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(54) Composition suitable for use as, or in, an acidic rinse aid.

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(73) Proprietor : **ROHM AND HAAS COMPANY**  
Independence Mall West  
Philadelphia Pennsylvania 19105 (US)

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(72) Inventor : **Zini, Paolo**  
34 Domaine Des Canebiers  
F-06550, Roquette Sur Siagne (FR)

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(74) Representative : **Tanner, James Percival et al**  
**ROHM AND HAAS (UK) LTD. European**  
**Operations Patent Department Lennig House**  
**2 Mason's Avenue**  
**Croydon CR9 3NB (GB)**

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**FR-A- 2 559 779**  
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**Description**

The present invention is concerned with compositions suitable for use as, or in, acidic rinse aids, particularly acidic rinse aids for machine dishwashers. However, the compositions may also be suitable for use as, or in, glass cleaning compositions, for example window cleaning compositions, metal cleaning compositions, textile production, finishing and wash-off compositions, and water treatment compositions, for example in cooling circuits.

Rinse aids are invariably used in commercial and institutional machine dishwashers and frequently in household dishwashers. A final rinse of fresh water serves to displace pre-final rinse water and its attendant detergent and soil residues. In large commercial machines the final rinse water is normally introduced at a temperature of 80°C or above; the high temperature being used to sanitize as well as to promote rapid flash drying of tableware, glassware or plasticsware (herein collectively referred to as "substrate") surfaces as they exit the machine. In some "low energy" commercial dishwashers the final rinse water may be used at a lower temperature of about 60°C, and may contain about 50 parts per million (ppm) of a conventional chlorine-releasing agent for sanitization. "Sanitization" in household dishwashers is achieved by effective batchwise cleaning with multiple wash and rinse cycles using fresh water.

Rinse aid formulations for machine dishwashers, are conveniently aqueous solutions containing a low foam nonionic surfactant, and may be injected into the final fresh water rinse at a concentration of about 50 to about 100 ppm. The surfactant in the rinse water lowers the surface tension of the rinse water and improves the wetting action of the rinse water on the somewhat hydrophobic substrate surfaces. Improved wetting reduces the tendency of the rinse water to form drops containing dissolved solids on the substrate surface which give rise to spots upon drying. Accordingly, the functions of the surfactant in the rinse aid are to effectively reduce the surface tension during the draining period and to be low foaming so as to avoid traces of foam on the rinsed substrate which result in a residue upon evaporation.

In commercial dishwashers, the final rinse water, after having been used to rinse the substrates, will be mixed with the circulated pre-final rinse water. The rinse water may also be fed back into the wash water or be used directly as the wash water for the next cycle. Consequently, when a rinse aid is formulated, the surfactant and any other additive should be chosen based on their effect in the wash bath as well as in the rinse water. An additional important aspect of a rinse aid, therefore, is the ability of the rinse aid to defoam food soils in the alkaline wash bath. Proteinaceous food soils are particularly prone to foam in agitated alkaline wash baths. Foam, or more specifically entrapped air, in the wash spray, will reduce the mechanical efficiency of the spray and interfere with maximum soil removal. Many low foam surfactants are effective soil defoamers. However, other additives may interfere with soil defoaming.

While low foam surfactants have improved the wetting of rinse water on substrates, they have not completely eliminated spotting and streaking problems. It is known that the addition of polycarboxylated polymers, such as polyacrylic acid, to the rinse water can further reduce spotting and filming or streaking. It is believed that these water-soluble polymers can adsorb onto slightly soiled substrates and make the surface more hydrophilic. A more hydrophilic surface can be more readily wetted by the surfactant-containing rinse water. Polycarboxylated polymers are especially useful because they do not contribute to foam formation and do not interfere with the soil defoaming activity of the low foam surfactants. Such polycarboxylated polymers also have the advantage, when used in hard water, that they aid in preventing precipitation of hardness ion salts.

A major obstacle, however, exists to the use of polycarboxylated polymers in rinse aids. This obstacle is due to the incompatibility of these polymers in aqueous rinse aid formulations containing low foam surfactants. Combining such polymers and surfactants in water results in phase separation. Upon standing for a short period of time the water containing these polymers and surfactants will form two or more layers of different compositions. This phase separation is obviously unsatisfactory since non-uniform addition of the desired components will occur as the formulation is injected into the machine. For example, the formulation may contain too little surfactant to provide adequate wetting or too much leading to excessive foam.

Hydrotropes such as sodium xylene sulfonate, cumene sulfonate and short chain alkyl sulfates have been used to permit the formulation of low foam nonionic surfactants into stable aqueous concentrates. (See, for example, US-A-3,563,901 and US-A-4,443,270). These hydrotropes have little effect, however, on compatibilizing low foam surfactants with polycarboxylated polymers in aqueous concentrates. Moreover, even in cases where hydrotropes give limited compatibility, they suffer from the major disadvantage of interfering with the food soil defoaming activity of the surfactants. Water-miscible solvents, such as isopropanol and propylene glycol, and hydrogen bond-breaking compounds, such as urea, have also been proposed for use in formulating rinse aids containing low foam nonionic surfactants. However, they have been found to have little or no effect on compatibilizing polycarboxylated polymers with low foam surfactants. Combinations of a hydrotrope and such solvents offer some improvement over the use of either compound alone, but the combinations still result in

rinse aids having limited compatibility and adversely affect food soil defoaming activity.

Low molecular weight polyelectrolytes have been combined with low foam surfactants in powder detergent formulations. US-A-4,203,858 discloses a low foaming, phosphate-free, dishwashing composition comprising an alkali metal or ammonium carbonate, such as sodium carbonate, a water-soluble salt of a polyelectrolyte having a molecular weight of from about 500 to 4,000, and optionally up to 10 weight percent of a foam-suppressing nonionic surfactant. The weight ratio of polyelectrolyte to carbonate ranges from 5:95 to 20:80. Typical of the polyelectrolytes are acrylic, methacrylic, maleic and itaconic acid polymers. Homopolymers and copolymers of acrylic and methacrylic acid having a molecular weight ranging from 504 to 1291 are preferred. US-A-4,203,858 discloses that the major differences between this composition and prior polyelectrolyte-built dishwashing compositions are the low concentration of polyelectrolyte and the poor metal ion sequestering capability of these polyelectrolytes. Other references disclosing (meth)acrylic acid polymers and their salts in detergent and cleaning applications include US-A-3,671,440; 3,853,981; 3,950,260; 3,933,673; 3,922,230, 4,521,332 and GB-A-965,215. GB-A-2,154,599 discloses detergent compositions comprising a nonionic surfactant and a phase stabilizer such as a maleic acid copolymer. None of these references, however, address or offer solutions for polyelectrolytes with low foam surfactants in rinse aid concentrates.

The desired nature of a rinse aid is dependent upon the hardness of the water used in the dishwashing machine. In the case of soft water which has a low level of hardness, e.g. below about 10 French degrees of hardness, the rinse aid conveniently has a pH of 7 or above (herein referred to as an alkaline rinse aid), and, in the case of hard water which has a high level of hardness, e.g. above about 30 French degrees of hardness, the rinse aid conveniently has a pH of less than 7 (herein referred to as an acidic rinse aid). In the case of alkaline rinse aids the problem of compatibilizing low foam nonionic surfactants with polycarboxylated polymers has been overcome, and stable alkaline rinse aids have been produced, by using, as compatibilizer or stabilizer, high molecular weight copolymer formed from monomers comprising methacrylic acid and one or more of C<sub>1</sub> to C<sub>6</sub> alkyl (meth)acrylates and in which at least 50 percent of the acid groups in the copolymer have been neutralized with alkali (see our EP-A-0245987). Such high molecular weight copolymers are, however, unsuitable for compatibilizing low foam nonionic surfactant with polycarboxylated polymer in an acidic rinse aid formulation as phase separation is found to occur.

We have now unexpectedly found that low foam nonionic surfactant can be compatibilized with polycarboxylated polymer, and a stable acidic rinse aid can be formed, by using, as compatibilizer or stabilizer, further nonionic surfactant.

According to the present invention there is provided a stable composition suitable for use as, or in, an acidic rinse aid, which comprises:-

- (i) low foam nonionic surfactant having a cloud point of less than 70°C;
  - (ii) polymer (hereinafter for convenience referred to as "polymer") having a weight average molecular weight of 1,000 to 250,000
- and being a homopolymer of acrylic acid, methacrylic acid, maleic acid, 2-acrylamido-2-methylpropane sulfonic acid or acrylamide, or being a copolymer comprising units derived from two or more of acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, hydroxyacrylic acid, C<sub>1</sub> to C<sub>4</sub> alkyl (meth)acrylates or amides, for example ethyl acrylate, 2 - acrylamido - 2 - methylpropane sulfonic acid (AMPS), styrene, acrylamide, isobutadiene, dimethylaminoethyl methacrylate (DMAEMA), and t-butyl acrylamide (t-BAM);
- (iii) further nonionic surfactant (nonionic cosurfactant) having a cloud point of 70°C or above, e.g. 80°C or above; and
  - (iv) water;

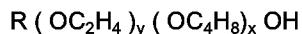
and wherein the composition has a pH of less than 7.

The present invention also provides a method of stabilizing an aqueous composition having a pH of less than 7 and comprising a mixture of low foam nonionic surfactant (which by its requirement of being low foaming will have a cloud point of less than 70°C) and polymer having a weight average molecular weight of 1,000 to 250,000 and being a homopolymer of acrylic acid, methacrylic acid, maleic acid 2-acrylamido-2-methylpropane sulfonic acid or acrylamide, or being a copolymer formed from two or more of acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, hydroxyacrylic acid, C<sub>1</sub> to C<sub>4</sub> alkyl (meth)acrylates or amides, e.g. ethyl acrylate, 2 - acrylamido - 2 - methylpropane sulfonic acid (AMPS), styrene, acrylamide, isobutadiene, dimethylaminoethyl methacrylate (DMAEMA), and t-butyl acrylamide (t-BAM), the method comprising incorporating in said composition nonionic cosurfactant having a cloud point of 70°C or above, e.g. 80°C or above.

In this specification, unless specifically stated otherwise, all quantities expressed as parts by weight for the low foam nonionic surfactant, polymer and further nonionic surfactant are per 100 parts by weight of low foam nonionic surfactant, polymer, further nonionic surfactant plus water.

The low foam nonionic surfactant may, for example, comprise any known low foam nonionic surfactant use-

ful in machine dishwashing or rinse aid applications. Suitable low foam nonionic surfactants include: C<sub>6</sub> to C<sub>22</sub> fatty alcohol/ethylene oxide condensates; polyoxypropylene - polyoxyethylene condensates; alkyl polyoxypolypropylene - polyoxyethylene condensates; alkyl polyoxyethylene - polyoxypropylene condensates; polyoxyalkylene glycols; benzyl ethers of polyoxyethylene condensates of alkyl phenols; and butylene oxide capped alcohol condensates, e.g. having the formula:



where R is a C<sub>8</sub> to C<sub>18</sub> alkyl group, y has an average value of 3.5 to 10, and x has an average value of 0.5 to 1.5. Typical commercially available low foam nonionic surfactants include: Triton CF-10 (an alkylaryl polyether) and Triton DF-16 (a modified polyoxyalkylated alcohol) manufactured by Rohm and Haas Company; Pluronic L-62 (a polyoxyethylene - polyoxypropylene block copolymer), Lutensol LF 403 and Lutensol LF 404 manufactured by BASF; and Antarox BL-330 (a modified linear aliphatic alcohol polyethoxylated and chloro-terminated compound) manufactured by GAF Corporation.

The composition of the invention may, for example, comprise at least 1 part by weight, preferably at least 5 parts by weight, and more preferably at least 10 parts by weight, of the low foam nonionic surfactant. Up to 60 parts by weight, preferably up to 50 parts by weight, and more preferably up to 40 parts by weight, of the low foam nonionic surfactant may, for example, be present in the composition.

In one embodiment of the invention, the polymer is a homopolymer of acrylic acid, methacrylic acid or maleic acid, or is a copolymer formed from two or more of acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, hydroxyacrylic acid, C<sub>2</sub> to C<sub>4</sub> alkyl (meth)acrylates or amides and 2-acrylamido - 2 - methylpropane sulfonic acid.

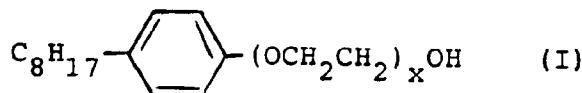
The polymer, used in the composition of the invention, may be a polycarboxylated polymer.

The weight average molecular weight of the polymer is at least 1,000 and is preferably up to 100,000, more preferably up to 70,000. The polymer may be used in the free acid form, or in the partially neutralised or neutralised, e.g. alkali metal or ammonium salt, form when producing the composition of the invention, but is preferably used in the partially neutralised form as it may then be unnecessary to carry out a pH adjustment step to achieve the desired acidic pH.

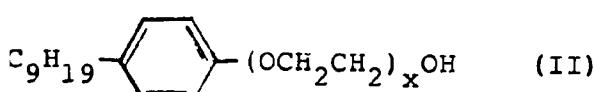
Suitable commercially available polymers include Acrysol LMW 45 (an acrylic acid homopolymer which is 20% neutralised and has a weight average molecular weight of 4500), and Acrysol LMW 45N (an acrylic acid homopolymer which is fully neutralised and has a weight average molecular weight of 4500).

The composition of the invention may, for example, comprise at least 0.5 parts by weight, preferably at least 1 part by weight, of the polymer. Up to 20 parts by weight, preferably up to 10 parts by weight, and more preferably up to 5 parts by weight, of the polymer may be present in the composition.

Suitable nonionic cosurfactants include alkyl aryl polyether alcohols having an average of at least ten ethylene oxide units per molecule; and alkyl polyether alcohols having an average of at least ten ethylene oxide units per molecule. Preferably, the cosurfactant is a reaction product of ethylene oxide with an octyl or nonyl phenol such as a compound of the formula:-



or



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in which x has an average value of at least 10.

Suitable commercially available materials having the formula (I) include: Triton X - 165 (average value of x = 16); Triton X - 305 (average value of x = 30); Triton X - 405 (average value of x = 40); and Triton X - 705 - 70% (average value of x = 70); and suitable commercially available materials having the formula (II) include: Triton N - 150 (average value of x = 15); Triton N - 302 (average value of x = 30); Triton N - 401 (average value of x = 40); Triton N - 998 - 70% (average value of x = 100); and Triton N 998 - 100% (average value of x = 100); all of these materials being manufactured by Rohm and Haas Company.

The composition of the invention may, for example, comprise at least 0.1 parts by weight, preferably at

least 0.5 parts by weight, of the nonionic cosurfactant. Up to 10 parts by weight, preferably up to 5 parts by weight, of the nonionic cosurfactant may, for example, be present in the composition.

It is to be understood that the composition of the invention may comprise one or more of each of the low foam nonionic surfactant, polymer and nonionic cosurfactant. In one embodiment of the invention, the total amount of low foam nonionic surfactant, polymer, nonionic cosurfactant and water is 100% by weight of the composition.

The composition of the invention may comprise other additives, for example, one or more of sequestrants such as nitrilo triacetic acid (NTA), ethylene diamine tetraacetic acid (EDTA), phosphonates, citric acid, or sodium citrate, and water-miscible solvents such as isopropanol or propylene glycol. Examples of suitable phosphonates include 1-hydroxy-ethylene-bis-phosphonic acid, nitrilo-tris(methylene phosphonic acid), ethylenediamine tetra (methylene phosphonic acid), diethylene triamine penta (methylene phosphonic acid), and hexamethylene diamine tetra (methylene phosphonic acid). Suitable commercially available phosphonates include Dequest-2006, -2016, -2046, -2056, and -2066, manufactured by Monsanto, and Mykon -P060, -P110, -P200, -P310, and -P400, manufactured by Warwick International. For example, based on the total weight of the composition, EDTA may be present in an amount of up to 2% by weight,

NTA may be present in an amount of up to 4% by weight, citric acid may be present in an amount of up to 10% by weight, or phosphonates may be present in an amount of up to 2% by weight. If more than one such sequestering additive is present, then the amounts of such additives present will require appropriate adjustment. The above-mentioned acidic materials, useful as optional additives, can be used in the acid, partially neutralized or fully neutralized form.

Table 1 below gives examples of a number of formulations according to the present invention, the figures quoted for each component being percentages by weight based on the total weight of the formulation and the balance being water.

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Table 1

Formul-	Low foam	Nonionic co-	Nonionic co-	Citric EDTA	Dequest	Dequest	Dequest	Dequest	Dequest
ation	nonionic	surfactant	surfactant	(Triton X-305)	2006	2016	2046	2056	2066
	surfactant	Polymer	(Triton DF16)	(Acrysol LMW45 or LMW45N)					
1	20	10	4	2	-	-	-	-	-
2	20	10	4	-	0.5	-	-	-	-
3	20	10	4	-	-	-	-	-	-
4	20	10	4	-	-	-	-	-	-
5	20	10	4	-	-	-	-	-	-
6	20	10	4	-	-	-	-	-	-
7	30	2	3	10	-	-	-	-	-
8	30	2	3	-	1	-	-	-	-
9	30	2	3	-	-	-	-	-	-
10	30	2	3	-	0.5	-	-	-	-
11	30	2	3	-	-	-	-	-	-
12	30	2	3	-	-	-	-	-	-
13	30	2	3	-	-	-	-	-	-

We have found that it is possible to make compositions according to the present invention which remain stable for several weeks at 40°C, for at least 90 days at room temperature, and pass five (5) freeze/thaw cycles. Whilst not wishing to be bound by theory, it is thought that this stability is due to the formation of a microemulsion by the addition of the nonionic cosurfactant. Two observations support the formation of a microemulsion. Firstly, 5 in the absence of the nonionic cosurfactant, the composition is turbid and quickly separates into two or more phases, but upon addition of the nonionic cosurfactant the composition becomes transparent. This transparency is believed to be due to the formation of a microemulsion in which the particle sizes are too small to result in scattering of the light. Secondly, upon addition of the nonionic cosurfactant, a stable dispersion is spontaneously formed, that is, is formed without input of mechanical energy, e.g. without agitation. In oil/surfactant- 10 /water systems, in which a homogenous phase is not formed, it is known that the addition of a cosurfactant can produce spontaneous formation of a stable dispersion due to the formation of a microemulsion, and it is believed that a similar situation is occurring in the case of the compositions of the present invention.

When used as, or in, a rinse aid, e.g. a rinse aid for automatic dishwashers, the composition of the invention may promote the wetting of a substrate, and may reduce spotting of the substrate when subsequently dried. 15 These properties of the composition may also make it suitable for other uses, for example, as, or in, glass (e.g. window) cleaning or metal cleaning compositions.

The present invention will now be further illustrated by way of the following examples in conjunction with the accompanying drawing, the examples being for illustrative purposes only and not to be construed as imposing any limitation on the scope of the invention:-

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Example 1

This example illustrates the need to utilise a nonionic cosurfactant to stabilise an aqueous composition comprising low foam nonionic surfactant and polymer. A number of formulations were prepared comprising low 25 foam nonionic surfactant, polymer, water, and, in some formulations, nonionic cosurfactant. The stability of these formulations against phase separation at 40°C for 24 hours (or longer) was measured and the results obtained are given in Table 2 below.

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Table 2

5	Formulation	1	2	3	4	5	6	7	8
10	Component	Parts By Weight							
15	Low foam nonionic surfactant (*)	10	10	30	30	50	50	20	20
20	polymer (**)	5	5	2	2	2	2	10	10
25	Water	85	84	68	65	48	44	70	66
30	Stable	No	Yes	No	Yes	No	Yes	No	Yes
35	*	Triton DF-16 (a modified polyalkoxylated alcohol)							
40	**	Acrysol LMW45 (acrylic acid homopolymer-20% neutralised - wt aver mol wt 4500)							
45	***	Triton X-305 (octylphenolethoxylate with an average 30 ethylene oxide units per molecule)							

The total weight of each of the formulations was 100 parts by weight.

From Table 2 it can readily be observed that the formulations in accordance with the present invention (i.e. formulations 2, 4, 6 and 8) were stable, whereas the comparative formulations (i.e. formulations 1, 3, 5 and 7), which did not contain nonionic cosurfactant, were not stable.

As previously stated, the presence of polymers, e.g. polycarboxylated polymers, in acidic rinse aids is advantageous as such polymers inhibit the precipitation of hardness ion salts from the water in which the rinse aid is used. However, prior art rinse aids have the disadvantage that none, or very little, polymer can be used otherwise phase separation of the low foam nonionic surfactant and polymer is found to occur in the rinse aid.

The presence of the cosurfactant, used in the present invention, enables greater concentrations of polymer to be present in the rinse aid, resulting in increased efficiency in inhibition of precipitation of hardness ion salts from water in which the rinse aid is used, without resulting in phase separation of the polymer and the low foam nonionic surfactant. That is, the cosurfactant enables stable compositions comprising low foam nonionic sur-

factant and polymer to be produced in which higher concentrations of polymer can be present than could be used in the prior art compositions.

The ability of the nonionic cosurfactants in enabling the production of stable aqueous compositions comprising low foam nonionic surfactant and polymer, e.g. polycarboxylated polymer, was investigated by comparing the light transmittance of formulations 4 and 8 of Table 2 (i.e. formulations according to the present invention) with a prior art formulation containing no nonionic cosurfactant, the prior art formulation being an aqueous composition of 30 percent by weight low foam nonionic surfactant, 10 percent by weight isopropanol and 60 percent by weight water. Light transmittance can be used as an indication as to whether or not precipitation of hardness ion salts is occurring in the formulations since any such precipitation will reduce the light transmittance.

The light transmittance of each of the three formulations, when added to soft water, medium hard water and hard water, was determined. The results are shown in the accompanying drawing which is in the form of a graph in which axis x is the degree of hardness of the water with A representing soft water, B representing medium hard water and C representing hard water, axis y is the percentage light transmittance, (i) is the line obtained for formulation 8 of Table 2, (ii) is the line obtained for formulation 4 of Table 2, and (iii) is the line obtained for the prior art formulation.

From the graph it can clearly be seen that the formulations according to the present invention (represented by lines (i) and (ii)) have a substantially higher light transmittance, i.e. greater inhibition of hardness ion salt precipitation, than the prior art formulation (represented by line (iii)) in medium and hard water.

The greater inhibition of hardness ion salt precipitation exhibited by the compositions of the present invention over the prior art composition is attributable to the ability to form, in accordance with the present invention, stable compositions having a higher concentration of polymer than can be used in the prior art composition.

Lines (i) and (ii) of the accompanying graph also demonstrate that, the higher the concentration of polymer in the rinse aid, the greater the inhibition of hardness ion salt precipitation, particularly in medium hard and hard water and hence the higher the light transmittance; line (i) representing the formulation comprising 10 parts by weight of polymer and line (ii) representing the formulation comprising 2 parts by weight of polymer.

## Example 2

This example illustrates two procedures for the preparation of the compositions of the present invention.

### Procedure A:-

To the water was added the polymer, then the low foam nonionic surfactant was added, and finally the nonionic cosurfactant was added.

### Procedure B:-

To the water was added the low foam nonionic surfactant, then the polymer was added, and finally the cosurfactant was added.

A number of formulations according to the invention were prepared using the above procedures and the stability of the formulations at 40°C for 24 hours (or longer) was determined. The results are given in Table 3.

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Table 3

5	Formulation	9	10	11	12	13	14
10	Procedure	A			B		
15	Component	Parts by Weight					
20	polyacrylate homopolymer wt aver mol wt 4,500	3.0	0	0	3.0	0	0
25	acrylic acid/ maleic acid copolymer, wt aver mol wt 30 10,000	0	3.0	0	0	3.0	0
35	acrylic acid/ ethacrylic acid copolymer, wt aver mol wt 40 3,500	0	0	3.0	0	0	3.0
45	low foam nonionic* surfactant nonionic cosurfactant**	20	20	20	20	20	20
50	Water	75	75	75	75	75	75
55	<u>Stable</u>	Yes	Yes	Yes	Yes	Yes	Yes

\* = Triton DF-16

\*\* = Triton X - 305

The total weight of each of the formulations was 100 parts by weight. From Table 3 it can be observed that, in the case of Triton DF-16 as low foam nonionic surfactant, either procedure A or procedure B can be used to prepare stable compositions in accordance with the present invention. Table 3 also indicates that stable compositions are still produced when the polycarboxylated polymer is varied.

In some cases, however, for example when alkoxypolyethoxy polypropoxy benzyl ether is used as the low foam nonionic surfactant, the order of addition of the components of the composition is important. Table 4 below illustrates the stability of compositions according to the present invention prepared using the above procedures A and B and two further procedures C and D, procedure C being the addition of polymer to the water, followed by the addition of nonionic cosurfactant and finally addition of low foam nonionic surfactant, and procedure D being the addition of nonionic cosurfactant to water, followed by the addition of low foam nonionic surfactant and finally polymer. In each of these compositions, the low foam nonionic surfactant was an alkoxypolyethoxy polypropoxy benzyl ether.

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Table 4

Formulation	15	16	17	18
Procedure	A	B	C	D
Stability	unstable	unstable	stable	stable

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This example illustrates that the procedure(s) by which formulations according to the present invention may be prepared may vary depending on the chemical structure of the low foam nonionic surfactant.

"Triton" and "Acrysol" are trademarks of Rohm and Haas Company; "Pluronic" and "Lutensol" are trademarks of BASF AG; "Antarox" is a trademark of GAF Corporation; "Dequest" is a trademark of Monsanto; and "Mykon" is a trademark of Warwick International.

### Claims

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1. A stable composition suitable for use as, or in, an acidic rinse aid, which comprises:-
  - (i) low foam nonionic surfactant having a cloud point of less than 70°C;
  - (ii) polymer having a weight average molecular weight of 1,000 to 250,000 and being a homopolymer of acrylic acid, methacrylic acid, maleic acid, 2-acrylamido-2-methylpropane sulfonic acid or acrylamide, or being a copolymer comprising units derived from two or more of acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, hydroxyacrylic acid, C<sub>1</sub> to C<sub>4</sub> alkyl(meth)acrylates or amides, 2-acrylamido-2-methylpropane sulfonic acid, styrene, acrylamide, isobutadiene, dimethylaminoethyl methacrylate, and t-butylacrylamide;
  - (iii) further nonionic surfactant having a cloud point of 70°C or above, for example 80°C or above; and
  - (iv) water;

and wherein the composition has a pH of less than 7.

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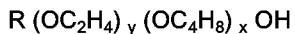
2. A composition as claimed in Claim 1, in which the polymer (ii) is a homopolymer of acrylic acid, methacrylic acid or maleic acid, or a copolymer formed from two or more of acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, hydroxyacrylic acid, C<sub>2</sub> to C<sub>4</sub> alkyl(meth)acrylates or amides and 2-acrylamido-2-methylpropane sulfonic acid.

3. A composition as claimed in Claim 1 or Claim 2, in which the polymer (ii) is a polycarboxylated polymer.

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4. A composition as claimed in any preceding claim, in which the low foam nonionic surfactant (i) comprises one or more of C<sub>6</sub> to C<sub>22</sub> fatty alcohol/ethylene oxide condensates; polyoxypropylene- polyoxyethylene condensates; alkyl polyoxypropylene- polyoxyethylene condensates; alkyl polyoxyethylene- polyoxypropylene condensates; polyoxyalkylene glycols; benzyl ethers of polyoxyethylene condensates of alkyl phenols; and butylene oxide capped alcohol condensates.

5. A composition as claimed in Claim 4, in which the butylene oxide capped alcohol condensates have the formula:-



where R is a C<sub>8</sub> to C<sub>18</sub> alkyl group, y has an average value of 3.5 to 10, and x has an average value of 0.5 to 1.5.

6. A composition as claimed in any preceding claim, in which the low foam nonionic surfactant (i) is present in an amount of at least 1 part by weight, preferably at least 5 parts by weight, more preferably at least 10 parts by weight, per 100 parts by weight of (i), (ii), (iii), plus (iv).

7. A composition as claimed in any preceding claim, in which the low foam nonionic surfactant (i) is present in an amount of up to 60 parts by weight, preferably up to 50 parts by weight, more preferably up to 40 parts by weight, per 100 parts by weight of (i), (ii), (iii) plus (iv).

10 8. A composition as claimed in any preceding claim, in which the polymer (ii) has a weight average molecular weight of up to 100,000, preferably up to 70,000.

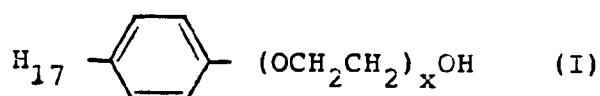
9. A composition as claimed in any preceding claim, in which the polymer (ii) is partially neutralised.

10 10. A composition as claimed in any preceding claim, in which the polymer (ii) is present in an amount of at least 0.5 parts by weight, preferably at least 1 part by weight, per 100 parts by weight of (i), (ii), (iii) plus (iv).

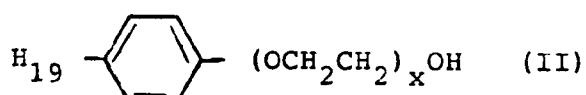
15 11. A composition as claimed in any preceding claim, in which the polymer (ii) is present in an amount of up to 20 parts by weight, preferably up to 10 parts by weight, more preferably up to 5 parts by weight, per 100 parts by weight of (i), (ii), (iii) plus (iv).

20 12. A composition as claimed in any preceding claim, in which the further nonionic surfactant (iii) comprises alkyl aryl polyether alcohols having an average of at least ten ethylene oxide units per molecule; and alkyl polyether alcohols having an average of at least ten ethylene oxide units per molecule.

13. A composition as claimed in claim 12, in which the alkyl aryl polyether alcohols comprise compounds of the formula:-



or



35 in which x has an average value of at least 10.

14. A composition as claimed in any preceding claim, in which the further nonionic surfactant (iii) is present in an amount of at least 0.1 parts by weight, preferably at least 0.5 parts by weight, per 100 parts by weight of (i), (ii), (iii) plus (iv).

40 15. A composition as claimed in any preceding claim, in which the further nonionic surfactant (iii) is present in an amount of up to 10 parts by weight, preferably up to 5 parts by weight, per 100 parts by weight of (i), (ii), (iii) plus (iv).

45 16. A method of stabilizing an aqueous composition having a pH of less than 7 and comprising a mixture of low foam nonionic surfactant having a cloud point of less than 70°C and polymer having a weight average molecular weight of 1,000 to 250,000 and being a homopolymer of acrylic acid, methacrylic acid, maleic acid, 2-acrylamido-2-methylpropane sulfonic acid or acrylamide, or being a copolymer comprising units derived from two or more of acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, hydroxyacrylic acid, C<sub>1</sub> to C<sub>4</sub> alkyl (meth)acrylates or amides, 2-acrylamido-2-methylpropane sulfonic acid, styrene, acrylamide, isobutadiene, dimethylaminoethyl methacrylate, and t-butylacrylamide, the method comprising incorporating in said composition further nonionic surfactant having a cloud point of 70°C or above, for example 80°C or above.

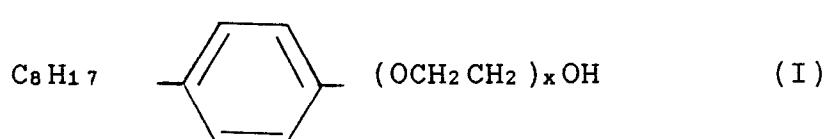
50 17. A method as claimed in Claim 16, in which the low foam nonionic surfactant, polymer, and further nonionic surfactant, and amounts thereof, are as defined in any of Claims 2 to 15.

55 18. The use of nonionic surfactant having a cloud point of 70°C or above, e.g. 80°C or above, to stabilise an aqueous composition having a pH of less than 7 and comprising low foam nonionic surfactant having a cloud point of less than 70°C and polymer, the polymer being as defined in Claim 1, 2 or 3.

**Patentansprüche**

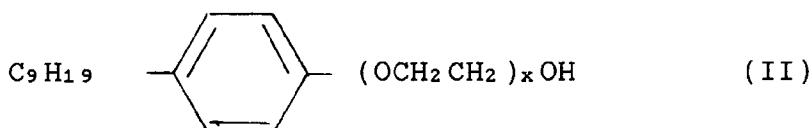
1. Stabile Zusammensetzung, geeignet zur Verwendung als oder in einem sauren Spülmittel, enthaltend:  
 5 (i) wenig schäumendes nichtionisches Tensid mit einem Trübungspunkt von weniger als 70 °C;  
 (ii) ein Polymer mit einem Gewichtsmittel des Molekulargewichts von 1.000 bis 250.000, welches ein Homopolymer darstellt aus Acrylsäure, Methacrylsäure, Maleinsäure, 2-Acrylamido-2-methylpropansulfonsäure oder Acrylamid oder ein Copolymer, welches Einheiten enthält, die abgeleitet sind aus zwei oder mehr aus Acrylsäure, Methacrylsäure, Ethacrylsäure, Maleinsäure, Itaconsäure, Hydroxyacrylsäure, C<sub>1</sub>-C<sub>4</sub>-Alkyl(meth)acrylaten oder -amiden, 2-Acrylamido-2-methylpropansulfonsäure, Styrol, Acrylamid, Isobutadien, Dimethylaminoethylmethacrylat und t-Butylacrylamid;  
 10 (iii) ein weiteres nichtionisches Tensid mit einem Trübungspunkt von 70 °C oder darüber, beispielsweise 80 °C oder darüber; und  
 (iv) Wasser;  
 und wobei die Zusammensetzung einen pH-Wert von weniger als 7 aufweist.
- 15 2. Zusammensetzung nach Anspruch 1, wobei das Polymer (ii) ein Homopolymer aus Acrylsäure, Methacrylsäure oder Maleinsäure ist, oder ein Copolymer, welches gebildet ist aus zwei oder mehr aus Acrylsäure, Methacrylsäure, Ethacrylsäure, Maleinsäure, Itaconsäure, Hydroxyacrylsäure, C<sub>2</sub>-C<sub>4</sub>-Alkyl(meth)acrylaten oder -amiden und 2-Acrylamido-2-methylpropansulfonsäure.
- 20 3. Zusammensetzung nach Anspruch 1 oder 2, wobei das Polymer (ii) ein polycarboxyliertes Polymer ist.
4. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei dem das wenig schäumende nichtionische Tensid (i) eines oder mehr enthält aus C<sub>6</sub>-C<sub>22</sub>-Fettalkohol/Ethylenoxid-Kondensaten; Polyoxypropen/Polyoxyethylen-Kondensaten; Alkylpolyoxypolyen/Polyoxyethylen-Kondensaten; Alkylpolyoxypolyen/Polyoxypropen-Kondensaten; Polyoxyalkylenglycolen; Benzylethern von Polyoxyethylen-Kondensaten von Alkylphenolen; und mit Butylenoxid gedeckten Alkoholkondensaten.
- 25 5. Zusammensetzung nach Anspruch 4, wobei die mit Butylenoxid gedeckten Alkoholkondensate die Formel R(OC<sub>2</sub>H<sub>4</sub>)<sub>y</sub>(OC<sub>4</sub>H<sub>8</sub>)<sub>x</sub>OH aufweisen, wobei R eine C<sub>8</sub>-C<sub>18</sub>-Alkylgruppe bedeutet; y einen mittleren Wert von 3,5 bis 10 hat und x einen mittleren Wert von 0,5 bis 1,5 hat.
6. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei dem das wenig schäumende nichtionische Tensid (i) anwesend ist in einer Menge von mindestens 1 Gewichtsteil, bevorzugt mindestens 5 Gewichtsteilen, bevorzugter mindestens 10 Gewichtsteilen, pro 100 Gewichtsteile von (i), (ii), (iii) plus (iv).
- 30 7. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei der das wenig schäumende nichtionische Tensid (i) anwesend ist in einer Menge von bis zu 60 Gewichtsteilen, bevorzugt bis zu 50 Gewichtsteilen, bevorzugter bis zu 40 Gewichtsteilen, pro 100 Gewichtsteile von (i), (ii), (iii) plus (iv).
8. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das Polymer (ii) ein Gewichtsmittel des Molekulargewichts von bis zu 100.000 aufweist, bevorzugt bis zu 70.000.
- 35 9. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das Polymer (ii) teilweise neutralisiert ist.
10. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das Polymer (ii) anwesend ist in einer Menge von mindestens 0,5 Gewichtsteilen, bevorzugt mindestens 1 Gewichtsteil, pro 100 Gewichtsteile von (i), (ii), (iii) plus (iv).
- 40 11. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das Polymer (ii) anwesend ist in einer Menge von bis zu 20 Gewichtsteilen, bevorzugt bis zu 10 Gewichtsteilen, bevorzugter bis zu 50 Gewichtsteilen pro 100 Gewichtsteile von (i), (ii), (iii) plus (iv).
- 45 12. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das weitere nichtionische Tensid (iii) Alkylarylpolyetheralkohole mit einem Mittel von mindestens zehn Ethylenoxideinheiten pro Molekül und Alkylpolyetheralkohole mit einem Mittel von mindestens zehn Ethylenoxideinheiten pro Molekül enthält.
13. Zusammensetzung nach Anspruch 12, wobei die Alkylarylpolyetheralkohole Verbindungen der Formel

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oder



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enthalten, wobei x einen Mittelwert von mindestens 10 hat.

14. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das weitere nichtionische Tensid (iii) anwesend ist in einer Menge von mindestens 0,1 Gewichtsteilen, bevorzugt mindestens 0,5 Gewichtsteilen, pro 100 Gewichtsteile von (i), (ii), (iii) plus (iv).

15. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das weitere nichtionische Tensid (iii) anwesend ist in einer Menge von bis zu 10 Gewichtsteilen, bevorzugt bis zu 5 Gewichtsteilen, pro 100 Gewichtsteile von (i), (ii), (iii) plus (iv).

16. Verfahren zum Stabilisieren einer wässrigen Zusammensetzung mit einem pH-Wert von weniger als 7, enthaltend ein Gemisch aus einem wenig schäumenden nichtionischen Tensid mit einem Trübungspunkt von weniger als 70 °C und ein Polymer mit einem Gewichtsmittel des Molekulargewichts von 1.000 bis 250.000, welches ein Homopolymer aus Acrylsäure, Methacrylsäure, Maleinsäure, 2-Acrylamido-2-methylpropansulfonsäure oder Arcylamid darstellt oder ein Copolymer, welches Einheiten enthält, die abgeleitet sind aus zwei oder mehr aus Acrylsäure, Methacrylsäure, Ethacrylsäure, Maleinsäure, Itaconsäure, Hydroxyacrylsäure, C<sub>1</sub>-C<sub>4</sub>-Alkyl(meth)acrylaten oder -amiden, 2-Acrylamido-2-methylpropansulfonsäure, Styrol, Acrylamid, Isobutadien, Dimethylaminoethylmethacrylat und t-Butylacrylamid, wobei man bei dem Verfahren in die Zusammensetzung außerdem ein nichtionisches Tensid mit einem Trübungspunkt von 70 °C oder darüber einbringt, beispielsweise 80 °C oder darüber.

17. Verfahren nach Anspruch 16, wobei das wenig schäumende nichtionische Tensid, das Polymer und das weitere nichtionische Tensid und deren Mengen so sind, wie in einem der Ansprüche 2 bis 15 definiert.

18. Verwendung eines nichtionischen Tensids mit einem Trübungspunkt von 70 °C oder darüber, beispielsweise 80 °C oder darüber, zum Stabilisieren einer wässrigen Zusammensetzung mit einem pH-Wert von weniger als 7, enthaltend ein wenig schäumendes nichtionisches Tensid mit einem Trübungspunkt von weniger als 70 °C und Polymer, wobei das Polymer so ist wie in den Ansprüchen 1, 2 oder 3 definiert.

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### Revendications

1. Composition stable utilisable à titre d'auxiliaire acide de rinçage ou dans un auxiliaire acide de rinçage, qui comprend:

- (i) un tensioactif non ionique de faible pouvoir moussant ayant un point de trouble inférieur à 70°C;
  - (ii) un polymère ayant une masse moléculaire moyenne en poids de 1 000 à 250 000 et étant un homopolymère d'acide acrylique, d'acide méthacrylique, d'acide maléique, d'acide 2-acrylamido-2-méthylpropanesulfonique ou d'acrylamide, ou étant un copolymère comprenant des motifs dérivés de deux ou plus de deux parmi l'acide acrylique, l'acide méthacrylique, l'acide éthacrylique, l'acide maléique, l'acide itaconique, l'acide hydroxyacrylique, les alkyl(méth)acrylates ou amides en C<sub>1</sub>-C<sub>4</sub>, l'acide 2-acrylamido-2-méthylpropanesulfonique, le styrène, l'acrylamide, l'isobutadiène, le méthacrylate de diméthylaminoéthyle et le t-butylacrylamide;
  - (iii) un autre tensioactif non ionique ayant un point de trouble supérieur ou égal à 70°C, par exemple supérieur ou égal à 80°C; et
  - (iv) de l'eau;
- et dans laquelle la composition a un pH inférieur à 7.

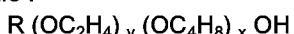
2. Composition selon la revendication 1, dans laquelle le polymère (ii) est un homopolymère d'acide acrylique, d'acide méthacrylique ou d'acide maléique, ou un copolymère formé à partir de deux ou plus de deux parmi l'acide acrylique, l'acide méthacrylique, l'acide éthacrylique, l'acide maléique, l'acide itaconique, l'acide hydroxyacrylique, les alkyl(méth)acrylates ou amides en C<sub>2</sub>-C<sub>4</sub> et l'acide 2-acrylamido-2-méthylpropanesulfonique.

3. Composition selon la revendication 1 ou la revendication 2, dans laquelle le polymère (ii) est un polymère polycarboxylé.

4. Composition selon l'une quelconque des revendications précédentes, dans laquelle le tensioactif non ionique de faible pouvoir moussant (i) comprend un ou plusieurs parmi les produits de condensation alcool gras en C<sub>6</sub> à C<sub>22</sub>/oxyde d'éthylène; les produits de condensation polyoxypropylène-polyoxyéthylène; les produits de condensation alkylpolyoxypropylène-polyoxyéthylène; les produits de condensation alkylpolyoxyéthylène-

polyoxypropylène; les polyoxyalkylèneglycols; les éthers benzyliques de produits de condensation polyéthoxy-lés d'alkylphénols; et les produits de condensation d'alcools coiffés à l'oxyde de butylène.

5. Composition selon la revendication 4, dans laquelle les produits de condensation d'alcools coiffés à l'oxyde de butylène répondent à la formule :



dans laquelle R est un groupe alkyle en C<sub>8</sub> à C<sub>18</sub>, y a une valeur moyenne de 3,5 à 10 et x a une valeur moyenne de 0,5 à 1,5.

6. Composition selon l'une quelconque des revendications précédentes, dans laquelle le tensioactif non ionique de faible pouvoir moussant (i) est présent en une quantité d'au moins 1 partie en poids, de préférence d'au moins 5 parties en poids, mieux encore d'au moins 10 parties en poids, pour 100 parties en poids de (i), (ii), (iii) plus (iv).

7. Composition selon l'une quelconque des revendications précédentes, dans laquelle le tensioactif non ionique de faible pouvoir moussant (i) est présent en une quantité allant jusqu'à 60 parties en poids, de préférence jusqu'à 50 parties en poids, mieux encore jusqu'à 40 parties en poids, pour 100 parties en poids de (i), (ii), (iii) plus (iv).

8. Composition selon l'une quelconque des revendications précédentes, dans laquelle le polymère (ii) a une masse moléculaire moyenne en poids allant jusqu'à 100 000, de préférence jusqu'à 70 000.

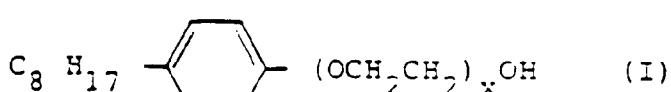
9. Composition selon l'une quelconque des revendications précédentes, dans laquelle le polymère (ii) est partiellement neutralisé.

10. Composition selon l'une quelconque des revendications précédentes, dans laquelle le polymère (ii) est présent en une quantité d'au moins 0,5 partie en poids, de préférence d'au moins 1 partie en poids, pour 100 parties en poids de (i), (ii), (iii) plus (iv).

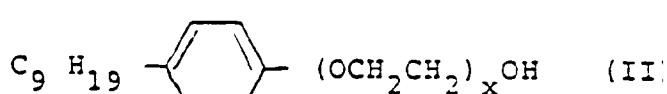
11. Composition selon l'une quelconque des revendications précédentes, dans laquelle le polymère (ii) est présent en une quantité allant jusqu'à 20 parties en poids, de préférence jusqu'à 10 parties en poids, mieux encore jusqu'à 5 parties en poids, pour 100 parties en poids de (i), (ii), (iii) plus (iv).

12. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'autre tensioactif non ionique (iii) comprend les alkylarylpolyétheralcools possédant une moyenne d'au moins dix motifs oxyde d'éthylène par molécule; et les alkylpolyétheralcools possédant une moyenne d'au moins dix motifs oxyde d'éthylène par molécule.

30 13. Composition selon la revendication 12, dans laquelle les alkylarylpolyétheralcools comprennent des composés de formule :



ou



45 où x a une valeur moyenne d'au moins 10.

14. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'autre tensioactif non ionique (iii) est présent en une quantité d'au moins 0,1 partie en poids, de préférence d'au moins 0,5 partie en poids, pour 100 parties en poids de (i), (ii), (iii) plus (iv).

15. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'autre tensioactif non ionique (iii) est présent en une quantité allant jusqu'à 10 parties en poids, de préférence jusqu'à 5 parties en poids, pour 100 parties en poids de (i), (ii), (iii) plus (iv).

16. Procédé de stabilisation d'une composition aqueuse ayant un pH inférieur à 7 et comprenant un mélange de tensioactif non ionique de faible pouvoir moussant ayant un point de trouble inférieur à 70°C et d'un polymère ayant une masse moléculaire moyenne en poids de 1 000 à 250 000 et étant un homopolymère d'acide acrylique, d'acide méthacrylique, d'acide maléique, d'acide 2-acrylamido-2-méthylpropanesulfonique ou d'acrylamide, ou étant un copolymère comprenant des motifs dérivés de deux ou plus de deux parmi l'acide acrylique, l'acide méthacrylique, l'acide éthacrylique, l'acide maléique, l'acide itaconique, l'acide hydroxyacrylique, les alkyl(méth)acrylates ou amides en C<sub>1</sub>-C<sub>4</sub>, l'acide 2-acrylamido-2-méthylpropanesulfonique, le sty-

rène, l'acrylamide, l'isobutadiène, le méthacrylate de diméthylaminoéthyle et le t-butylacrylamide, le procédé comprenant l'incorporation, dans ladite composition, d'un autre tensioactif non ionique ayant un point de trouble supérieur ou égal à 70°C, par exemple supérieur ou égal à 80°C.

17. Procédé selon la revendication 16, dans lequel le tensioactif non ionique de faible pouvoir moussant, 5 le polymère et l'autre tensioactif non ionique, et leurs quantités, sont tels que définis dans l'une quelconque des revendications 2 à 15.

18. Utilisation d'un tensioactif non ionique ayant un point de trouble supérieur ou égal à 70°C, par exemple supérieur ou égal à 80°C, pour stabiliser une composition aqueuse ayant un pH inférieur à 7 et comprenant un tensioactif non ionique de faible pouvoir moussant ayant un point de trouble inférieur à 70°C et un polymère, 10 le polymère étant tel que défini dans la revendication 1, 2 ou 3.

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