#### Method of Manufacture

The liquid skin cleanser compositions of the present invention are made using mixing techniques disclosed herein. A method of making the present invention is shown in the examples which follow.

A method which can be used to make the exemplary compositions of the present invention is as follows:

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- 1. The polymer is hydrated in the main mix tank by dispersing in purified water at ambient temperature, then lowering the solution pH to about 6 via addition of citric or other suitable acid, to aid hydration. Sodium sulfate may also be added to reduce the potential for polymer/surfactant coacervate formation when the surfactants are mixed with the polymer.
- 2. A separate premix of the purified water, sodium alkyl sulfate, cocoamidopropyl betaine, lauramide diethanol amine, and ethyleneglycol distearate is mixed at a temperature of about 76°C, then chilled to about 26° to 38°C to crystallize the ethyleneglycol distearate. The crystallized ethyleneglycol distearate gives the final product a pearlized appearance.
- 3. The contents of the premix in step (2) are added to the hydrated polymer in the main mix.
- 4. The sodium laureth-3 sulfate is added to main mix.
- 5. The preservatives are added to the main mix.
- 6. Citric acid is added to adjust the pH of the finished product to about pH 6.0 to 6.5.
- 7. The TCS is predissolved in the perfume. This mix is then added to the main mix.
  - 8. Colorants are added to the main mix.
  - 9. Sodium sulfate is added to adjust the finished product viscosity to about 6,000 to 9,000 cps.

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#### Composition Use

In its method aspect, the present invention comprises a method of washing the skin by contacting the skin with an amount of the cleanser compositions herein which is effective to clean the skin and rinsing the excess cleanser from the skin. An effective amount for any individual will depend upon variable factors such as amount of soil on the skin, type of soil on the skin, level of surfactant in the cleanser composition, etc. Generally, an effective amount will be from about 0.5 to about 5 grams per use.

The following examples will illustrate the invention, but are not intended to be in any way limiting thereof. All percentages and temperatures and data are approximations or estimations unless

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otherwise specified. Tables 3, 4, 6 and 7 cite degerming results obtained with the Minimum Inhibitory Concentration Disk Test, which procedure is set out below.

### Minimum Inhibitory Concentration Disk Test

The degerming performance of the products was evaluated using the Minimum Inhibitory Concentration Disk Test ("MIC Test") for antimicrobial liquid soap products. The MIC Test is a modification of a disk diffusion test method used by clinical laboratories to determine the susceptibility of infectious organisms to antibiotics. In this method, 50 microliters of a 1% solution of the antimicrobial products is added to filter paper disks 13 mm in The disks are then applied to the surface of agar plates which have been inoculated with microorganisms. disk is applied to an agar plate, the antimicrobial diffuses through the agar medium. The result is a gradual changing gradient of antimicrobial concentration in the agar surrounding each disk. The organisms that are not inhibited by the antimicrobial multiply on the agar plate forming a lawn of growth which can be visualized. No growth will occur in the area around the disk where the antimicrobial is present in inhibitory concentrations. The more susceptible the microorganism and soluble the antimicrobial, the larger the zone of inhibition surrounding the disk.

The agar plates in the testing that follows were innoculated with <u>Staphylococcus aureus</u> and, in some cases, <u>Escherichia coli</u>. Products are typicallly tested in a random block design. The agar plates are incubated for 18 to 24 hours. The diameters of the circular zones of inhibition are then measured in two directions in millimeters and averaged to establish the zone of inhibition size reported.

To account for the variability in zone size across MIC Tests for any given product, which can occur as a result of variations in the bacteria inoculated on the agar plates, products are only compared within the same test.

Tables 5 and 7 cite clinical mildness results obtained using the method below.

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#### Mildness Methodology

A four-day forearm wash test among 40 panelists was conducted to evaluate mildness. The methodology was similar to that discussed in "Forearm Wash Test to Evaluate the Clinical Mildness of Cleansing Products," by Lukacovic, Dunlop, Michaels, Visscher, and Watson, in <u>J. Soc. Cosm. Chem.</u>, 39, 355-366, Nov./Dec. 1988; and "Effects of Bar Soap Constituents on Product Mildness," by Dahlgren, Lukacovic, Michaels, and Visscher, in Proceedings of the Second World Conference on Detergents, Montreux, Switzerland, A.R. Baldwin, Ed. (American Oil Chemists Society, 1987), pp. 127-134. After four days of treatment, visual grades for skin dryness and redness (0 = perfect skin, 5 = degraded skin) are assigned. Also the conductance of the skin is measured by a Skicon instrument (higher conductance is indicative of higher levels of moisture in Finally, a Scopeman Fiber Optic Magnifying Video Camera was used to visually record the skin condition, and the video images are later graded using the same "dryness" scale referenced above.

A logical way to achieve a milder antibacterial liquid cleanser would be to increase the level of mild surfactant vs. harsher cosurfactants. However, as Comparative E2 shows, this approach results in a significant reduction in degerming vs. Example 7, as set out in Table 6.

the level of antibacterial relative to E3, does resolve the degerming deficiency. In sharp contrast, Examples 1 and 2 of Table 3 show preferred levels of ethoxylated surfactant and cosurfactants. Example 1 shows comparable degerming to Comparative A, a leading commercially available antibacterial hand soap.

Example 2 is superior to "A" in degerming. Example 2 has more TCS, 0.5% than Example I, 0.2%. This increase in degerming is unexpected and surprising in view of E4 of Table 7. Example 5 in Table 4 is the more preferred execution of the present invention.

TABLE 3

Degerming Examples 1, 2, vs. Comparative Composition A

	<u>begerming examples 1.</u>	2, V3. CU	mipar acree oo	Compara-
	<u>Ingredients</u>	<u>Ex. 1</u>	Ex. 2	tive A*
5	Ammonium Lauryl Sulfate	-	-	7.00
	Sodium Lauryl Sulfate	6.00	6.00	-
	Sodium Laureth Sulfate	4.00	4.00	4.30
	Cocamidopropyl Betaine	1.20	1.20	-
	Lauramide Diethanol			
10	Amine (DEA)	1.20	1.20	2.00
	Guar Hydroxypropyl-			
	trimonium Chloride	0.25	0.25	•
	Triclosan	0.20	0.50	0.20
	Disodium Ricinoleamido			
15	MEA-Sulfosuccinate	-	-	1.50
	Isostearamidopropyl			
	Morpholine Lactate	-	-	1.20
	Glycerin	**	-	1.00
	Styrene/Acrylate Copolymer	0.40	0.40	. <del>-</del>
20	Sodium Sulfate	0.75	0.75	-
	Sodium Chloride	-	-	0.50
	Tetrasodium EDTA	0.10	0.10	0.10
	DMDM Hydantoin	0.20	0.20	0.20
	Perfume	0.30	0.30	0.25
25	Dye	0.01	0.01	0.01
	Citric Acid	0.08	0.08	0.23
	Water	<u>85.31</u>	<u>85.01</u>	<u>81.51</u>
	Totals	100.00	100.00	100.00
	<b>*Comparative</b> "A" is an	estimate (	of a leading	commercially
30	available liquid antib	pacterial:	soap.	
	MIC Test Results			
	Zone of Inhibition*	40.57	51.14	42.86
	Difference vs. "A"	-2.29	+8.28	
	p-value: probability			
35	difference equals zero	0.19	0.00	

\*Average of seven repetitions. Diameter of zone measure in millimeters.

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TABLE 4

	Degerming Examples 3-5 vs. Comparative A				
	<u>Ingredients</u>	<u>Ex. 3</u>	Ex. 4	<u>Ex. 5</u>	
	Ammonium Lauryl Sulfate	-	-	-	
5	Sodium Lauryl Sulfate	6.00	6.00	6.00	
	Sodium Laureth Sulfate	4.00	4.00	4.00	
	Cocamidopropyl Betaine	1.20	1.20	1.20	
	Lauramide DEA	1.20	1.20	1.20	
	Guar Hydroxypropyl-				
10	trimonium Chloride	0.25	0.50	0.25	
	Triclosan	0.30	0.30	0.30	
	Disodium Ricinoleamido				
	MEA-Sulfosuccinate	-	-	-	
	Isostearamidopropyl				
15	Morpholine Lactate	-	-	-	
	Glycerin	-	-	-	
	Ethylene Glycol				
	Distearate	-	-	1.50	
	Styrene/Acrylate				
20	Copolymer	0.40	0.40	-	
	Sodium Sulfate	0.75	0.75	0.75	
	Sodium Chloride	-	-	-	
	Tetrasodium EDTA	0.10	0.10	0.10	
	DMDM Hydantoin	0.20	0.20	0.20	
25	Perfume	0.30	0.30	0.30	
	Dye	0.01	0.01	0.01	
	Citric Acid	0.08	0.08	0.08	
	Water	<u>85.21</u>	<u>84.96</u>	<u>84.11</u>	
	Totals	100.00	100.00	100.00	
30					
	MIC Test Results: Note that	in this test	Comparative A	s	
		nhibition = 3	88.86		
	Zone of Inhibition*	38.57	40.71	39.00	
	Difference vs. "A"	-0.29	+1.85	-0.14	
35	p-value: probability				
	difference equals zero	0.77	0.09	0.90	
	Difference vs. Ex. 3		2.14	0.43	

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p-value: probability
difference equals zero 0.01 0.63
\*Average of seven repetitions.

5 <u>TABLE 5</u> <u>Mildness Examples</u>

			Experi-	
			mental	Compara-
	<u>Ingredients</u>	Ex. 6*	Comp. E1	<u>tive A</u>
10	Ammonium Lauryl Sulfate	-	-	7.00
	Sodium Lauryl Sulfate	6.00	6.00	-
	Sodium Laureth Sulfate	4.00	4.00	4.30
	Cocamidopropyl Betaine	1.20	1.20	-
	Lauramide DEA	1.20	1.20	2.00
15	Guar Hydroxypropyl-			
	trimonium Chloride	0.25	-	-
	Triclosan	0.20	0.20	0.20
	Disodium Ricinoleamido			
	MEA-Sulfosuccinate	-	-	1.50
20	Isostearamidopropyl			
	Morpholine Lactate	-	-	1.20
	Glycerin	-	-	1.00
	Styrene/Acrylate Copolymer	0.40	-	-
	Sodium Sulfate	0.75	0.75	-
25	Sodium Chloride	-	-	0.50
	Tetrasodium EDTA	0.10	0.10	0.10
	DMDM Hydantoin	0.20	0.20	0.20
	Perfume	0.30	0.30	0.25
	Dye	0.01	0.01	0.01
30	Citric Acid	0.08	0.08	0.23
	Water	<u>85.31</u>	<u>85.96</u>	81.51
	Totals	100.00	100.00	100.00

<sup>\*</sup>This is the same composition as Example 1.

<sup>35</sup> Mildness results reported below.

TABLE 6

Effect of the Ratio of Sodium Lauryl Sulfate to

Sodium Laureth Sulfate

		Experi-	
5		mental	
	<u>Ingredients</u>	Comp. E2	<u>Ex. 7</u>
	Ammonium Lauryl Sulfate	-	-
	Sodium Lauryl Sulfate	4.00	8.00
	Sodium Laureth Sulfate	8.00	4.00
10	Cocamidopropyl Betaine	1.50	1.50
	Lauramide DEA	1.50	1.50
	Polyquaternium-10	0.50	0.50
	Triclosan	0.20	0.20
	Ethylene Glycol		
15	Monostearate	1.50	1.50
	Disodium Ricinoleamido		
	MEA-Sulfosuccinate	-	-
	Isostearamidopropyl		
	Morpholine Lactate	-	-
20	Glycerin	-	-
	Sodium Acetate	0.40	-
	Tetrasodium EDTA	0.10	0.10
	DMDM Hydantoin	0.20	0.20
	Perfume	0.25	0.25
25	Dye	0.01	0.01
	Citric Acid	0.08	0.08
	Water	<u>82.76</u>	<u>83.26</u>
	- Totals	100.00	100.00
	MIC Test Results		
30	Zone of Inhibition	32.91	35.09
	Difference vs. E2		2.18
	p-value: probability that		
	the difference in the zor	ne	
	at inhibition for E2 and		
35	Ex. 7 is equal to zero		0.01

Referring to the MIC test results in Table 6, E2 vs. Example 7, shows E2 has too much ethoxylated surfactant, sodium laureth sulfate. E2 is lower in degerming via a lower zone of inhibition.

<u>TABLE 7</u>

<u>Table of Comparative Examples</u>

		Experi-	- Experi-
		mental	mental
	<u>Ingredients</u>	Comp. E3	Comp. E4
10	Ammonium Lauryl Sulfate	4.00	4.00
	Ammonium Laureth Sulfate	8.00	8.00
	Cocamidopropyl Betaine	1.50	1.50
	Lauramide DEA	1.50	1.50
	Polyquaternium-10	0.50	0.50
15	Triclosan (TCS)	0.25	0.50
	Ethylene Glycol		
	Monostearate	1.50	1.50
	Sodium Acetate	0.40	0.40
	Tetrasodium EDTA	0.10	0.10
20	DMDM Hydantoin	0.20	0.20
	Perfume	0.25	0.25
	Dye	0.01	0.01
	Citric Acid	0.08	0.08
	Water	<u>82.76</u>	82.26
25	Totals	100.00	100.00

Referring to the Comparative MIC Performance below, E3 and E4 are formulae which would be expected to be milder than "A" based on higher levels of milder surfactants and lower levels of harsher surfactants. However, their degerming efficacies are compromised, that is to say, reduced.

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## <u>Comparative MIC Performance for Experimental</u> <u>Comparative E3 vs. Experimental Comparative E4</u>

100% Product Concentrations tested on Staphylococcus aureus (N=4	100%	Product	<u>Concentrations</u>	tested	on Staphy	lococcus	aureus	(N=4)
--	------	---------	-----------------------	--------	-----------	----------	--------	-------

5	Comp. E3	Comp. E4	Comp. A
Mean	49.75	48.50	62.75
p-value vs. E3		0.66	0.01
p-value vs. E4			0.00

### 10 1% Product Concentrations tested on Escherichia coli (N=4)

	<u>Comp. E3</u>	Comp. E4	<u>Comp. A</u>
Mean	28.50	29.25	37.75
p-value vs. E3		0.79	0.04
p-value vs. E4			0.06

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Conclusion: The point is that higher levels of antibacterial in these formulae (E3 and E4) do not fix reduced degerming which results from increased level of mild ethoxylated surfactant. See Referring to Table 6 and its MIC test results, Example 7 vs. E2, also demonstrate this point more clearly, for the only variables are the levels of the harsh and mild surfactants.

### <u>Paired Comparison Forearm Clinical Mildness Test</u> <u>Paired Comparison #1: Comparative El vs. Example 6</u>

			Jempa, doite	LI TO. LAUM	<u> </u>
25					Diff.
	<u>Attribute</u>	Comp. E1	<u>Ex. 6</u>	<u>Diff.</u>	<u>p-Value</u>
	Visual Dryness	2.00	1.16	0.84	0.0001*
	Scopeman Dryness	2.24	1.74	0.50	0.0001*
	Visual Redness	2.16	1.37	0.79	0.0002*
30	Skicon	67.45	75.23	-7.78	0:0450*

<sup>\*</sup>Significant at 95% confidence.

Paired Comparison #2: Comparative Composition A vs.

Experimental Comparative El

					Diff.
	<u>Attribute</u>	"A"_	Comp. El	<u>Diff.</u>	<u>p-Value</u>
5	Visual Dryness	1.89	1.97	-0.08	0.6083
	Scopeman Dryness	2.14	2.11	0.03	0.8067
	Visual Redness	2.02	2.35	-0.32	0.0746
	Skicon	69.60	67.88	1.72	0.7291

# 10 <u>Comparison #3: Example 6 vs. Comparative Composition A</u> <u>Statistical Evaluation Across Pairs\*\*</u>

					Diff.
	<u>Attribute</u>	<u>Ex. 6</u>	"A"	Diff.	<u>p-Value</u>
	Visual Dryness	1.15	1.91	-0.76	0.0012*
15	Scopeman Dryness	1.67	2.19	-0.52	0.0015*
	Visual Redness	1.47	1.94	-0.47	0.0736
	Skicon	75.9	69.62	6.28	0.3171

\*Significant at 95% confidence.

\*\*Between pair estimate of (Example 6 vs. "A") obtained as the difference of the two within-pair estimates, (Example 6 vs. E1) - ("A" vs. E1). The means are adjusted to compensate for difference in the means of E1 from one pair to another.

Referring to the MIC test results in Table 3, Example 1 demonstrates equivalent degerming to Comparative "A". The liquid cleansing compositions of the present invention also demonstrate superior mildness to the skin as measured by a clinical mildness test, the results of which are set out in Paired Comparisons # 1 and #2, and Comparison #3. These significant improvements in degerming and mildness are unexpected and surprising in view of the higher ratio of harsher cosurfactant to mild ethoxylated surfactant. The preferred executions are Examples 1, 2, and 5, which contain cationic polymer. Specifically, Paired Comparison #1 demonstrates that the addition of 0.25% Jaguar C-14-S in

the formula of Example 1 improves mildness over E1, which is formulated with the same surfactant base but without polymer and opacifier. Paired Comparison #2 demonstrates that E1 has equal mildness performance to "A". Finally, Comparison #3 is a statistical evaluation across Paired Comparisons #1 and #2 demonstrating that Example 1 (also appears as Example 6 in Table 5) is milder to the skin than "A".

It is important to note that the cationic polymer also improves the antibacterial activity of the product. Referring to Table 4, it is shown with Example 3 and Example 4 that increasing the polymer level from 0.25% to 0.5% significantly increases the antibacterial activity at a constant 0.3% level of TCS.

WHAT IS CLAIMED IS:

- 1. An antibacterial liquid personal cleansing composition comprising:
  - (A) from about 0.5% to about 5.8% of a mild ethoxylated surfactant;
  - (B) from about 1% to about 40% of an antibacterial compatible non-ethoxylated cosurfactant;
  - (C) from about 0.01% to about 4% of antibacterial agent;
  - (D) from about 0.05% to about 5% of water-soluble cationic polymer, and wherein said cationic polymeric has a molecular weight of from 1000 to 3,000,000; and
- (E) from about 35% to about 97% water; and wherein said cosurfactant (B) contains harsh lathering surfactant at a level to provide a ratio of harsh lathering surfactant to said mild ethoxylated surfactant (A) of from about 20:1 to about 1:5.8; and wherein the total level of said (A) and said (B) is at least 4% by weight of said composition.
- 2. The antibacterial liquid personal cleansing composition of Claim 1 wherein:
  - (A) said mild ethoxylated surfactant is present at a level of from about 2% to about 5%; and wherein said mild ethoxylated surfactant is selected from the group consisting of alkali metal and ammonium salts of the sulfuric acid esters of the reaction product of 1 mole of a C8-C22 alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 20 moles of ethylene oxide (ethoxy groups);
  - (B) said non-ethoxylated cosurfactant is present at a level of from about 4% to about 20%;
  - (C) said antibacterial agent is present at a level of from about 0.5% to about 2%;
  - (D) said polymer is present at a level of from about 0.1% to about 2%; and
  - (E) said water is present at a level of from about 50% to about 95%; and

wherein said ratio of said harsh lathering surfactant and said (A) is from about 5:1 to about 1:2.

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- 3. The antibacterial liquid personal cleansing composition of Claim 1 wherein:
  - (A) said mild ethoxylated surfactant is present at a level of from about 3% to about 5%; and wherein said mild ethoxylated surfactant is selected from the group consisting of alkali metal and ammonium salts of the sulfuric acid esters of the reaction product of 1 mole of a C8-C22 alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 13 moles of ethylene oxide (ethoxy groups);
  - (B) said non-ethoxylated cosurfactant is present at a level of from about 5% to about 10%;
  - (C) said antibacterial agent is present at a level of from about 0.2% to about 1%;
  - (D) said polymer is present at a level of from about 0.2% to about 1%; and
  - (E) said water is present at a level of from about 75% to about 90%; and

wherein said harsh surfactant and said (A) has a ratio of from about 2:1 to about 1:1.

- 4. The antibacterial liquid personal cleansing composition of Claim 1 wherein:
  - (A) said mild ethoxylated surfactant is selected from the group consisting of anionic and nonionic; and wherein said mild anionic ethoxylated surfactant is selected from the group consisting of alkali metal and ammonium salts of the sulfuric acid esters of the reaction product of 1 mole of a C8-C22 alcohol (e.g., tallow or coconut oil alcohols) and about 2 to 6 moles of ethylene oxide (ethoxy groups);
  - (B) said non-ethoxylated cosurfactant is selected from the group consisting of anionic, nonionic, zwitterionic, and amphoteric surfactants and mixtures thereof;
  - (C) said antibacterial agent is selected from the group consisting of 3,4,4'-trichlorocarbanilide (TCC); 3-tri-fluoromethyl-4,4'-dichlorocarbanilide (TFC); 2-hydroxy-4,2',4'-trichlorodiphenylether (TCS); and mixtures thereof;

- (D) said polymer is selected from the group consisting of: (I) cationic polysaccharides;
  - (II) cationic copolymers of saccharides and synthetic cationic monomers; and
  - (III) synthetic polymers selected from the group consisting of:
    - (A) cationic polyalkylene imines;
    - (B) cationic ethoxypolyalkylene imines; and
- 5. The composition of Claim 1 wherein said antibacterial agent is selected from the group consisting of 3,4,4'-trichlorocarbanilide (TCC); 3-trifluoromethyl-4,4'-dichlorocarbanilide (TFC); 2-hydroxy-4,2',4'-trichlorodiphenylether (TCS); and mixtures thereof.
- 6. The composition of Claim 1 wherein said antibacterial agent is 2-hydroxy-4,2',4'-trichlorodiphenylether (TCS).
- 7. The composition of Claim 1, 2, 3, 4, 5 or 6 wherein said cationic polymeric has a molecular weight of from 1000 to 3,000,000 and a typical aqueous viscosity at 1-2% of from about 125 cps to about 3200 cps and wherein said cationic polymer is selected from the group consisting of:
  - (I) cationic polysaccharides;
  - (II) cationic copolymers of saccharides and synthetic cationic monomers; and
  - (III) synthetic polymers selected from the group consisting of:
    - (A) cationic polyalkylene imines;
    - (B) cationic ethoxypolyalkylene imines; and
    - (C) cationic poly(N-(3-(dimethylammonio)propyl)-N'-(3-(ethyleneoxyethylene dimethylammonio)propyl)urea dichloride).
- 8. The composition of Claim 1, 2, 3, 4, 5, 6, 7 or 8 wherein said polymer comprises a cationic guar gum polymer; preferably wherein the

polymer is selected from the group consisting of the cationic guar gum and cationic guar gum derivatives of a molecular weight from 2,500 to 350,000.

191. The composition of Claim 1, 2, 3, 4, 5, 6, 7, 8, or 9 wherein said composition contains from about 4% to about 20% of total surfactants selected from the group consisting of: alkyl sulfates, alkyl glyceryl ether sulfonates, anionic acyl sarcosinates, methyl acyl taurates, N-acyl glutamates, alkyl glucosides, acyl isethionates, alkyl sulfosuccinates, alkyl phosphate esters, ethoxylated alkyl phosphate esters, methyl glucose esters, protein condensates, mixtures of ethoxylated alkyl sulfates and alkyl amine oxides, betaines, sultaines, the alkyl ether sulfates with 1 to 12 ethoxy groups, and mixtures thereof, wherein said surfactants contain  $C_8$ - $C_{22}$  alkyl chains; preferably wherein said cosurfactant has an alkyl chain length of  $C_{10}$ - $C_{18}$ .

#### INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/02847

I. CLASSIFICATION OF SUBJECT MATTER (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 A61K7/50	; A61K7/48;	A61K7/08;	C11D3/48			
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II. FIELDS	SEARCHED						
		Minimum Documen	station Searched <sup>7</sup>				
Classificatio	on System	` C	lassification Symbols				
Int.Cl.	Int.Cl. 5 A61K; C11D						
		Documentation Searched other to to the Extent that such Documents a					
				:			
III. DOCUM	IENTS CONSIDERE	D TO BE RELEVANT <sup>9</sup>					
Category o	Citation of D	ocument, 11 with indication, where appropria	te, of the relevant passages 12	Relevant to Claim No. <sup>13</sup>			
Х	cited i	761 418 (J.J. PARRAN) 29 n the application whole document	5 September 1973	1-5,7-9			
X A	US,A,4 329 336 (D. T. SU) 11 May 1982 see column 2, line 20 - line 68 see column 3, line 38 - line 68 see column 4, line 1 - line 63 see column 5, line 20 - line 25 see claims 1-7						
P,X P,Y							
			-/				
"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 filing date.  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means  "P" document published prior to the international filing date but later than the priority date claimed							
IV. CERTIE	TCATION						
Date of the		the International Search GUST 1992	Date of Mailing of this Internat 0 4. 09, 92	•			
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International	International Searching Authority  EUROPEAN PATENT OFFICE  Signature of Authorized Officer  SIERRA GONZALEZ ierre ierre						

	International Application No		
	NTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SI		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages		
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(	EP,A,O 417 501 (J.A. BENCKISER GMBH) 20 March	1	
	1001	1,4-6,9	
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