11) Publication number:

0 256 343 A1

(12)

Ш

EUROPEAN PATENT APPLICATION

21) Application number: 87110667.0

(5) Int. Cl.4: **C11D 17/00** , C11D 3/39 , C11D 3/00

2 Date of filing: 23.07.87

③ Priority: 12.08.86 IT 1253186

Date of publication of application: 24.02.88 Bulletin 88/08

Designated Contracting States:
AT BE CH DE ES FR GB GR LI LU NL SE

Applicant: MIRA LANZA S.p.a. Via Rivarolo 14 I-16161 Genova(IT)

2 Inventor: Nistri, Ugo
4, Via Coriolano Bozzo
I-16030 Pieve Ligure(IT)
Inventor: Colombo, Paolo
12, Via Avogadro
I-21047 Saronno(IT)
Inventor: Franzolin, Giorgio
8, Largo S. Luca

I-30034 Mira (VE)(IT)
Inventor: Pizzato, Luciano
5, Via Monti
I-35100 Padova(IT)
Inventor: Dallavalle, Roberto

43, Via Ognisanti I-35100 Padova(IT)

Representative: Porsia, Attilio et al c/o Succ. Ing. Fischetti & Weber-Dr. Porsia Via Caffaro 3/2 I-16124 Genova(IT)

Two-phases, non aqueous liquid detergent composition.

Enduid detergent comprising a non-aqueous liquid base, containing, in solution and/or dispersion and/or emulsion, the other solid and liquid components of the detergent. The detergent comprises two different and separated phases (A,B), to be mixed together at the time of use or just before, wherein one of the two phases (phase A) contains the oxidizing agents and the other phase (phase B) contains enzymes and activation agents for the oxidizing agents contained in the other detergent phase (A). Other components, chosen from the agents listed below are furthermore present in both the detergent phases (A,B): builders, pigments, stabilizers, perfumes, dyes, optical brighteners, anti-redeposition agents, anionic and/or cationic surfactants, anti-foaming agents. The non-aqueous liquid base is formed by a mixture of non-ionogenic surfactants with a possible addition of a polar solvent for viscosity control purposes. By mixing the two phases (A,B), a liquid detergent composition is obtained which is complete in all its cleansing functions, action on oxidizable stains, on protein stains, sequestration of alkaline-earth metal and heavy-metal ions, etc. The solid material content in the two phases (A,B) is suitably comprised in the concentration range between 40-60% by weight.

Xerox Copy Centre

Two-phases, non-aqueous, liquid detergent composition

The present invention relates to heavy duty and light duty liquid detergents.

5

Liquid detergents have been gaining an ever increasing importance as they are more convenient to us than powder detergents. They are divided in two main groups, namely water based liquid detergents and non-aqueous liquid detergent, whose base is formed by an organic liquid medium.

Most aqueous liquid detergents consists of solutions or microsuspensions of anionic, cationic and non-ionic surfactants, enzymes, perfumes, stabilizers and various adjuvants.

They have a limited washing action, as they contain limited amounts of substances (so called "builders") apt to sequester the alkaline-earth metal ions, which cause the hardness of the washing waters, as well as the ions of the heavy metals.

Furthermore, they do not contain stain removing agents of the peroxide type (hydrogen peroxide, inorganic peroxides such as sodium perborate, organic peroxides, organic peracids etc.), as not only such oxidizing agents are not stable in aqueous suspension or solution, but they also interfere with the added enzymes, disactivating them.

Said aqueous based detergents for machine and hand washing are, therefore mainly founded on the suface-active action and on the stain removing action on stains of protein type, whereas they do not act on oxidizable stains, which constitute the main portion of the soils which are most frequently found.

The oxidizing action is only possible with non-aqueous detergents, consisting of an organic liquid medium based on polar solvents and surfactants containing in suspension an oxidizing agent of the organic or inorganic peroxide type, in conditions and in presence of other co-formulating agents such that interaction and therefore the decomposition of the oxidizing agent be impossible.

The DE-C-1 279 878 (Unilever) relates to a non-aqueous base liquid detergent, comprising a mixture of non-ionic and anionic surfactants, ethyl alcohol, builders such as sodium tripolyphosphate, suspending agents such as calcinated silica or calcinated aluminum oxide, optical brighteners and sodium perborate.

US-A-3 850 831 (Hellsten et al.) refers to essentially anhydrous liquid detergent compositions, consisting of ionic, anionic and polyhydric solvents, stain removing agents of the persalt type, builders such as sodium tripolyphosphate and chelating agents such as polyamino-carboxylic acids.

US-A-4 316 812 (Hancock et al) refers to the use of non-ionic surfactants with no solvents (pour point about 10°C), mixed with builders such as sodium tripolyphosphate, stain removing agents such as sodium percarbonate and perborate as well as with an alkalizing agent such as metasilicate and other typical detergent components, such as CMC (carboxymethyl cellulose), sodium borate, carbonate and bicarbonate, kaolin, bentonites etc. to obtain an essentially water free fine grain paste detergent.

EP-B-0028 849 (Unilever) refers to a non-aqueous based liquid detergent containing a maleic anhydride copolimer with ethylene or methylvinyl ether, an essentially polyhydric solvent acting as a suspending agent together with non-ionic surfactants, as well as solid agents such as alkalizing agents, builders, oxidizing agents, bleach activators, enzymes and softeners.

EP-B-0120 659 (Imperial Chemical Industries) relates to essentially anhydrous liquid detergent compositions, consisting essentially of a non-ionic surfactant, polar solvents with viscosity lowering functions and dispersing agents, builders, alkalizers, persalts, optical brighteners, carboxymethyl cellulose, enzymes, such compositions being substantially anhydrous.

DE-A-3 511 516 (Colgate-Palmolive) refers to a substantially anhydrous laundry detergent, comprising non-ionic surfactants, acid surfactants, sodium tripolyphsphate, sodium perborate, TAED and a copolymer such as SOKALAN CP5®.

DE-A-3 511 515 (Colgate Palmolive) refers to a substantially anhydrous laundry detergent, comprising non-ionic surfactants, acid surfactants, sodium tripolyphosphate, sodium phosphonate, sodium perborate, SOKALAN CP5®-copolymer, sodium carbonate, TAED, optical brightener and protease.

The above mentioned DE-C-1 279 878, US-A-3 850 831 and US-A-4 316 812 all refer to non-aqueous liquid detergent compositions, having a stain removing action based on non-activated persalts. Said compositions have a limited action on oxidizable stains at low temperatures due to the absence of bleach activators. Furthermore, they have a limited stain removal properties on protein stains, due to the absence of enzymes, particularly of the proteolytic type. Said absence of enzymes is due to the difficulty in introducing enzymes into this type of compositions, as they would be rapidly disactivated by the action of the oxidizing agent, enhanced by the traces of humidity inevitably to be found in the raw materials during the preparation and the packaging, and anyway easily picked up during the use with the consumer.

EP-B-0 028 849, EP-B-0120 659, DE-A-3 511 515 and and DE-A-3 511 516 are based on the combined use of oxidizing agents, bleach activators and enzymes to achieve the desired detergency effect.

It is however known that bleach activator and persalt, if simultaneously present in solvents and polar surfactants based formulations, give rise to early reactions, with formation of peracid and water and possibly developing oxygen. Said reaction is assisted both by the partial solubility of the two components, but mainly by the presence of traces of water.

It is also well known that the simultaneous presence of enzymes in a system containing oxidizing agents in non-protected form causes the enzyme rapid disactivation.

Consequently, the detergent compositions described in EP-B-0028 849, EP-B-0120 659, DE-A-3 511 515 and DE-A-3 511 516 do not provide a satisfactory solution to the problem of formulation of a complete liquid detergent.

It is therefore the object of the present invention to provide a non-aqueous liquid detergent, able to remove oxidable stains as well as protein stains and free from the disadvantages of the known detergents of this kind.

10

55

According to a characteristic of the present invention, said object is achieved by providing the said detergent in form of two physically separared phases, one containing the oxidizing agent and the other the bleach activator and the enzyme, in combination with surfactants, builders, optical brighteners, anti-redeponent agents, alkalizing substances, dyes, perfumes, stabilizing agents etc., all said components being dissolved and/or dispersed and/or emulsified in a suitable non-aqueous liquid base.

Said liquid base preferably is formed by mixtures of liquid non-ionic surfactants and solvents of the polar type, the latter having the function of lowering the viscosity and the freezing point as well as that of enhancing the dispersibility in water during washing.

Surfactants of the anionic or cationic type can be also included, if a textiles softening effect is desired.

The builder consists of anhydrous salts of the kind of the polyphosphates, NTA (nitrilo-triacetic acid), sodium citrate, zeolites, bentonites, montmorillonites, and so on.

The oxidizing agents are chosen among the inorganic persalts, of the kind of the monohydrate sodium perborate, tetrahydrate sodium perborate, sodium percarbonate, sodium, potassium and ammonium persulphate, sodium and potassium monopersulphate, perphosphate, percarbammide, peracids and organic peroxides and so on.

The bleach activator, which is used whenever inorganic persalts are employed, can consist of TAED (tetra-acetyl diamine), PAG (penta-acetyl glucose), ESA (sorbitol hexa-acetate), TAGU (tetra-acetyl glycol urile) NAOFS (octyl phenol sulfonate sodium salt) and other known bleach activators.

The enzymes are mainly of the proteolytic type, also in combination with lipase, amylase and cellulase.

The optical brighteners employed are of the stilbene-morpholine, distril diphenyl and pyrazole type, and anyway of the type normally used in detergents.

The preferred anti-redeponent substances are of the cellulose derivative type, such as carboxymethyl cellulose and etherified non-ionic celluloses. Furthermore, acrylic acid homopolymers and acrylic acid copolymers with maleic anhydride and the maleic anhydride polar copolimers with methyl-vinyl ether, methyl propenyl ether and so on, are also employed.

Persalt stabilizing agents are of type of the phosphonate and amino polycarboxylic complexants, such as EDTA (ethylen diamino tetracetyc acid), DTPA (diethylen triamino pentacetyc acid) etc.

The enzymes used in the present invention, protease, lipase, amylase, cellulase, can be introduced in the detergent in solid form, as slurry, or in the form of solution, in the organic liquor.

With respect to the presence of water and other agents having a destabilizing action on the enzymes, stabilizers, such as calcium and magnesium organic and inorganic salts, polar solvents such as ethyl alcohol and polyglycols, borum organic and inorganic compounds such as boric acid and borates, nitrogenous compounds such as EDTA, NTA (nitrilo triacetyc acid), glycine, monoethanolamine, diethanolamine, triethanolamine, acetamide or glutamic acid can be suitably added.

According to a preferred form to introduce the enzyme in the detergent composition, the proteolytic enzyme is introduced in form of a slurry in non-ionic surfactant or polar solvent, in fine particles, in post-admixture, to the residual composition, after milling, to avoid undesired degradation. The simultaneous presence of oxidizing agents such as inorganic persalts and peracids or organic peroxides can give rise to interaction between activator and enzyme respectively, with a rapid decay of these compounds.

Also the simultaneous presence of persalt and bleach activators, in non-protected form, give rise to exothermic decomposition reaction.

The two phases can be prepared according to any suitable procedure.

The dosing of the liquid detergent in the washing machine may be effected by using the dosing cup provided in the machine or directly into the washing machine.

The composition of liquids and solids of the two separate phases shall be such as to provide similar final density, viscosity and pour point, so as to ensure the same physical stability at low temperatures and constant supply ratio.

The various solid components of the detergent can be partly soluble or insoluble in the liquid system. In order to ensure a perfect physical stability in time, the unsolved solids must have a very fine grain size, for instance lower than 10 μ m.

Each phase consists of liquid components, solvents and ionic surfactants, solid components which can be dissolved in the system and suspended solid components, as well as emulsified liquid components.

The ratio between solids and liquids ranges between 1:3 and 9:1, preferably between 1:1.5 and 3:1.

The liquid phase is composed of preferably non-ionic surfactants and polar solvents. The ratio between solvents and surfactants ranges between 1:9 and 3:1.

C₁ to C₄ lower alcohols, ethylene, propylene glycols, olygomers and copolymers thereof, even partly esterified with C₁-C₄ alcohol, glicerine and aprotic polar solvents such as dimethyl sulphoxide are particularly suitable solvents.

The most suitable non-ionic surfactants are the primary and secondary, natural or synthetic alcohol derivatives, with a number of carbon atoms ranging between C_6 and C_{22} , and preferably between C_8 and C_{18} , condensed with ethylene oxide, having 3 to 25 monomer units and preferably 5 a 15, or condensed with propylene oxide, with a monomer unit content between 2 and 10, and preferably between 3 and 6, or condensed together with oxyethylene and oxypropylene units. Non ionic surfactants of the mentioned type can contain the final hydroxyl esterified with C_1 - C_3 organic acids.

Other non-ionic surfactants suitable for the formulation of the liquid detergents according to invention are those derived from condensation of alkyl phenols with alkylene oxides and where the type and content of monomer units is similar to those of the alcohol-based non-ionic ones mentioned above.

The physical and chemical stability of the two phases composing the detergent shall be suitably ensured by a limited presence of water in the two phases.

Therefore, as regards the phase in which, inter alia, the oxidizing agents of the composition are contained, the free water content shall not exceed 6% and preferably be lower than 3%.

For the preparation of the two phases of the detergent, the liquid and solid components containing crystallization free water need to be dehydrated, in order to fulfill the above mentioned conditions.

The two phases forming the detergent are in form of suspensions of solids in liquids, having a viscosity ranging between 100 and 2000 mPa.s, and preferably between 500 and 100 mPa.s; in order to fulfill this requirement and in order to obtain the same viscosity for the two phases, to ensure a uniform delivery, the solid particles must be adequately fine, for instance smaller than $10 \, \mu m$.

This result is obtained by milling the suspension in a suitable machine, such as a ball mill or a bead mill, with a duration and a number of stages apt to ensure that the desired result is achieved.

A modification of the above procedure can consist in the previous milling in solid phase the single solid components, to be then added to the liquid, so as to obtain a fine suspension (grain size lower than $10 \mu m$) stable to decantation.

The physical stability, that is to say, non-decantation of the suspensions corresponding to the two detergent phases, must be ensured for periods of time between between production and consumption, that is to say, at least for a period of time ranging between 6 and 12 months.

It is therefore useful to add suspending agents, such a calcinated silica, calcinated allumina, hydrosoluble polymers such as polyvinyl pyrrolidone, to the suspension, before or after milling. The added amounts range between 0.1 and 2.0%, and preferably between 0.3 and 1.0%.

Calcinated silica is silicium dioxide obtained through pyrohydrolisis of chlorosilanes and it is marketed as a low density powder unsoluble in water, with very small particles and superficial area comprised between 50 and 400 m²/g. Commercially available types of pyrogenic silica are the HDK® by Waker and AEROSIL® by Degussa.

Polyvynil pyrrolidone is used in the 30,000 molecular weight range.

The invention will be further described by the following examples, given only by way of illustration and not of limitation of same. In the examples, the detergent phase containing the oxidizing agents will be referred to as "Phase A", and that containing enzymes and the bleach activators will be referred to as "Phase B".

55

50

15

Phase A and phase B are separately prepared as described below, by mixing in a mixer provided with a stirrer the liquid and solid components.

In order to obtain sufficient physical stability, the solid components of the two phases are subsequently milled in a bead mill, until a 6.6 μ m average value of the solid particles is obtained.

The composition of the two phases is the following, in % by weight:

10	Phase A	Weight %
	Propylene glycol	14.5
	C_9-C_{15} alcohols with 5 EO (ethylene oxide) moles	20.0
15	Nonyl phenol with 6 EO moles	20.0
	Dried zeolite	10.0
	Sodium tripolyphosphate	10.0
20	Monohydrated sodium perborate	19.4
	EDTA (ethylen-diaminotetracetic acid) sodium salt	1.0
	K polyvynil pyrrolidone	0.5
25	Optical brightener	0.1
	cumene sulphunate	3.0
30	Other additives (perfumes, dyes, pigments, anti-foam)	1.5
	Phase B	Weight %
35	Propylene glycol	14.5
	Secondary C ₉ -C ₁₅ alcohols with 5 EO moles	20.0
	Nonyl phenol with 6 EO moles	20.0
40	TAED	8.0
	NTA sodium salt	4.0
	Sodium citrate	18.0
45	Sodium phosphonate (EDTMPA) * Methylvynilether-maleic anhydride copolimer	1.0 7.0
	Polyvynil pyrrolidone	0.5
	Proteolytic enzyme	2.4
50		0.1
	Optical brightener Other additives (perfumes, dyes, pigments, anti foam)	1.5
55		
	*(ethylen diamino tetra methyl phosphonic acid Na s	al + \

The two phases have the following chemical-physical characteristics:

			Phase A	Phase B
5				
	Density	g/ml	1.25	1.18
	Brookfield LVF viscosity			
10	Spindle = 20 r.p.m.	mPa-s	850	800
	Free water	%	0.8	1.1
	Average grain size	microns	6.3	6.6
<i>1</i> 5	Freezing point (solvent + surfacta	nts) °C	-2	-2

Following the same operation procedures as in Example 1, the phase A and phase B are prepared, with the following compositions:

25

30	Phase A	Weight %
	Ethanol	8.0
05	$^{\mathrm{C}}_{8}$ - $^{\mathrm{C}}_{16}$ alcohols with 8 EO moles	30.0
35	Octyl phenol with 6 EO moles	15.0
	A zeolite	15.0
40	sodium tripolyphosphate	10.0
	monohydrated sodium perborate	24.0
	Sodium diethylen diamino pentaacetate	2.0
45	Colloidal silica	0.4
	Xylene sulphonate	4.0
	Optical brightener	0.1
50	Other additives (perfumes, dyes, pigments, anti-foam)	1.5

0 256 343

	Phase B	Weight %
	Ethanol	8.0
5	C ₈ -C ₁₆ alcohols with 8 EO moles	30.0
	Octyl phenol with 6 EO moles	15.0
10	Penta acetyl glucose	6.0
70	Sodium citrate	22.0
	NTA sodium salt	4.0
15	Acrylic acid-maleic anhydride copolymer	6.0
	Colloidal silica	0.4
	Proteolytic enzyme	2.0
20	Optical brightener	0.1
	Xylene sulphonate	4.0
	CMC	1.0
25	Other additives (perfumes, dyes, pigments, anti-foam)	1.5
	The two phases in Example 2 have the following chemical-physical characteristics:	

			Phase A	Phase B
40	Density	g/ml	1.28	1.17
	Brookfield LVF viscosity			
	Spindle = 20 r.p.m.	mPa-s	700	750
4 5	Free water	%	0.7	1.2
	Average grain size	microns	5.5	5.9
	Freezing point (solvent + surfacta	nts) °C	-1.5	-1.5

After milling, two parts of phase A and phase B of Example 1 are thoroughly mixed, in a 1:1 ratio, to obtain a single phase liquid detergent having the following composition:

10

15

5

Single phase liquid detergent as per Example 1

		weight %
20	Propylene glycole	14.5
	Secondary C_9^{-C} alcohols with 5 EO moles	20.0
	Nonyl phenol with 6 EO moles	20.0
25	A Zeolite .	5.0
	Sodium tripolyphosfate	5.0
	Sodium perborate monohydrate	9.7
30	EDTA	0.5
	Polyvynil pyrrolidone	0.5
05	Optical brightener	0.1
35	Cumene sulphonate	3.0
	TAED	4.0
40	NTA sodium salt	2.0
	Sodium citrate	9.0
	Sodium phosphonate (EDTMPA)	0.5
45	Methylvynilether-maleic anhydryde copolimer	3.5
	Proteolytic enzyme	1.2
	Other additives (perfumes, dyes, pigments, anti-foam)	1.5

50

After milling, two parts of phase A and phase B preparations as per Example 2, have been thoroughly mixed in a 1:1 ratio, to obtain a single phase liquid detergent, having the following composition, in weight %

Single phase liquid detergent as per Example 2

10

5

		Weight %
	Ethanol	8.0
15	Linear C ₈ -C ₁₆ alcohols with 8 EO moles	30.0
	Octyl phenol with 6 EO moles	15.0
	A Zeolite	7.5
20	Sodium perborate monohydrate	12.0
	Diethyl amino penta acetate	1.0
25	Colloidal silica	0.4
20	Xylene sulphonate	4.0
	Optical brightener	0.1
30	Penta acetyl glucose	3.0
	Sodium citrate	11.0
	NTA Sodium salt	2.0
35	Acrylic acid-maleic anhydryde copolimer	3.0
	Proteolytic enzyme	1.0
	CMC	0.5
40	Other additives (perfumes, dyes, pigments, anti-foam)	1.5

EXAMPLE 5

Formulations A and B as per Examples 1 and 2 and the new formulations deriving from their mixture as per Examples 3 and 4, were tested in time and at different temperatures, as regards sodium perborate, bleach activator and proteolytic enzyme stability. The products were kept in sealed glass containers. The test results are shown in the following Tables I and II

5

10

15

20

25

30

TABLE I

35

40

45

50

55

ดู 4 as | Formulation per Example 11.6 35.3 39.3 88.9 2 8 0.1 a 1.95 5.9 2.0 7.5 5.7 3.4 Formulation as Formulation as Formulation per Example М 23.8 23.0 3.4 4 ſ 1 ო 1 |per Example 81.8 9,5 9.9 30.5 28.9 3.8 2.7 0.2 7.7 ري دي 2.4 2 2 8.3 per Example Д 19.2 18.7 2.6 ∢ ı months months 2 months Q a 0 0 0 اا ۳ <u>ا</u> ٦ ا % % Storage temperature % % % \triangleleft \triangleleft 23°C monohydrate proteolytic perborate activator Sodium Enzyme Bleach

TABLE II

Storage temperature 37°C	tempe 37°C	rature	Formulation per Example		as Formulation as	as Formulation 3 per Example	i	as Formulation as 2 per Example 4
			A	æ		A	В	
Sodium	\\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\	t= 0	19.2		9.5	23.8	t	11.6
monohydrate	°	t= 7 days	19.0		7.6	23.4	ŧ	6 6
	γ 		\ \ 1	1	20.0	1.7	ı	18.1
	. , ,	t= 0	1	7.9	3.8	1	5.9	2.8
bleach activator	% 	t= 7 days	!	7.6	2.6	1	5.7	2.1
	% 			3.8	31.6	1	3.4	25.0
	} 	t= 0		.2.4	1.1	 -	2.0	6.0
proteolytic Enzyme	% 	 t= 7 days	!	2.0	0.16	l	1.7	0.05
	% ∇		1	16.7	85.5	· ·	15.0	94.4

It should be noted that, opening the containers where formulations as per Examples 3 and 4 were stored to carry out the analyses, an inner pressure caused by gas formation due to a remarkable decomposition of the oxidizing agent was observed.

EXAMPLE 6

5

15

With the liquid detergents as per Examples 1, 2, 3 and 4, stored for 2 months at 23°C, washing tests were carried out in a washing machine.

Meanwhile, a washing test using a market water-based detergent containing enzymes was carried out under the same operating conditions. The amounts of detergent used in the washing tests are shown in the following table:

TABLE III

20		Protein stains	Oxidi- zable stains	Grease stain	Doses
	DETERGENT A + B	R%	R%	R%	Gr.
25	as per Ex. 1	77	82	53	110
	DETERGENT A + B as per Ex. 2	78	83	54	110
30	DETERGENT as per Ex. 3	51	65	51	110
35	DETERGENT as per Ex. 4	49	59	50	110
40	COMMERCIAL WATER-BASED DETERGENT	77	71	48	200

R% = reflectivity % value measured by means of ELREPHO reflectometer - filter number 11.

Detergents A + B as per Examples 1 and 2 where dosed by mixing equal weight of the two phases just before testing.

Claims

- A two-phases, non-aqueous liquid detergent composition comprising a non-aqueous liquid base containing in solution and/or dispersion and/or emulsion, the liquid and solid components of the detergent, characterized in that it consists of two different and separate liquid base phases, to be joined at the moment of use or immediately before, wherein a first phase (phase A) contains oxidizing agents and the second phase (phase B) contains enzymes and activation agents for said oxidizing agents, both phases (A,B) containing a number of further components selected among builders, pigments, dyes, stabilizers, optical brighteners, perfumes and anti-redeponent agents, anionic and/or cationic surfactants and anti-foam agents.
 - 2. A two-phases, non-aqueous liquid detergent composition according to claim 1, characterized in that said non-aqueous liquid base consists of one or more non ionogenic surfactants and one or more polar solvents.

- 3. A two-phases, non-aqueous liquid detergent composition according to claim 1, wherein said oxidizing agents are contained in said first phase (A) in amounts ranging between 2 to 35% and preferably between 10 to 25%.
- 4. A two-phases, non-aqueous liquid detergent composition according to claim 1, wherein the bleach activators are contained in said second phase (B) in amounts ranging between 1 to 15% and preferably between 5 to 10%.
- 5. A two-phases, non-aqueous liquid detergent composition according to claim 1, wherein the enzymes contained in the second phase (B) of the detergent are of the proteolytic and/or amyolitic and/or lipolytic and/or cellulase type, said enzymes being contained in said second phase (B) in amounts ranging between 0.2 to 5%, and preferably between 0.5 to 2%.
- 6. A two-phases, non-aqueous liquid detergent composition according to claims 1 to 5, wherein said oxidizing agents, said bleach activators and said enzymes are contained in said liquid bases of said two detergent phases (A,B) in the form of suspension of solid particles having average diameter smaller than 10 μ m.
- 7. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein the ratio between the liquid base and the solid agents suspended and/or dispersed and/or emulsified in said two detergent phases (A,B) ranges between 1:3 and 9:1 and preferably between 1:1.5 and 3:1.
- 8. A two-phases, non-aqueous liquid detergent composition according to claim 2, wherein the polar solvents and surfactants ratio in said liquid base ranges between 0.5:9 and 3:1, and preferably between 1:9 and 1:1.
 - 9. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein said builders are contained in said two detergent phases (A,B) in amounts ranging between 5 and 50%, and preferably between 10 and 30%.
- 10. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein said optical brighteners are contained in said two phases (A,B) in amounts ranging between 0.01 and 0.5% and preferably between 0.05 and 0.2%.
 - 11. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein said first phase (A) contains a persalt stabilizer, of the amino polycarboxilic acid and/or alkali phosphonate type.
 - 12. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein said two detergent phases (A,B) furthermore contain stabilizers of the calcinated silica, calcinated alumina or suspending polymer type.
 - 13. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein the free water content in said first phase (A) is lower than 2% and preferably lower than 1%.
 - 14. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein the free water content in said second phase (B) is lower than 5% and preferably lower than 3%.
- 15. A two-phases, non-aqueous liquid detergent composition according to claim 2, wherein the liquid base of the solution and/or dispersion and/or suspension of the components of the said two detergent phases (A,B) consists of a non-ionic surfactant, formed by a primary or secondary alcohol, condensed with alkylene oxides.
- 16. A two-phases, non-aqueous liquid detergent composition according to claim 2, wherein the liquid base of the solution and/or dispersion and/or suspension of the components of the said two detergent phases (A,B) consists of a non-ionic surfactant, formed by alkylphenol condensed with alkylene oxides.
 - 17. A two-phases, non-aqueous liquid detergent composition according to claim 2, wherein the solvent of the liquid base of the solution and/or dispersion and/or suspension of the components of the said two detergent phases (A,B) is propylene glycol, ethylene glycol or olygomers with 3 to 100 monomeric units, and preferably 5 to 20.
 - 18. A two-phases, non-aqueous liquid detergent composition according to claim 2, wherein said solvent is ethanol.
 - 19. A two-phases, non-aqueous liquid detergent composition according to claim 2, wherein said solvent is dimethyl sulphoxide.
- 20. A two-phases, non-aqueous liquid detergent composition according to claim 15, wherein the alcohol constituting the non-ionic surfactant is formed by a number of C atoms ranging between C_6 - C_{22} , and preferably between C_8 - C_{18} .

- 21. A two-phases, non-aqueous liquid detergent composition according to claims 15 and 16, wherein the primary and/or secondary alcohol and the alkyl phenols are condensed with 3-25 ethylene oxide units, and preferably 5 to 15 units.
- 22. A two-phases, non-aqueous liquid detergent composition according to claims 15 and 16, wherein the primary and/or secondary alcohol and the alkyl phenols are condensed with 2-10 propylene oxide units, and preferably 3-6 units.
- 23. A two-phases, non-aqueous liquid detergent composition according to claims 15 and 16, wherein the primary and/or secondary alcohol and the alkyl phenols are condensed with 3-25 units of ethylene oxide and propylene oxide simultaneously present, and preferably 5-15 units.
- 24. A two-phases, non-aqueous liquid detergent composition according to claim 15 and 16, wherein the primary and/or secondary alcohol and alkyl phenols condensed with ethylene oxide and/or propylene oxide can be esterified on the terminal hydroxil with organic acids containing 1 to 3 carbon atoms.
- 25. A two-phases, non-aqueous liquid detergent composition according to claim 3, wherein the oxidizing agent employed as stain removing agent is monohydrate sodium perborate.
- 26. A two-phases, non-aqueous liquid detergent composition according to claim 4, wherein the bleach activator employed in said second phase (B) is tetra-acetyl diamine.
- 27. A two-phases, non-aqueous liquid detergent composition according to claim 4, wherein the bleach activator employed in said second phase (B) is penta-acetyl glucose.
- 28. A two-phases, non-aqueous liquid detergent composition according to claim 9, wherein the builder employed is A Zeolite.
- 29. A two-phases, non-aqueous liquid detergent composition according to claim 9, wherein the builder employed is a potassium or sodium polyphosphate or pyrophosphate.
- 30. A two-phases, non-aqueous liquid detergent composition according to claim 29, wherein said polyphosphate is sodium or potassium tripolyphosphate.
- 31. A two-phases, non-aqueous liquid detergent composition according to claim 9, wherein the builder employed is nitrilo-triacetic acid, sodium salt.
- 32. A two-phases, non-aqueous liquid detergent composition according to claim 9, wherein the builder employed is sodium citrate.
- 33. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein the anti-redeponent agent is sodium polyacrylate.
- 34. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein the anti-redeponent agent is a maleic anhydride copolimer with methyl-vynil ether.
- 35. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein the anti-redeponent agent is a maleic anhydride copolymer with acrylic acid.
- 36. A two-phases, non-aqueous liquid detergent composition according to claim 5, wherein the enzymes contained in said second phase (B) are post-admixed in the detergent composition after milling, in form of solution or of fine particle slurry in non-ionic surfactant or in non-reagent polar solvent.
- 37. A two-phases, non-aqueous liquid detergent composition according to claim 36, wherein said enzymes are proteolytic enzymes of the type of the maxatase, mexacal, savinase, espernase, alkalase, cellulase SP 227®, thermamyl L type A.
- 38. A two-phases, non-aqueous liquid detergent composition according to any one of the preceding claims, wherein said two detergent phases (A,B) contain anionic and/or cationic surfactants.
- 39. Use of a two-phases, non-aqueous liquid detergent composition according to claims 1 to 38 above, wherein the two phases (A,B) forming the detergent are mixed together in a fixed ratio, ranging between 1:4 and 4:1, and preferably 1:1.5 and 1.5:1.
- 40. Use of a two-phases, non-aqueous liquid detergent composition according to claims 1 to 38 above, wherein the mixture of the two detergent phases (A,B) takes place when the detergent is introduced in the washing machine or immediately before.

50

35

10

15

EUROPEAN SEARCH REPORT

EP 87 11 0667

	DOCUMENTS CONS	DERED TO BE RELEYA			
Category		n indication, where appropriate, ant passages	Relevant to claim		ICATION OF THE ATION (Int. Cl.4)
A	EP-A-0 151 678 GAMBLE CO.) * example 1 *	(PROCTER &	1,2,5,	C 11 : C 11 : C 11 :	D 17/00 D 3/39 D 3/00
A	FR-A-2 069 073	- (UNILEVER N.V.)	1,2,5, 10,13- 15,18- 21,25, 30,37		
	* page 5, line: 2-8 *	s 24-28, examples			
A,P	GB-A-2 173 224 (COLGATE-PALMOLIV	- VE CO.)	1,2,4, 5,10, 13-15, 20,25, 26,30,		
	* abstract, examp	ole 1 *	37		NICAL FIELDS CHED (Int. Cl.4)
O,A	EP-A-0 028 849 ** * examples N-R, 0	·	1,2,15 ,18,20 ,25,29	C 11	D 17/00 D 3/00
A	EP-A-0 133 566 * examples, clair	- (HENKEL KGaA)	33		
		· 	·		
·	The present search report has b	een drawn up for all claims			
	Place of search BERLIN	Date of completion of the sear 23-10-1987	- 1	Exam LTZE D	iner
Y: p	CATEGORY OF CITED DOCL articularly relevant if taken alone articularly relevant if combined w ocument of the same category schnological background	E: earlier after ti ith another D: docum	or principle under patent document, ne filing date nent cited in the ap nent cited for other	, but publish polication	vention ed on, or