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54 **Detergent composition.**

57 A remarkably stable alkaline built liquid detergent composition is provided, containing in an aqueous medium:

- a) 0 to 25% by weight of nonionic detergent active;
- b) 5 to 40% by weight of alkaline agent;
- c) 0.1 to 2% by weight of structuring polymeric agent; and
- d) 2.5 to 20% by weight of a copolymer of acrylic acid and maleic acid,

the composition containing not more than 15% by weight of phosphate detergency builder. Preferably, the copolymer has a molecular weight of at least 5,000.

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DETERGENT COMPOSITION

The invention relates to built aqueous alkaline liquid detergent compositions.

Aqueous alkaline built liquid detergent compositions for use in fabric or dishwashing machines are well known. They are often considered to be more convenient to the user than the equivalent dry powdered or particulate products, as they are easier to dose, dissolve more readily, are non-dusting and usually occupy less storage space. Their formulation, however, is difficult since, on the one hand, considerable quantities of builder salts and alkaline agents should be incorporated to provide consumer-satisfactory detergency and, on the other hand, liquid products should be stable under a wide range of storage conditions and should have good pourability for consumer convenience.

It is known, for example, from EP-A-120533 to provide alkaline liquid detergent compositions containing relatively substantial amounts of an alkaline agent and a detergency builder together with rather smaller quantities of a nonionic detergent active and a structuring polymeric agent which may be cross-linked polyacrylate. The detergency builder used in such a composition may be a phosphate builder, in particular sodium tripolyphosphate. There is nowadays a general desire to reduce the phosphate content of detergent products and indeed the above-mentioned EP-A-120533 does mention the possibility of using other builders.

US-A-6.608.188 describes a low phosphate machine dishwashing composition in which an acrylic acid/maleic acid copolymer is employed as builder. This composition also contains nonionic detergent active, some phosphate and an alkaline agent, but the compositions specifically described are solid, presumably in powder form.

A difficulty in providing aqueous alkaline built liquid detergent compositions is that of keeping the liquid stable against sedimentation. Commercial compositions in accordance with the above-mentioned European application have tripolyphosphate and nonionic detergent active present in the liquid as a dispersed phase. The polyacrylate acts to stabilise the dispersion against sedimentation.

It has been known to include in such compositions a small percentage of linear polyacrylate having a molecular weight of around 4,500. The use of linear polyacrylates in detergent compositions has been suggested by P. Zini in "Seifen-Oele-Fette-Wachse" 83, 45-48 (1987) and also in US-A-4,579,676. Experimentation with such polyacrylates of varying molecular weight, however, reveals that polyacrylate with molecular weights of 4,500 and above are detrimental to the stability of built aqueous alkaline liquid compositions, the loss of physical stability becoming much worse as the molecular weight increases. It would be expected that acrylic acid/maleic acid copolymers of the type referred to in US-A-4,608,188 would behave in a similar way to linear polyacrylates and be highly detrimental to stability.

We have now found that, unexpectedly, acrylic acid/maleic acid copolymers can be utilised successfully in these liquid compositions and moreover are advantageous as a builder to replace tripolyphosphate.

These acrylic acid/maleic acid copolymers do have some detrimental effect on physical stability of the liquid compositions but much less than would be predicted. Moreover, at low percentages of the copolymer, stability actually increases with the quantity of copolymer included until a maximum stability is reached, after which the stability begins to reduce with increasing quantity of copolymer.

These copolymers are advantageous as builders in that they can replace tripolyphosphate, giving adequate building performance, at reasonable cost, without bringing other problems of scaling or excessive foaming. They do not fall foul of current environmental protection regulations and also allow the products to contain active chlorine.

According to the present invention there is provided an alkaline built liquid detergent composition containing in an aqueous medium:

- a) 0 to 25% by weight of nonionic detergent active;
- b) 5 to 40% by weight of alkaline agent;
- c) 0.1 to 2% by weight of structuring polymeric agent; and
- d) 2.5 to 20% by weight of a copolymer of acrylic acid and maleic acid,

the composition containing not more than 15% by weight of phosphate detergency builder.

The copolymer employed in this invention will generally contain acrylic acid and maleic acid in a mole ratio of 1:0.2 up to 1:1. Copolymers with more maleic acid are not stable. The molecular weight of the copolymer will generally be at least 5,000, may be at least 40,000 and may extend up to 100,000 or even more. It is preferred to employ copolymer in which the ratio of acrylic acid to maleic acid is 1:0.25 to 1:1. Suitable copolymers are produced by BASF under their designations Sokalan CP5 and Sokalan CP7. In the former, the mole ratio of acrylic acid to maleic acid is 1:0.3 and the average molecular weight is 70,000.

while in Sokalan CP7 the mole ratio is 1:0.6 and the average molecular weight is 50,000.

The preferred amount of the copolymer is in the range from 5 to 15% by weight of the composition.

The nonionic detergent active which may be used in the composition is preferably of the type consisting of a fatty alcohol condensed with an alkylene oxide or a mixture of alkylene oxides. It is particularly preferred to employ a nonionic detergent active of the type called for in EP-A-120553, that is to say fatty alcohol condensed with an ethylene oxide and propylene oxide and/or butylene oxide. It is desirable to select the alkoxylated fatty alcohol or mixture thereof such that the overall ratio between the number of ethylene oxide units and the propylene and/or butylene oxide units is below 9, preferably below 2.5 or even 1.8. The term "overall ratio" refers to the fact that either a single alkoxylated alcohol may be used having in its alkylene oxide radical a suitable ratio of ethylene oxide to propylene and/or butylene oxide units or a mixture of alkoxylated alcohols may be used having a suitable ratio only on an average.

The nonionic detergent is normally present in an amount of at least 1% by weight, the amount preferably ranging from 1 to 15% by weight of the total composition.

Nonionic detergents for use in compositions of the present invention can be readily obtained commercially, such as e.g. those sold under the trade names Lutensol LF 400 to 1300 (ex BASF AG) and Plurafac RA 30 to 343 (ex Produits Chimiques Ugine-Kuhlmann).

The nonionic detergents can be used as sole detergent but other detergent-active ingredients, such as e.g. water-soluble anionic sulphate or sulphonate detergents, can be tolerated provided their amount does not exceed 50% by weight, preferably 3% by weight or even 1% by weight of the total composition.

The alkaline agent is preferably present in an amount of at least 10% by weight, more preferably 15 to 30% by weight of the total composition. The preferred alkaline agents are the alkali metal hydroxides. Other agents may be used, such as alkali metal orthosilicates, metasilicates and disilicates. Of these, sodium metasilicate is preferred. Also mixtures of alkaline agents may be used, such as a combination of approximately equal weights of sodium orthosilicate and potassium hydroxide which is another preferred possibility.

The present compositions are externally structured and for this purpose they contain a structuring or thickening polymeric agent, which may be essentially a single such agent. Suitable agents are found among the alkali-stable polymers, notably cross-linked polymers of acrylic acid, having molecular weights of 500,000 to 4,000,000, preferably 1,000,000 to 1,500,000. Especially suitable are the water-soluble polymers of acrylic acid, cross-linked with about 1% of a polyallyl ether of sucrose having an average of about 5.8 allyl groups for each sucrose molecule, the polymer having a molecular weight in excess of 1,000,000. Examples of such polymers are Carbopol 934 and 941. Carbopol is the Registered Trademark of B.F. Goodrich Co. Ltd, the manufacturers of these polymers. The preferred polymer is Carbopol 941. Depending on the viscosity which is desired, they may be included in the range of from 0.1% to 1% by weight, but preferably their amount varies from 0.2% to 0.8% by weight, and in particular from 0.2 to 0.6% by weight of the total composition.

The liquid detergent composition of the invention may further contain any of the adjuvants normally used in fabric-washing detergent compositions, e.g. sequestering agents such as ethylene diamine tetraacetate and diethylene tetramine methylene phosphoric acid, soil-suspending and anti-redeposition agents such as carboxymethylcellulose, polyvinylpyrrolidone and the maleic anhydride/vinylmethylether copolymer; fluorescent agents, hydrotropes, conditioning agents, lather boosters; lather-depressors such as liquid polysiloxane anti-foam compounds; alkaline-stable enzymes; perfumes, germicides and colourants.

In addition to the acrylic acid/maleic acid copolymer, the compositions of this invention may include from 0 to 15% of phosphate builder. Preferably the amount of phosphate builder is in the range 0 to 10% by weight of the composition. One possibility within the invention is to omit phosphate builder entirely and rely on the copolymer as sole builder. Another possibility is to include some phosphate builder, with the copolymer then being a second builder employed to give adequate detergency building while keeping the quantity of phosphate down to within the maximum of 15% (preferably 10%) by weight of the composition. In compositions containing phosphate a quantity of phosphate may be within the range of 1 to 15%, preferably 1 to 10%, by weight of the composition, with the preferred phosphate being alkali metal tripolyphosphate.

The compositions of this invention may contain a source of active chlorine such as hypochlorite bleach. If a source of active chlorine is present, it is preferred that the amount of active chlorine is 0.2 to 2%, preferably 0.5 to 1% by weight of the composition.

Compositions of the present invention normally have viscosities within the range of 400 to 3,000 mPa.s at 21 sec⁻¹ at 20° C and preferably within the range of 500 to 1500 mPa.s at 21 sec⁻¹ at 20° C.

Compositions of the present invention are especially advantageous having pH-values within the high alkaline region, in particular values equal to or above 11, but preferred are pH-values above 12 or even

above 13.

The invention will be further illustrated in the following examples. All percentages used therein are by weight unless otherwise specified.

Example 1A (comparative)

A series of liquid compositions was prepared, all containing the following:

Sodium hydroxide	22.8%
Plurafac RA 340 (nonionic)	3.6%
Carbopol 941	0.71%
Linear polyacrylate	5.0%
Water	balance

Polyacrylates of various molecular weights were used, and the viscosity at 10^{-5}sec^{-1} was determined with a Rheodeer viscometer. (Viscosity is a good indication of physical stability of the composition.) The results were as follows:

Molecular weight of Polyacrylate	Viscosity (kPa.s)
1,000	29
2,000	32
4,500	12
15,000	1.3
29,000	0.04
90,000	0.008
Control, no polyacrylate	32

Thus it can readily be seen that at molecular weights of 4,500 and above, the polyacrylate leads to loss of physical stability which worsens with increasing molecular weight.

Example 1B

When the linear polyacrylate used in Example 1A was replaced with Sokalan CP5 or CP7 the viscosity was surprisingly much higher.

Example 2

Built liquid detergent compositions were prepared, and their viscosities at 10^{-5}sec^{-1} determined, as set out in the following Table:

	A	B	C	D	E	F
Sodium tripolyphosphate (anhydrous)	10.0%	10.0%	10.0%	10.0%	10.0%	10.0%
Sokalan CP7	5.0%	7.5%	10.0%	5.0%	7.5%	10.0%
Sodium hydroxide	16.0%	16.0%	16.0%	20.0%	20.0%	20.0%
Plurafac RA340	2.5%	2.5%	2.5%	2.5%	2.5%	2.5%
Carbopol 941	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%
Water	balance					
Viscosity (kPa.s)	2.9	6.4	3.3	16	22	14

It can be seen that the viscosity rises to a maximum, that with 7.5% of Sokalan CP7 being greater than with 5% or 10%.

The compositions A, B and C were each dissolved in samples of water of varying hardness, at 1.5 g./litre and at 20 ° C. The residual calcium ion concentration was measured. The results are shown in the attached Figure 1 which is a graph of pCa against hardness in French Hardness units. These results indicate that building capacity depended directly on the concentration of Sokalan CP7.

Example 3

Built liquid detergent compositions without phosphate were prepared, and their viscosities at 10^{-5} sec⁻¹ determined, as set out in the following Table:

Water	72.0%	69.5%	67.0%	64.5%	62.0%
NaOH	20.0%	20.0%	20.0%	20.0%	20.0%
Sokalan CP7	5.0%	7.5%	10.0%	12.5%	15.0%
Plurafac RA340	2.5%	2.5%	2.5%	2.5%	2.5%
Carbopol 941	0.5%	0.5%	0.5%	0.5%	0.5%
S(kPa.s)	1.2	1.0	2.1	1.8	1.4

Viscosity and hence stability were greatest at around 10 to 12% Sokalan CP7.

The compositions of this Example were dissolved in 7 French Hardness water at 1.5 g./litre and at 20 ° C. In Figure 2 the resulting residual calcium ion concentration as pCa is plotted against the level of Sokalan CP7. Values of pCa for equivalent compositions where Sokalan CP7 is replaced by sodium tripolyphosphate are also shown. It can be seen that on weight basis Sokalan CP7 is more effective as a builder.

Example 4

Sokalan CP5 was used in built liquid detergent products with low, but some, phosphate. The compositions and viscosities are set out below:

Water	61.2%	56.2%	51.2%
Sokalan CP5	5.0%	10.0%	15.0%
NaOH	20.0%	20.0%	20.0%
STP	8.0%	8.0%	8.0%
Plurafac RA340	5.0%	5.0%	5.0%
Carbopol 941	0.8%	0.8%	0.8%
S(kPa.s)	15	36	31

Viscosity and hence stability were greatest at around 10% Sokalan CP5.

Claims

1. An alkaline built liquid detergent composition containing in an aqueous medium:

- 0 to 25% by weight of nonionic detergent active;
 - 5 to 40% by weight of alkaline agent;
 - 0.1 to 2% by weight of structuring polymeric agent; and
 - 2.5 to 20% by weight of a copolymer of acrylic acid and maleic acid,
- the composition containing not more than 15% by weight of phosphate detergency builder.

2. A composition according to claim 1, containing 5 to 15% by weight of the copolymer of acrylic acid and maleic acid.

3. A composition according to claim 1 or claim 2, wherein the copolymer has a molecular weight of at least 5,000.

4. A composition according to any one of the preceding claims, wherein the copolymer contains acrylic acid and maleic acid in a mole ratio of 1:0.25 to 1:1.

5. A composition according to any one of the preceding claims, containing 15 to 30% by weight alkali metal hydroxide.

5 6. A composition according to any one of the preceding claims, containing not more than 10% by weight of phosphate detergency builder.

7. A composition according to any one of the preceding claims, containing 1 to 15% by weight of nonionic detergent active.

8. A composition according to claim 7, wherein the nonionic detergent active is alkoxylated fatty alcohol nonionic detergent or mixture thereof having in the alkylene oxide radical an overall ratio between the number of ethylene oxide units and the number of propylene and/or butylene oxide units of less than 9.

9. A composition according to any one of the preceding claims, wherein the structuring polymeric agent is cross-linked polyacrylic acid having a molecular weight of at least 500,000.

10. A composition according to claim 9, wherein the amount of cross-linked polyacrylic acid is 0.3 to 15 1% by weight of the composition.

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