



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

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<b>(21) International Application Number:</b> PCT/EP97/00914 <b>(22) International Filing Date:</b> 25 February 1997 (25.02.97) <b>(30) Priority Data:</b> 08/616,942 18 March 1996 (18.03.96) US <b>(71) Applicant (for AU BB CA GB IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). <b>(71) Applicant (for all designated States except AU BB CA GB IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). <b>(72) Inventors:</b> HE, Mengtao; 9 Tuxedo Drive, Wayne, NJ 07470 (US). FAIR, Michael, Joseph; 290 Anderson Road, Hackensack, NJ 07601 (US). MASSARO, Michael; 39 Dover Road, Congers, NY 10920 (US). <b>(74) Agent:</b> ELLIOTT, Peter, William; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BI, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> With international search report.
<b>(54) Title:</b> BAR COMPOSITION COMPRISING COPOLYMER MILDNESS ACTIVES <b>(57) Abstract</b> <p>The present invention is directed to synthetic bar compositions wherein relatively small amounts of specified polyoxyethylene-polypropylene nonionic polymer has been found to enhance mildness of bar compositions.</p>		

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## FIELD OF THE INVENTION

The present invention relates to synthetic bar compositions (i.e., bars in which at least some fatty acid soap has been replaced by synthetic surfactants, such as anionic surfactants).

Traditionally, soap has been utilized as a skin cleanser. Notwithstanding its many advantages (e.g., inexpensive, easy to manufacture into bars, having good lathering properties), soap is a very harsh chemical. Irritated and cracked skin often result from the use of soap, especially in colder climates.

In order to maintain cleaning effectiveness and reduce harshness, the art has used synthetic surfactants to replace some or all of the soap. In particular, anionic surfactants have been used because these tend to most clearly mimic the lather generation which soap readily provides.

Anionic surfactants, however, are still harsh. One method of reducing the harshness of anionic surfactants is to utilize other surfactants such as nonionic or other mildness surfactants (e.g., amphoteric). The use of surfactants other than anionics, however, can introduce other problems. For example, nonionic surfactants generally do not generate creamy thick lather as do anionics; and both nonionics and amphoterics, for example can be sticky and introduce processing difficulties.

For this reason, the art is always searching for materials which are milder than anionic and/or which can be used to replace at least some of the anionic surfactants, yet, which do not simultaneously seriously compromise lather generation or processing efficiency. Further, even if the anionic is not substituted, the art is always searching for materials which can substitute for inerts and/or other fillers and produce enhanced mildness.

Unexpectedly, applicants have found that the use of relatively low levels of specific nonionic polymeric surfactants can be used to obtain these goals. That is, at levels no higher than 10% by wt. of the bar composition, the polymers provide enhanced mildness without sacrificing processability or lather. While not wishing to be bound by theory, it is believed that the copolymers may be interacting with anionic surfactant to form polymer-surfactant complexes thereby reducing free anionic surfactant (known for its harshness) from the bar.

The use of polyoxyethylene polyoxypropylene (EO-PO) nonionic polymeric surfactants in bar compositions per se is not new.

U.S. Patent No. 3,312,627 to Hooker, for example, teaches bars substantially free of anionic detergents comprising 0 to 70% by weight EO-PO polymer, polyethylene glycol (PEG) or derivatives of these compounds as base; and 10 to 70% of a nonionic lathering component. In order to give these bars more "soap-like" characteristics, the reference contemplates use of 10%-80% lithium soap. It is clear that use of lithium soap is unique to the invention (column 8, lines 20-23) and that use of other soaps or anionic (other than fatty acid lithium soap) is not contemplated. Thus, this reference clearly differs from the

composition of the invention which comprise 10 to 50% of a surfactant system of which at least 50% (though no more than 40% total of total composition) is anionic surfactant.

5 U.S. Patent No. 3,766,097 to Rosmarin discloses the use of 30%-50% of a specified EO-PO copolymer (Pluronic F-127) in a bar using sodium cocoyl isethionate as primary anionic surfactant. Here again, the polymer is being used as a bar  
10 structurant at levels well above the 10% upper limit of the subject invention. There is no teaching or suggestion that the polymers can be used in combination with anionic at much lower levels to unexpectedly and remarkably enhance mildness (e.g., reduce irritation) at these low levels.

15 U.S. Serial No. 08/213,287 to Chambers et al. (assigned to Lever Brothers) teaches that certain solid EO-PO polymers can be used as alternatives to solid polyethylene glycols (PEGs) as bar structurants for synthetic bar formulations. Once more, the polymers are contemplated for use as  
20 structurants, i.e., at much higher levels than the levels under 10% by wt. of the subject application. There is again no teaching or suggestion that the polymers can be used at much lower levels (both as total percentage of compositions and as ratio to total level of anionics) to provide enhanced  
25 mildness (i.e., reduced skin irritation).

#### BRIEF SUMMARY OF THE INVENTION

30 Applicants have now found that the use of relatively small amounts of defined polyoxyethylene-polyoxypropylene nonionic polymer surfactants in bar compositions comprising primarily anionic surfactant systems remarkably and unexpectedly enhances the mildness of these bars.

More specifically, applicants' invention relates to bar compositions comprising:

(a) 10% to 70% by wt. total composition of a surfactant system selected from the group consisting of anionic surfactants, nonionic surfactants (other than the nonionic EO-PO polymer), cationic surfactants, amphoteric surfactants and mixtures thereof;

wherein the anionic surfactant comprises at least 50%, preferably at least 60% of said surfactant system and wherein the anionic component further comprises no more than about 40% by wt. of total composition;

(b) 20% to 85% by wt., preferably 30 to 70% total composition of a bar structurant selected from the group consisting of alkylene oxide compounds having a molecular weight of from about 2000 to about 25,000, preferably 3,000 to 10,000;  $C_8$ - $C_{22}$  free fatty acids, paraffin waxes; water soluble starches (e.g., maltodextrin); and  $C_8$ - $C_{20}$  alkanols; and

(c) 3% to 10% by wt. total composition of a polyoxyethylene-polyoxypropylene nonionic polymer surfactant (EO-PO polymer);

wherein ratio of anionic surfactant to EO-PO polymer is between 2.5:1 to 10:1, preferably 4:1 to 7:1.

The composition may optionally comprise 0% to 25%, preferably 2% to 15% by wt. solvent such as ethylene oxide or propylene oxide.

Figure 1 shows the Zein % dissolved by acyl isethionate/cocoamidopropyl betaine as a function of Pluronic (EO-PO polymer) concentration. In contrast to PEG 8000,

Pluronic F88 and 25R8 significantly reduced the Zein % dissolved at even quite low levels, such as 0.3 wt.% (at sodium acyl isethionate (SAI) to EO-PO weight ratio at 1:0.15, this is equivalent to about 4% EO-PO in the bar of Formulation (a) in Table 2, Example 1). Therefore the irritation potential of a personal washing bar can be further reduced by including relatively low levels (i.e. 10% and under in a full bar composition; this would correspond to about 0.74% in the liquor as shown in Figure 1) of Pluronics in the bar formulation. The data also showed that EO-terminated Pluronic F88 is potentially a better mildness enhancer than the PO-terminated Pluronic 25R8.

Figure 2 shows the EO-PO polymer of the invention significantly reduces skin irritation caused by DEFI.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to synthetic bar compositions wherein the majority of the surfactant system of the bar comprises anionic surfactant; and to specific nonionic copolymers which can be used in such bar compositions to significantly enhance bar mildness.

More specifically, the bar compositions comprise

- (a) 10% to 70% by weight total composition of a surfactant system wherein said surfactant system is selected from the group consisting of anionic surfactants, nonionic surfactants (other than the EO-PO polymer), amphoteric surfactants, cationic surfactants and mixtures thereof, wherein the anionic comprises 50% or more, preferably 60% or more, of the surfactant system and the anionic further comprises no more than 40% of the total

composition;

(b) 20% to 85% by wt. total composition of a bar  
structurant selected from the group consisting of  
polyalkylene glycols having a MW of from about  
2,000 to 25,000 (which may optionally include 1% to  
5% higher molecular weight polyalkylene glycols  
having MW from 50,000 to 500,000, especially around  
100,000); C<sub>8</sub> to C<sub>24</sub>, preferably C<sub>12</sub> to C<sub>24</sub> fatty  
acids; paraffin waxes; water soluble starches  
(e.g., maltodextrin); and C<sub>8</sub> to C<sub>20</sub> alkanols (e.g.,  
cetyl alcohol); and

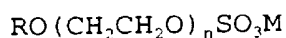
(c) 3% to 10% by weight total composition of a  
polyoxyethylene, polyoxypropylene nonionic polymer  
surfactant

wherein ratio of anionic surfactant to EO-PO polymers is  
between 2.5:1 to 10:1, preferably 4:1 to 7:1.

#### Surfactant System

The anionic detergent active which may be used may be  
aliphatic sulfonates, such as a primary alkane (e.g., C<sub>8</sub>-C<sub>22</sub>)  
sulfonate, primary alkane (e.g., C<sub>8</sub>-C<sub>22</sub>) disulfonate, C<sub>8</sub>-C<sub>22</sub>  
alkene sulfonate, C<sub>8</sub>-C<sub>22</sub> hydroxyalkane sulfonate or alkyl  
glycerol ether sulfonate (AGS); or aromatic sulfonates such  
as alkyl benzene sulfonate.

The anionic may also be an alkyl sulfate (e.g., C<sub>12</sub>-C<sub>18</sub>  
alkyl sulfate) or alkyl ether sulfate (including alkyl  
glycerol ether sulfates). among the alkyl ether sulfates are  
those having the formula:

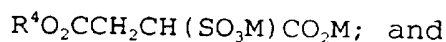




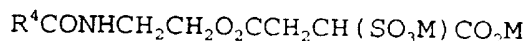
wherein R is an alkyl or alkenyl having 8 to 18 carbons, preferably 12 to 18 carbons, n has an average value of greater than 1.0, preferably greater than 3; and M is a solubilizing cation such as sodium, potassium ammonium or substituted ammonium. Ammonium and sodium lauryl ether sulfates are preferred.

The anionic may also be alkyl sulfosuccinates (including mono- and dialkyl, e.g., C<sub>8</sub>-C<sub>22</sub> sulfosuccinates); alkyl and acyl taurates, alkyl and acyl sarcosinates, sulfoacetates, C<sub>8</sub>-C<sub>22</sub> alkyl phosphates and phosphates, alkyl phosphate esters and alkoxyl alkyl phosphate esters, acyl lactates, C<sub>8</sub>-C<sub>22</sub> monoalkyl succinates and maleates, sulphoacetates, alkyl glucosides and acyl isethionates.

Sulfosuccinates may be monoalkyl sulfosuccinates having the formula:

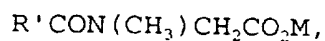


amide-MEA sulfosuccinates of the formula:



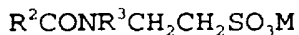
wherein R<sup>4</sup> ranges from C<sub>8</sub>-C<sub>22</sub> alkyl and M is a solubilizing cation.

Sarcosinates are generally indicated by the formula:



wherein R ranges from C<sub>8</sub>-C<sub>20</sub> alkyl and M is a solubilizing cation.

Taurates are generally identified by formula:

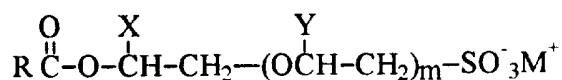


5            wherein  $R^2$  ranges from  $C_8$ - $C_{18}$  alkyl,  $R^3$  ranges from  $C_1$ - $C_4$   
a alkyl and M is a solubilizing cation.

10            Particularly preferred are the  $C_8$ - $C_{18}$  acyl isethionates.  
These esters are prepared by reaction between alkali metal  
isethionate with mixed aliphatic fatty acids having from 6 to  
18 carbon atoms and an iodine value of less than 20. At  
least 75% of the mixed fatty acids have from 12 to 18 carbon  
atoms and up to 25% have from 6 to 10 carbon atoms.

15            Acyl isethionates, when present, will generally range  
from about 10% to about 70% by weight of the total  
composition. Preferably, this component is present from  
about 30% to about 60%.

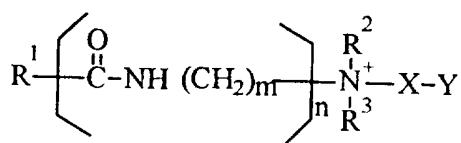
20            The acyl isethionate may be an alkoxylated isethionate  
such as is described in Ilardi et al., U.S. Patent No.  
5,393,466, hereby incorporated by reference. This compound  
has the general formula:



30            wherein R is an alkyl group having 8 to 18 carbons, m is  
an integer from 1 to 4, X and Y are hydrogen or an alkyl  
group having 1 to 4 carbons and  $M^+$  is a monovalent cation  
such as, for example, sodium, potassium or ammonium.

35            The anionic surfactant comprises 50% or more of the  
total surfactant system, but should comprise no more than 40%  
by wt. of the total composition.

Amphoteric detergents which may be used in this invention include at least one acid group. This may be a carboxylic or a sulphonic acid group. They include quaternary nitrogen and therefore are quaternary amido acids. They should generally include an alkyl or alkenyl group of 7 to 18 carbon atoms. They will usually comply with an overall structural formula.



where  $R^1$  is alkyl or alkenyl of 7 to 18 carbon atoms;

$R^2$  and  $R^3$  are each independently alkyl, hydroxyalkyl or carboxyalkyl of 1 to 3 carbon atoms;

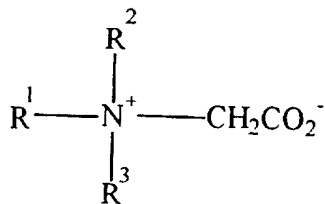
$m$  is 2 to 4;

$n$  is 0 to 1;

$X$  is alkylene of 1 to 3 carbon atoms optionally substituted with hydroxyl, and

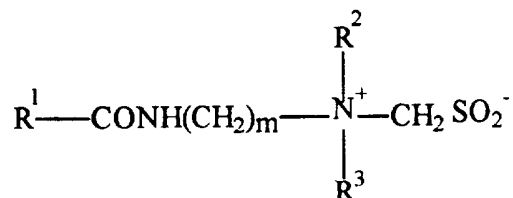
$Y$  is  $-CO_2^-$  or  $-SO_3^-$

Suitable amphoteric detergents within the above general formula include simple betaines of formula:



10

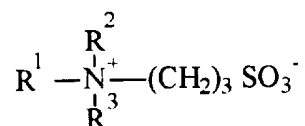
and amido betaines of formula:



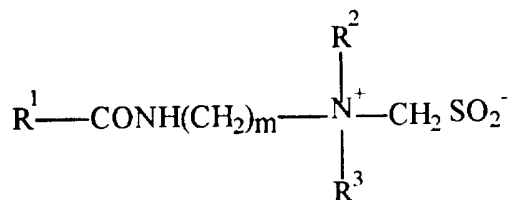
wherein m is 2 or 3.

In both formulae  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are as defined previously.  $\text{R}^1$  may in particular be a mixture of  $\text{C}_{12}$  and  $\text{C}_{14}$  alkyl groups derived from coconut so that at least half, preferably at least three quarters of the groups  $\text{R}^1$  are preferably methyl.

A further possibility is that the amphoteric detergent is a sulphobetaine of formula

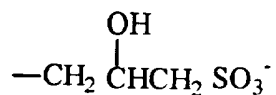


or



wherein m

is 2 or 3, or variants of these in which  $-(\text{CH}_2)_3 \text{SO}_3^-$  is replaced by



5 in these formulae  $R^1$ ,  $R^2$  and  $R^3$  are as discussed previously.

10 The nonionic which may be used includes in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene  
15 oxide. Specific nonionic detergent compounds are alkyl ( $C_6$ - $C_{22}$ ) phenols-ethylene oxide condensates, the condensation products of aliphatic ( $C_8$ - $C_{18}$ ) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamene. Other so-called nonionic  
20 detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

25 The nonionic may also be a sugar amide, such as a polysaccharide amide. Specifically, the surfactant may be one of the lactobionamides described in U.S. Patent No. 5,389,279 to Au et al. which is hereby incorporated by reference or it may be one of the sugar amides described in Patent No. 5,009,814 to Kelkenberg, hereby incorporated into  
30 the subject application by reference.

Other surfactants which may be used are described in U.S. Patent No. 3,723,325 to Parran Jr. which is also incorporated into the subject application by reference.

Nonionic and cationic surfactants which may be used include any one of those described in U.S. Patent No. 3,761,418 to Parran, Jr. hereby incorporated by reference into the subject application. Those included are the  
5 aldobionamides taught in U.S. Patent No. 5,389,279 to Au et al. and the polyhydroxy fatty acid amides as taught in U.S. Patent No. 5,312,934 to Letton, both of which are incorporated by reference into the subject application.

10 The surfactants generally comprise 10 to 50% of the total composition except, as noted that anionic comprises 50% or more of the surfactant system and no more than 40% total.

15 A preferred surfactant system is one comprising acyl isethionate and a amphoteric, i.e., betaine, as co-surfactant.

### Structurant

20 The structurant of the invention can be a water soluble or water insoluble structurant.

25 Water soluble structurants include moderately high molecular weight polyalkylene oxides of appropriate melting point (e.g., 40° to 100°C, preferably 50° to 90°) and in particular polyethylene glycols or mixtures thereof.

30 Polyethylene glycols (PEG's) which are used may have a molecular weight in the range 2,000 to 25,000, preferably 3,000 to 10,000. However, in some embodiments of this invention it is preferred to include a fairly small quantity of polyethylene glycol with a molecular weight in the range from 50,000 to 500,000, especially molecular weights of around 100,000. Such polyethylene glycols have been found to  
35 improve the wear rate of the bars. It is believed that this

is because their long polymer chains remain entangled even when the bar composition is wetted during use.

5 If such high molecular weight polyethylene glycols (or any other water soluble high molecular weight polyalkylene oxides) are used, the quantity is preferably from 1% to 5%, more preferably from 1% or 1.5% to 4% or 4.5% by weight of the composition. These materials will generally be used jointly with a large quantity of other water soluble  
10 structurant such as the above mentioned polyethylene glycol of molecular weight 2,000 to 25,000, preferably 3,000 to 10,000.

15 Water insoluble structurants also have a melting point in the range 40-100°C, more preferably at least 50°C, notably 50°C to 90°C. Suitable materials which are particularly envisaged are fatty acids, particularly those having a carbon chain of 12 to 24 carbon atoms. Examples are lauric, myristic, palmitic, stearic, arachidic and behenic acids and  
20 mixtures thereof. Sources of these fatty acids are coconut, topped coconut, palm, palm kernel, babassu and tallow fatty acids and partially or fully hardened fatty acids or distilled fatty acids. Other suitable water insoluble structurants include alkanols of 8 to 20 carbon atoms,  
25 particularly cetyl alcohol. These materials generally have a water solubility of less than 5 g/litre at 20°C.

30 Soaps (e.g., sodium stearate) can also be used at levels of about 1% to 15%. The soaps may be added neat or made in situ by adding a base, e.g., NaOH, to convert free fatty acids.

35 The relative proportions of the water soluble structurants and water insoluble structurants govern the rate at which the bar wears during use. The presence of the

water-insoluble structurant tends to delay dissolution of the bar when exposed to water during use and hence retard the rate of wear.

5           The structurant is used in the bar in an amount of 20% to 85%, preferably 30% to 70% by wt.

#### EO - PO Polymer

10           The polyoxyethylene polyoxypropylene nonionic copolymers (EO-PO copolymers) of the subject invention are generally commercially available polymers having a broad molecular weight range and EO/PO ratio and a melting temperature of from about 25° to 85°C, preferably 40° to 65°C.

15           Generally, the polymers will be selected from one of two classes of polymers, i.e., (1)  $(EO)_m(PO)_n(EO)_m$  type copolymers or  $(PO)_n(EO)_m(PO)_n$  type copolymers of defined m/n ratio and optional hydrophobic moieties (e.g., decyltetradecanol ether) attached to either EO or PO compounds (such products are  
20           commercially available for example, from BASF under the Trademark Pluronic<sup>(R)</sup> or Pluronic-R<sup>(R)</sup>, respectively); or (2) EO-PO polymers with amine constituents such as  $N_2C_2H_4(PO)_{4n}(EO)_{4m}$  or  $N_2C_2H_4(EO)_{4m}(PO)_{4n}$  with defined values of m  
25           and n and optional hydrophobic moieties [for example?] attached to either EO or PO components (such products are commercially available, for example from BASF as Tetronic<sup>(R)</sup> and Tetronic-R<sup>(R)</sup>, respectively).

30           Specifically, examples of various Pluronic and Tetronic EO-PO polymers are set forth in Table 1 below wherein  $T_m$  (°C) and Ross Miles foam height data (measured at 0.1% and 50°C) were digested from literature from BASF.



TABLE 1

Polymer		$T_m(^{\circ}\text{C})$	Foam Heights (ml)	EO and PO Number
Pluronic:	$(\text{EO})_m - (\text{PO})_n - (\text{EO})_m$			m/n
	F38	48	35	46/16
	F68	52	35	75/30
	F77	48	47	52/35
	F87	49	44	62/39
	F88	54	48	97/39
	F98	58	43	122/47
	F108	57	41	128/54
	F127	56	41	98/67
Pluronic-R:	$(\text{PO})_n - (\text{EO})_m - (\text{PO})_n$			
	10R8	46	20	90/9
	17R8	53	2	155/15
	25R8	54	15	227/21
Tetronic:	$\text{N}_2\text{C}_2\text{H}_4 - (\text{PO})_{4n}(\text{EO})_{4m}$			
	707	46	60	35/12
	1107	51	50	64/20
	908	58	40	85/16
	1307	54	40	78/25
	1508	60	40	159/30
Tetronic-R:	$\text{N}_2\text{C}_2\text{H}_4 - (\text{EO})_{4m}(\text{PO})_{4n}$			
	90R8	47	0	90/17
	110R7	47	0	64/21
	150R8	53	0	12/29

In general, the molecular weight of the copolymers used ranges from 2,000 to 25,000 (preferably 3,000 to 10,000). The EO-terminated polymers (Pluronic and Tetronic) are preferred to the PO-terminated ones (Pluronic-R and Tetronic-R) for the advantages of mildness enhancement and lather generation. To ensure water solubility, we prefer that the portion of ethylene oxide moiety per mole is between 50% to 90% wt., more preferably 60-85% wt. In other words, 2m:n (for Pluronic) or m:n (for Tetronic) ranges from 1.32 to 11.9, preferably 2.0 to 7.5.

As noted, melting temperature of the compounds must be about 25°-85°, preferably 40° to 65°C, the latter being more favorable for processing (e.g., chips form more easily and logs plod more readily).

Bars of the invention may comprise 0% to 25%, preferably 2% to 15% by wt. of an emollient such as ethylene glycol, propylene glycol and/or glycerine.

#### Other Ingredients

Bar compositions of this invention will usually contain water, but the amount of water is only a fairly small proportion of the bar. Larger quantities of water reduce the hardness of the bars. Preferred is that the quantity of water is not over 15% by weight of the bars, preferably 1% to about 10%, more preferably 3% to 9%, most preferably 3% to 8%.

Bars of this invention may optionally include so-called benefit agents - materials included in relatively small proportions which confer some benefit additional to the basic cleansing action of the bars. Examples of such agents are: skin conditioning agents, including emollients such as fatty alcohols and vegetable oils, essential oils, waxes,

phospholipids, lanolin, anti-bacterial agents and sanitizers, opacifiers, pearlescers, electrolytes, perfumes, sunscreens, fluorescers and coloring agents. Preferred skin conditioning agents comprise silicone oils, mineral oils and/or glycerol.

The examples below are intended to better illustrate the invention, but are not intended to be limiting in any way.

All percentages, unless otherwise noted, are intended to be percentages by weight.

### EXAMPLES

#### Methodology

#### Mildness Assessments

Zein dissolution test was used to preliminarily screen the irritation potential of the formulations studied. In an 8 oz. jar, 30 mLs of an aqueous dispersion of a formulation were prepared. The dispersions sat in a 45°C bath until fully dissolved. Upon equilibration at room temperature, 1.5 gms of zein powder were added to each solution with rapid stirring for one hour. The solutions were then transferred to centrifuge tubes and centrifuged for 30 minutes at approximately 3,000 rpms. The undissolved zein was isolated, rinsed and allowed to dry in a 60°C vacuum oven to a constant weight. The percent zein solubilized, which is proportional to irritation potential, was determined gravimetrically.

#### The Protocol of 3-Day Patch Test

Patch test was used to evaluate skin mildness of aqueous dispersions containing 1% DEFI active (sodium cocoyl

isethionate) and different levels of the structurant/coactives. Patches (Hilltop<sup>(R)</sup> Chambers, 25 mm in size) were applied to the outer upper arms of the panelists under bandage type dressings (Scanpor<sup>(R)</sup> tape). After each designated contact periods (24  
5 hrs. for the first patch application, 18 hrs. for the second and third applications), the patches were removed and the sites were visually ranked in order of severity (erythema and dryness) by trained examiners under consistent lighting.

10

### Formulation Processing

Bar formulations were prepared in a 2-liter Patterson mixer with a sigma type blade. The components were mixed  
15 together at ~95°C, and the water level was adjusted to approximately 8-10 wt.%. The batch was covered to prevent moisture loss, and mixed for about 15 minutes. Then the cover was removed and the mixture was allowed to dry. The moisture content of the samples taken at different times during the  
20 drying stage was determined by Karl Fisher titration with a turbo titrator. At the final moisture level (~5%), the formulation was dropped onto a heated applicator roll and then was chipped over a chill roll. The chill roll chips were plodded under vacuum in a Weber Seelander duplex refiner with  
25 screw speed at ~20 rpm. The nose cone of the plodder was heated to 45-50°C. The cut billets were stamped into bars using a Weber Seelander L4 hydraulic press with a nylon, pillow-shaped die in place.

30 Bars were also prepared by a cast-melt process. First, the components were mixed together at 80-120°C in a 500 ml beaker, and the water level was adjusted to approximately 10-15 wt.%. The batch was covered to prevent moisture loss and was mixed for about 15 minutes. Then the cover was removed, and  
35 the mixture was allowed to dry. The moisture content of the

samples taken at different times during the drying stage and was determined by Karl Fisher titration with a turbo titrator. At the final moisture level (~5%), the mixture in the beaker (in the form of a free-flow liquid) was dropped into bar-molds and was allowed to be cooled at room temperature for four hours. Upon solidification, the mixture was casted in the bar mold into a bar.

#### Example 1

Components as listed in Table 2 below were melted together at 80°C-120°C to produce a material consisting predominantly of a liquid phase. All amounts are provided in percentage by weight. On cooling to 10°C-50°C by a chill-roll, the formulations formed plastic-like solids that were plodded using the extrusion equipment described above (i.e., formulation processing section) and pressed into bars using the single bar press. Identical formulations were also formed into bars by using the casting process from the hot melt. These bars contain a major DEFI active and an optional cocoamidopropyl betaine coactive. These bars provided rich, creamy and slippery lather; the skin-feel of the bars were found to be smooth and non-tacky.

TABLE 2

Formulation	A	B	C	D
Sodium acyl isethionate (from DEFI*)	27.8%	27.0%	27.0%	27.8%
Cocoamidopropyl betaine	5.2	5.0	5.0	5.2
PEG 8000**	32.1	29.5	35.0	45.1
PEG 4000***	3.1	0.0	0.0	0
Stearic-palmitic acid	11.6	8.6	9.0	11.6
Maltodextrin	10.3	10.0	0.0	4.4
Pluronic F88	4.0	5	10	0.0
Tetronic 1107	0	5	0	0
Perfume	0	0.3	0.3	0
Sodium Stearate	0	0	5.0	0
Titanium Dioxide	0	0	0.5	0
EHDP	0	0.1	0.1	0
EDTA	0	0.1	0.1	0
Misc. Salts	0	2.9	2.9	0
Water	5.9	6.5	5.1	5.9

\*DEFI: directly esterified fatty acid isethionate, which is a mixture containing about 74% by weight of fatty acyl isethionate, 23% stearic-palmitic acid and small amounts of other materials, manufactured by Lever Brothers Co., U.S.

\*\* PEG 8000: polyoxyethylene glycol with mean molecular weight at 8000; PEG 4000: polyoxyethylene glycol with mean molecular weight at 4000.

Example 2

Components as listed in Table 3 below were preferably processed using a cast-melt approach described in the methodology section. All amounts are given in percentage of weight. These bars used sodium lauryl sarcosinate (formulation E, G) and sodium lauryl sulphate (formulation F) as the major anionic detergent with optional cocoamidopropyl betaine as a coactive. These bars provided rich, creamy and slippery lather and smooth skin feel.

TABLE 3

Formulation	(E)	(F)	(G)
Sodium Lauryl Sarcosinate	15	0.0	27.0
Cocoamidopropyl Betaine	5.0	5.0	5.0
SLES (3EO)	5.0	20.0	0.0
Stearic-palmitic Acid	5.0	5.0	5.0
PEG 8000	25.0	44.0	39.0
PEG 6000	27.0	8.0	5.0
Pluronic F88	10.0	10.0	10.0
Paraffin Wax	2.0	2.0	3.0
Perfumes	1.0	1.0	1.0
Water	5.0	5.0	5.0

Example 3

The irritation reduction potential of Pluronics was investigated using Zein dissolution experiments. As indicated in Tables 4 and 5, Pluronic surfactants, as a class, are significantly more effective than PEG in reducing the Zein % dissolved by a 1% aqueous DEFI suspension (DEFI is a sodium

acyl isethionate/fatty acid mixture defined in the Table 2 of Example 1). The data in Tables 4 and 5 also showed that EO terminated Pluronic F127 is potentially a better mildness enhancer than the PO-terminated Pluronic 25R8. Table 6 showed that EO-PO can significantly reduce the Zein % dissolved by even a quite mild detergency system (DEFI/cocoamidopropyl betaine): Tables 4, 5 and 6 are set forth below.

TABLE 4

Component	% Zein Dissolved
1% DEFI	23.9
1% DEFI + 0.8% PLU.F127*	17.8
Water	9.0

TABLE 5

Component	% Zein Dissolved
PEG 8K	20.8
5% PLU.25R8**	8.9
5% PLU.F127*	4.1

TABLE 6\*\*\*

Component	% Zein Dissolved
5% PEG	17.4
5% PLU.F127	3.6

\* Structure of PLU F127 is  $\text{EO}_{28} \text{PO}_{67} \text{EO}_{56}$

\*\* Structure of PLU 25R8 is  $\text{PO}_{21} \text{EO}_{227} \text{PO}_{21}$

\*\*\* Components tested in mild system comprising 1% DEFI/0.8% cocoamidopropyl betaine



Example 4

Three day skin patch tests showed that Pluronic F88 significantly reduced the skin irritation caused by DEFI, even at low levels of addition. As shown in Figure 2, at a Sodium acyl isethionate (SAI) Pluronic F88 weight ratio around 1:0.37 (equivalent to 10% EO-PO in the bar of Formulation (B) or (C) in Table 2 of Example 1), Pluronic F88 reduced the skin irritation of a DEFI/betaine liquor significantly. In contrast, even at SAI/PEG 8000 weight ratio as low as 1:1.67 (effectively 45% PEG 8000 in the bar of formulation D, Table 2) PEG 8000 made no measurable mildness contribution to the SAI/CAP betaine aqueous liquor.

Example 5

Zein dissolution experiments (Table 7 below) revealed that Pluronic F88 can significantly reduce the amount of Zein dissolved by many different types of anionic surfactants commonly used in personal washing products. Thus inclusion of EO-POs in the bar formulations containing the anionic surfactants listed in Table 7 can effectively enhance the mildness of the bars.

TABLE 7

5	Formulation (in distilled water) Anionic Surfactant	Pluronic F88	Zein % Dissolved (w/w) (Standard dev. 2%)
	1% Sodium Lauryl Sarcosinate	0.73%	37.1%
10	1% Sodium Lauryl Sarcosinate	0	43.8
	1% SLES (3EO)	0.73%	28.6
	1% SLES (3EO)	0	35.8
	1% Sodium Lauryl Sulfate	0.73%	59.0
	1% Sodium Lauryl Sulfate	0	66.9
15	1% Sodium Soap (82:18 Tallowate/Cocoate)	0.73%	49.7
	1% Sodium Soap	0	59.7
	1% Sodium Lauryl Isethionate	0.73%	38.5
20	1% Sodium Lauryl Isethionate	0	46.5

**CLAIMS**

1. A bar composition comprising

(a) 10% to 70% by weight of total composition of a surfactant system selected from anionic surfactants, nonionic surfactants other than the nonionic polymer surfactant of item (c) below, cationic surfactants, amphoteric surfactants and mixtures thereof, wherein the anionic surfactant comprises 50% or greater of the surfactant system, and wherein anionic comprises no more than about 40% by wt. of the total composition.

(b) 20% to 85% by wt. of the composition of a bar structurant selected from the group consisting of alkylene oxide components having a molecular weight of from about 2,000 to about 25,000; and C<sub>8</sub>-C<sub>22</sub> free fatty acids; C<sub>2</sub> to C<sub>20</sub> alkanols, paraffin waxes; water-soluble starches; and

(c) 3% to 10% by wt. total composition of a polyoxyethylene polyoxypropylene nonionic polymer surfactant (EO-PO polymer) wherein ratio by weight total composition of anionic surfactant to EO-PO polymer is between 2.5:1 to 10:1.

2. A composition as claimed in claim 1, wherein said surfactant system comprises anionic, amphoteric or mixtures thereof.

3. A composition as claimed in either claim 1 or claim 2, wherein said surfactant comprises acyl isethionate and betaine.

4. A composition as claimed in any preceding claim, wherein structurant (b) comprises 30% to 70% of the bar.

5. A composition as claimed in any preceding claim, wherein molecular wt. of structurant (b) is 3,000 to 10,000.

5 6. A composition as claimed in any preceding claim, wherein melting temperature of (c) is 25°C to 85°C.

7. A composition as claimed in any preceding claim, additionally comprising a polyol.

10 8. A composition as claimed in claim 7, wherein said polyol is selected from ethylene glycol, propylene glycol, glycerol and mixtures thereof.

Fig.1.

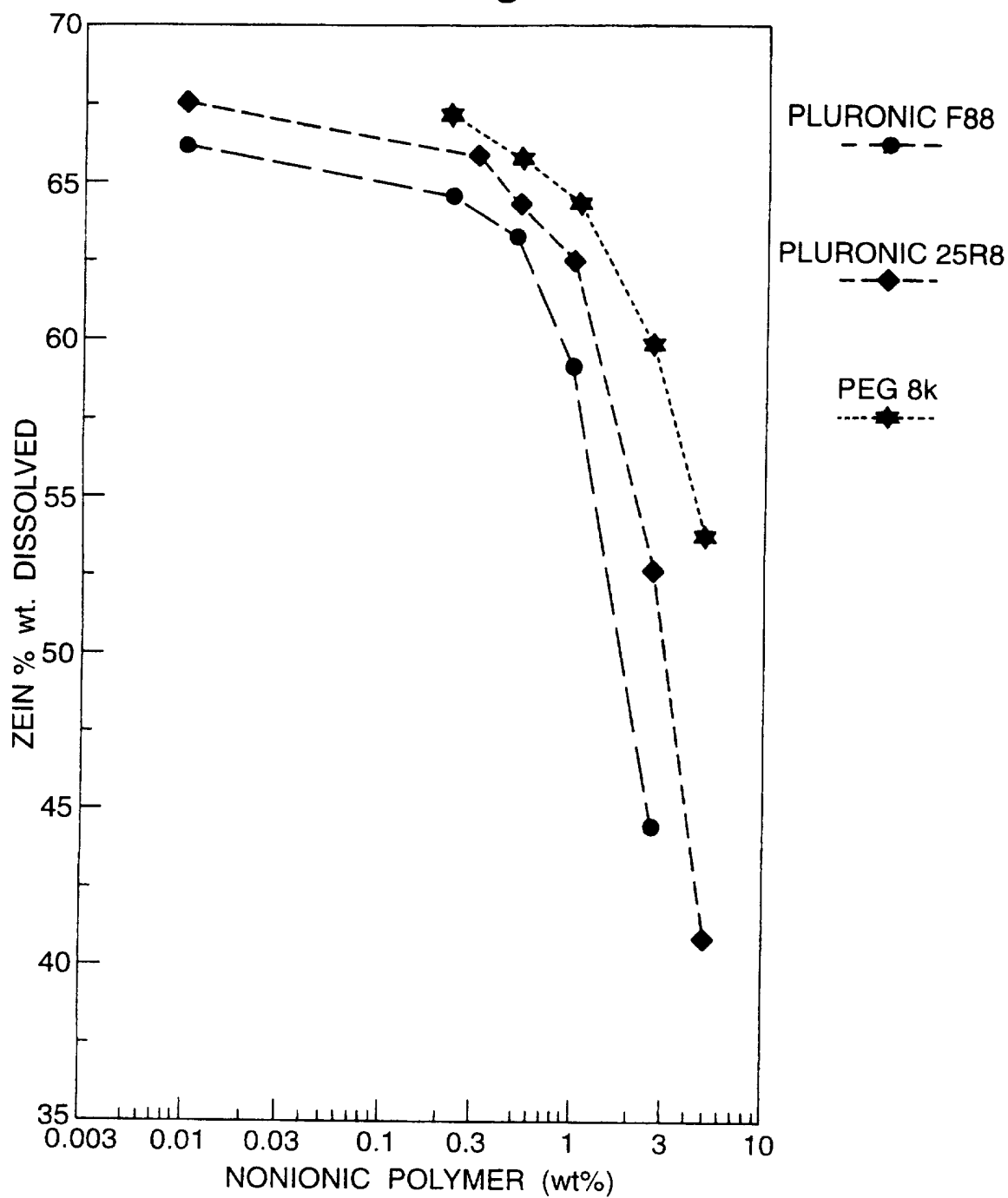
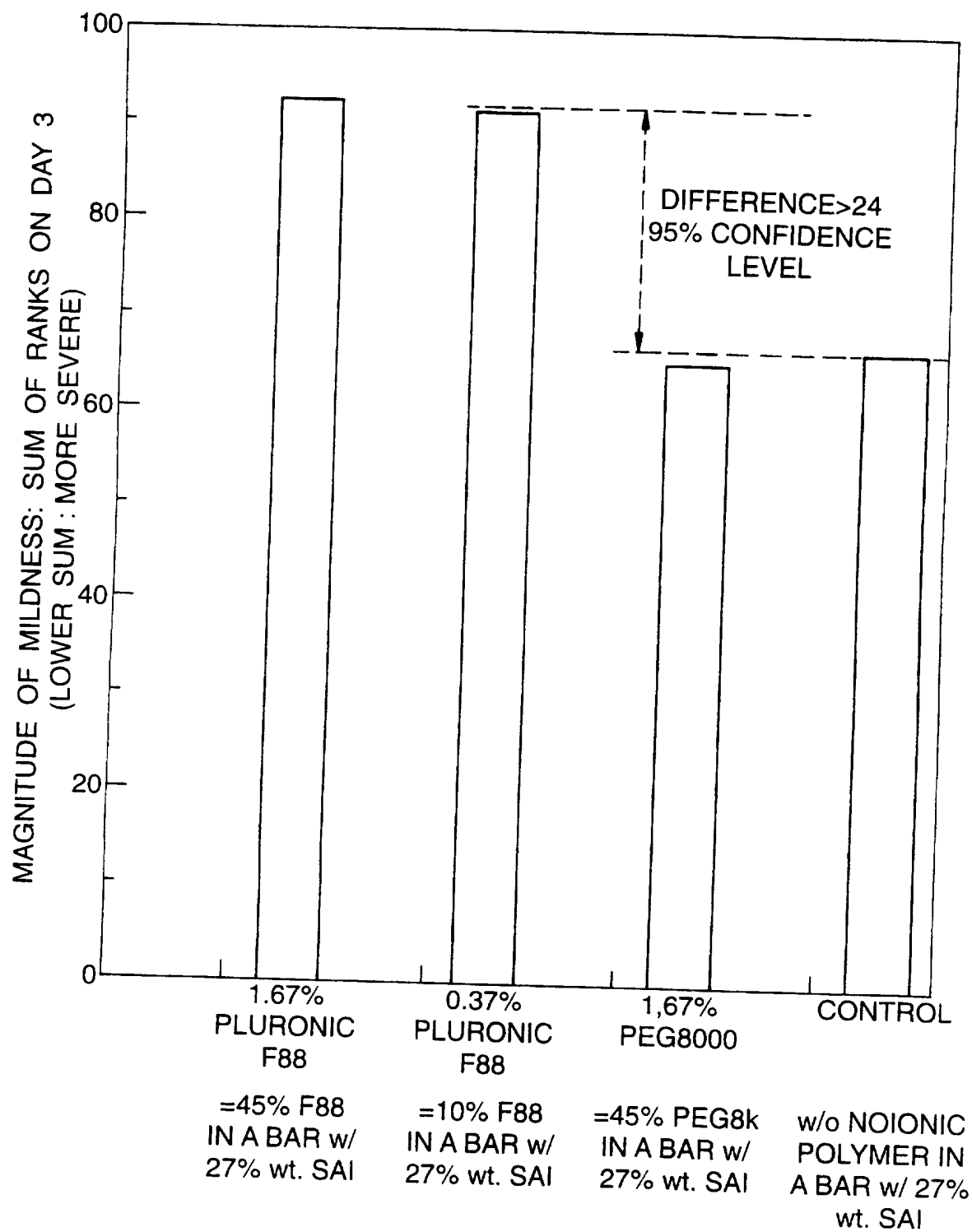


Fig.2.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 97/00914

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D17/00 C11D1/94 C11D3/37 C11D3/18 C11D3/22  
C11D3/20

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

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

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 21778 A (UNILEVER PLC. ) 29 September 1994 see page 5, line 3 - page 7, line 16 see page 11, line 14 - line 23 see claims 1-9; examples 6,7 ---	1-5,7,8
P,A	US 5 520 840 A (MASSARO MICHAEL ET AL. ) 28 May 1996 see claims; example 1 see column 3, line 60 - line 67 ---	1-8
A	US 3 312 627 A (HOOKER D.T. ) 4 April 1967 cited in the application see column 2, line 57 - column 4, line 7 see claim 1 --- -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 97/00914

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92 13060 A (THE PROCTER & GAMBLE CO. ) 6 August 1992 see page 3, line 5 - page 6, line 37 see page 10, line 12 - line 18 see claims 1-7 ---	1-5
A	WO 91 09106 A (THE PROCTER & GAMBLE CO.) 27 June 1991 see page 10, line 6 - page 11, line 16 see page 20, line 17 - page 21, line 6 see claims 1-8 ---	1-3
A	WO 94 17172 A (UNILEVER PLC. ) 4 August 1994 see page 8, line 26 - page 12, line 9 see claims 1-4 ---	1-3
A	US 3 766 097 A (ROSMARIN P) 16 October 1973 cited in the application see claims 1,15 -----	1



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/00914

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9421778 A	29-09-94	AU 6377194 A BR 9406008 A CZ 9502359 A EP 0689584 A HU 73042 A JP 8507816 T PL 310619 A ZA 9401813 A	11-10-94 26-12-95 17-01-96 03-01-96 28-06-96 20-08-96 27-12-95 15-09-95
US 5520840 A	28-05-96	AU 5101796 A WO 9629388 A	08-10-96 26-09-96
US 3312627 A	04-04-67	NONE	
WO 9213060 A	06-08-92	AU 1350192 A CN 1063894 A TR 26616 A	27-08-92 26-08-92 15-03-95
WO 9109106 A	27-06-91	CA 2068423 A EP 0505435 A	15-06-91 30-09-92
WO 9417172 A	04-08-94	AU 5884594 A EP 0631615 A	15-08-94 04-01-95
US 3766097 A	16-10-73	NONE	