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(54) Detergent compositions.

(57) A stable, viscous, liquid detergent composition comprises a detergent builder at least partially present in insoluble form, a soluble alkali-metal silicate having a (silica-to-alkali) ratio of from 0.5 to 3.0, and water. The composition is not structured by conventional agents such as clay or polymer.

The composition is of particular use as a machine dishwashing cleanser.

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DETERGENT COMPOSITIONS

The present invention relates to detergent compositions. In particular, it relates to liquid machine dishwashing detergent compositions suitable for use in cleansing food soils from cooking utensils, dishes, glasses and similar ware.

More particularly, the present invention relates to a stable, pourable, aqueous system comprising at least partially undissolved builder salts and a dissolved alkali silicate, the composition being essentially free of conventional structuring agents. The system is characterised by its thixotropic nature.

Detergents for use in domestic machine dishwashers are generally available in powdered or granular forms. However, such solid compositions exhibit a number of disadvantages for the producer and user. In manufacture, the compositions cannot generally be spray-dried, and thus separate manufacturing facilities to those generally used for powdered detergents must be built. The powders often incorporate large lumps caused by caking during storage at high humidity. This can cause difficulties in dispersion. Powdered forms of the product are often very dusty, which can affect dispensing as well as causing irritation.

The use of liquid forms of detergent for machine dishwashing eliminates many of the above disadvantages solely attributable to powders. However, liquid detergents must meet certain requirements. Firstly, the liquid must be a uniform mixture of ingredients in order to deliver the optimum combination of active components to the wash with each dose. By active components, we mean those components which actually take part in the cleaning, rather than those acting as fillers. In many formulations described in the art, this requires that the liquid be shaken before each use in order to re-mix the different components.

A preferred product should be stable against physical separation and segregation of the active components during storage. Particulate solids, for example detergency builders, should remain suspended in liquid detergents. To keep the solids in suspension, some kind of structuring system is necessary. In aqueous detergent liquids this may be achieved either by "external structuring", ie adding an additional component such as a polymer or clay, or using the interaction of the water in the liquid and the detergent actives themselves, to form an "internal structure" to support the solids (eg secondary alkane sulphonates and phosphonates). In all cases, microscopic investigation indicates that some type of suspending network is formed.

Accordingly, it should be understood that the phrase 'structuring agent' as used herein is taken to mean any component, e.g. clay, polymer or biocellulosic, which at suitable amounts within a liquid imparts a structure to said liquid, usually by network formation. The use of such agents, particularly clay, in lower amounts is not to be taken as being excluded from compositions. Such low amounts may act as builders or rinse aids. The critical amount of the component in question may only be determined by reference to experiments or the prior art.

For use with machine dishwashers, the detergent must be compatible with the dishwashing equipment presently available. Home dishwashing machines use a detergent cup which has been designed to house powdered or granular solid detergent and deliver it to a specific wash cycle. The cups are usually held vertically on the dishwasher door and are not designed to contain low viscosity liquids. Consequently, liquids for use as machine dishwashing detergents must possess sufficient viscosity to be effectively retained in the cup and avoid leakage into the machine during cycles which precede the wash. Excessive leakage will lead to under-dosing in the wash cycle and may affect cleaning performance. However, they must not be so viscous that they cannot be washed out of the dispensing cup at the appropriate time.

The prior art has disclosed a number of methods for thickening liquid machine dishwashing compositions and for providing some degree of stability. GB 1 527 706 discloses a slurry structured by the addition of synthetic polymers. However, it is thought that the low yield point in liquids containing, eg polyacrylate as the only structuring agent, causes poor cup retention.

GB 2 140 450 discloses liquids structured with clay. The clay lowers the amount of active component which can be delivered in each dose. Furthermore, the presence of insoluble clay minerals can negatively affect glass spotting and filming performance. The use of biopolymers or cellulosics within a liquid detergent base has also been proposed to provide thickened systems, eg US 4 226 736 and US 4 260 528. Since most biopolymers react readily with hypochlorite, these systems are unstable and exhibit a gradual loss in viscosity if hypochlorite is present. GB 2 185 037 has disclosed the use of long-chain fatty acids to provide a thickening effect.

The systems described in the prior art are all, in principle, structured by the use of external, network-forming structurants and, in general, these liquids possess a shear thinning character, ie they exhibit a high viscosity at low shear rate and a low viscosity at high shear rate. Furthermore, and this illustrates the thixotropic nature of the liquids, the viscosity of these liquids is time-dependent after distortion has taken

place.

The present invention makes use of different principles to obtain pourable and stable liquid systems. In contrast to the prior art the present invention does not involve the use of a network-forming structurant. Due to the absence of such a structurant, which in the current state of the art is judged to be essential for keeping the solid particles well suspended, the present invention involves liquid systems (dispersions) which are Newtonian (eg not shear thinning) over a broad range of shear rate values: 1-100 sec^{-1}. It appears that at extremely low shear rates, which require special equipment (controlled stress Deer rheometer) for measurement, the deviation from Newtonian behaviour becomes more pronounced, which is in line with a theory ("Inleiding in de Reologie, Reometrie, Disperstereologie en Polymeerreologie", Blom C, Jongschaap RJJ, Mellema J, Technische Hogeschool Twente Kluwer Technische Boeken, 1 Druk 1986) developed to describe the rheological behaviour of concentrated dispersions. Hence, it could not be expected according to the current state of art that these dispersions would be physically stable. Rapid sedimentation should occur.

Without being bound to any theory we assume that in compositions of the present invention the solids are present as individual particles and not as flocculates. By selecting a water-soluble alkali-metal silicate with a suitable ratio SiO_2/M_2O (M = K, Na) this phenomenon, a deflocculated system as indicated by pseudo-Newtonian behaviour, can be obtained. Addition of an electrolyte may broaden the range in which the desired rheological behaviour is observed. The deflocculation effect can be illustrated by the following observation: the addition of 40% zeolite 4A to a 20% sodium disilicate (ratio 3.6) solution results in the formation of a viscous, shear thinning unusable paste outside the scope of the invention. Adjusting the silicate ratio with NaOH or KOH the viscosity will drop considerably and a thin, pourable, pseudo-Newtonian system is obtained by deflocculation of the particles.

According to the present invention there is provided a stable, viscous, liquid detergent composition comprising:

(a) a detergent builder at least partially present in insoluble form;

(b) a soluble alkali-metal silicate having a (silica-to-alkali) ratio of from 0.5 to 3.0; and

(c) water

characterised in that the composition has a Thixotropic Index of from 2.5 to 0.5, the composition being essentially free of a structuring agent.

The ratio of the alkali-metal silicate is between 0.5 and 3.0, preferably between 0.5 and 2.2 and more preferably between 0.6 and 1.9.

The preferred rheological behaviour is identified by the Thixotropic Index (TI) which has to be between 0.5 and 2.5. The Thixotropic Index is herein defined as the ratio of the apparent LVT Brookfield viscosity of a sample after 3 minutes at room temperature using a No 4 spindle at (a) 3 rpm and (b) 30 rpm.

To explain the surprisingly good physical stability of the liquid systems according to the present invention, it might be speculated that by selecting the proper concentration and ratio of alkali-metal silicate, the electrostatic force between the particles, which causes them to flocculate, are more than compensated by repulsion forces. Hence, the individual particles sediment out slowly at a rate determined by Stokes' law, whereby at high solids levels (>20%) the phenomenon of hindered settling will result in even lower settling rates. Overall this will lead to liquid systems with a good physical stability.

The compositions according to the present invention may be used in formulating detergent liquid cleaning products. These may be formulated in a very wide range of specific forms, according to the intended use. They may be formulated as cleaners for hard surfaces (with or without abrasive) or as agents for ware washing (cleaning of dishes, cutlery etc) either by hand or mechanical means, as well as in the form of specialised cleaning products, such as for cleaning surgical apparatus or artificial dentures.

Products formulated for ware washing, in particular for use in machine dishwashers, constitute a preferred form of the present invention.

The composition according to the present invention has improved rheology and stability in comparison to compositions of the prior art and can deliver a high and uniform dosage of active ingredients to the machine wash cycle.

The detergent builder material may preferably be a non-phosphate builder salt. Such builders include water-soluble inorganic carbonate and bicarbonate. Water-soluble organic builders which may be used include polyacetates, carboxylates, polycarboxylates and polyhydroxy sulphonates, at least a proportion of the salt remaining undissolved. Particularly preferred as builders are zeolite and amorphous silica/alumina builders. Aluminosilicates of the zeolite type may be prepared as described in US 2 882 243 (Union Carbide) or of the amorphous type as described in EP 0 097 512 (Unilever). The aluminosilicate is preferably of the formula 0.8-1.5 Na_2O; Al_2O_3; 1.7 - 3.0 SiO_2; 2 - 6 H_2O.

Examples of other suitable builders are NTA, EDTA, CMOS and DPA.

In terms of weight percentage of the total composition, the builder may constitute from 5-60%, most preferably from 20-40%.

The second essential component of the present invention is a silicate material. When in combination with an alkali material, disilicates are particularly preferred, although metasilicates may also be included. The alkali-metal silicates which are used serve as anti-corrosion agents, protecting metal and china surfaces against harshly alkaline environments present during a dishwashing cycle.

In terms of weight percentage of the total composition, the silicate-based material may constitute from 3-40%, most preferably from 5-20%.

In its broadest sense, the present invention comprises compositions which do not necessarily contain any detergent surfactants. In the absence of such surfactants, the compositions may be used for the delivery of caustic agents to the wash liquor during mechanical dishwashing operations. However, it is generally preferred to include one or more detergent surfactant agents. In general, these may be selected from one or more of nonionic, anionic, cationic, zwitterionc and amphoteric agents. Such agents are commercially available and will be well known by those skilled in the art; for instance, they are fully described in the literature, such as in "Surface Active Agents and Detergents", Volumes I and II by Schwarz, Perry and Berch. Preferably, any detergent active material comprises one or more nonionic agents, for example the condensation products of alcohols having from 8-16 carbon atoms, and alkyl phenols with alkylene oxides including ethylene oxide, propylene oxide, butylene oxide and mixtures thereof. Preferably the alcohols are linear, having from 12-15 carbon atoms, and are condensed with 2-10 mols of ethylene oxide. Most preferred are those compounds which are generally regarded as "low-foaming", especially those where the alkylene oxide chain is terminated by a moiety other than hydrogen.

The compositions according to the present invention may be prepared by admixture of the various components.

Conventional additives such as colourants and perfumes may be present in the composition in conventional amounts.

An alkali-metal hypochlorite may be present in the formula as an agent for removing tea, coffee and other food stains from cups, dishes, flatware, etc. The bleach source may be present in the mixture at from 0.1-10 wt %, with the most preferred range being from 0.1-2 wt % (percentages as active chlorine).

Electrolytes such as NaCl, NaI, Na_2SO_4 may be included in the composition at from 0.1 to 10 wt %.

Defoamers may be included in the composition. These defoamers may be of the general type of slightly soluble alkyl carboxylates, alkyl phosphates, hydrophobic silicas, silicone defoamers, or many others. In addition to being an effective defoamer, the species should be stable to hypochlorite. The defoamer may optionally be present in the composition at from 0-5 wt %, more preferably from 0.1-1 wt %, and most preferably from 0.1-0.5 wt %.

The products according to the present invention exhibit a high degree of stability at room temperature, in comparison to other systems. Unlike known liquids, the products produced in accordance with the present invention do not require shaking in order to redisperse the ingredients. Furthermore, compositions formulated in accordance with the present invention exhibit a higher density (1.7-1.8) than comparable products of the prior art. This is particularly important when considering transportation. A more concentrated liquid benefits from lower packing and transport costs. Also, a unit dose will deliver more active ingredients per unit dose than products produced in accordance with the art.

The absence of network formation, due to the deflocculation forces within the system, has also important consequences for the nature of the product before dosing. Liquid systems according to the present invention are not susceptible to setting after storage. Even after prolonged storage the product does not solidify and no setting has been observed. The inference is that the product can be dosed without shaking or squeezing the bottle which is required for the current liquids with an external structurant. Dealing with bottles of 1.5-2.5 kg this benefits the convenience aspect of the product.

The compositions of the present invention provide a liquid system which is very convenient for consumers whilst being also perfectly suitable for an automatic dosing application. The automatic dosing principle can be used for domestic as well as industrial dishwashing machines.

Unlike compositions of the prior art, compositions according to the present invention are pourable from rest without need for shear thinning. Dispenser behaviour is strongly determined by the rheological properties of the liquid. In the prior art, Newtonian liquids are not considered to be suitable. Some of the liquids according to the present invention have been tested to measure dispenser cup leakage in a number of commercially-available dispenser types. It was found that the degree of dispenser cup leakage was acceptable if the liquid had a viscosity of at least 2000 mPAS.

The dosing of the machine dishwashing liquids which are currently available on the market makes use of bottles with a small aperture to realise high shear rates to break down the network. Because the liquid

system according to the present invention is pseudo-Newtonian this high shear rate regime is not required during dosing so that a selection can be made out of a wide range of bottles. Hence a broad conventional spout, eg 0.5-1.0 cms diameter, optionally equipped with a self-draining device, may be used for a bottle containing the liquid system according to the present invention. Less spillage, an optimal dosing and less undesired skin contact result from the lack of need to shake, squeeze or squirt the bottle.

It has been found that dishwashing compositions formulated according to the present invention show less tendency to cause spot formation on glass than other conventionally structured (eg by polymers or clays) liquid detergent systems. This is particularly noticeable after a number of wash cycles.

A further possible use of the system of the invention arises when considering systems incorporating zeolite as the builder. Zeolite slurrys of the prior art are known to be unstable. The liquids of the present invention provide a stable zeolite slurry which does not separate on standing. The slurry can be spray dried as a basis for formulating powders for, e.g. fabric or ware washing.

The invention will now be further illustrated by means of the following non-limiting examples, wherein all percentages are given by weight unless otherwise stated.

Examples

1.1-1.3

Using a basic composition of 40% zeolite and 20% disilicate, the viscosity of different compositions was measured as varying amounts of KOH were added. Viscosity was measured with respect to shear rate for each system.

Base :	40% zeolite	20% disilicate	
Addition :	0% KOH	10% KOH	20% KOH
Log shear rate	log visc	log visc	log visc
-0.75	5.0	-	-
-0.45	4.7	4.1	-
-0.06	4.3	4.2	3.7
0.25	4.1	4.2	3.7
0.55	3.8	4.1	3.8
0.85	3.4	4.2	3.8
1.15	3.4	4.1	3.8
1.45	3.4	4.1	3.8

With the addition of KOH to lower the silicate ratio, the composition exhibits pseudo-Newtonian behaviour. When no KOH is added, the liquid is shear thinning.

2.1-2.3

Using a base composition of 20% disilicate and 10% KOH, log viscosity was measured as a function of log shear rate for varying additions of zeolite to the system.

Base :	20% disilicate		10% KOH
Addition :	35% zeolite	40% zeolite	45% zeolite
Log shear rate	log visc	log visc	log visc
-1.06	-	-	-
-0.75	-	-	4.5
-0.45	-	4.1	4.4
-0.06	-	4.1	4.4
0.25	3.5	4.2	4.5
0.55	3.6	4.2	4.5
0.85	3.5	4.1	4.5
1.15	3.5	4.1	4.5
1.45	3.5	4.1	4.5

As zeolite is added, the viscosity increases, but a pseudo-Newtonian behaviour is exhibited.

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The stability of liquid compositions according to the present invention was measured as the percentage of separation at 1, 2, 3 and 4 weeks after storage at 20 ° C.

Zeolite	Disilicate	KOH	t (weeks)	1	2	3	4
				% Separation			
13	20	10		3	6	13	12
36	20	10		0	1	1	1
46	20	10		0	1	1	1
50.	20	10		0	0	0	0
32	20	5		1	2	2	2
48	20	5		1	1	1	1

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The build-up of spots on glasses was measured over a number of washes using different compositions formulated according to the present invention. Comparisons were made with a commercially-available polymer structured machine dishwashing liquid.

Formulation	A	B	C
Zeolite 4A	30	10	30
Disilicate	20	20	20
KOH	10	10	5
Hypochlorite	1	1	1
Water	---------- to 100% ----------		

The build-up of spots over 4 washes is measured as the number of spots on a glass tumbler:

0	1
1-5	2
6-10	3
11-20	4
>20	5

Washing was carried out in a Bauknecht GS 870 S machine on a normal 55° C programme, dosing at 30 g/machine. (Water 15° French hardness.)

An average score for 20 glasses was made.

	Spot Score			
Wash No	A	B	C	Comparison
1	1.0	1.6	2.0	5.0
2	3.4	1.4	4.0	5.0
3	3.9	2.4	4.9	5.0
4	4.0	3.2	5.0	5.0

It can be seen that spot build-up is considerably reduced using compositions formulated in accordance with the present invention in comparison to compositions which are "externally" structured.

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The following composition was prepared:

	wt%
Zeolite 4A	42
Sokalan Polymer (20% slurry)	5
Disilicate (ratio 2.0)	20
K OH (85% soln)	5
HOCl (as Cl_2)	1
Water	to 100

The composition was found not to have separated over a period of weeks and was suitable for cleaning dishes in a machine dishwasher.

Claims

1. A stable, viscous, liquid composition comprising:
(a) a detergent builder at least partially present in insoluble form;
(b) a soluble alkali-metal silicate having a (silica-to-alkali) ratio of from 0.5 to 3.0; and
(c) water.
characterised in that the composition has a Thixotropic Index of from 2.5 to 0.5, the composition being essentially free of a structuring agent as herein defined.

2. A composition as claimed in claim 1, characterised in that the detergent builder is an aluminosilicate.

3. A composition as claimed in claim 3, characterised in that the aluminosilicate is a zeolite.

4. A composition as claimed in any one of claims 1 to 3 characterised in that the composition comprises:
(a) 20-45 wt % of a detergent builder;
(b) 5-25 wt % of a silicate;
(c) 30-70 wt % of water.

5. A composition as claimed in claim 1 comprising
(a) 35-45 wt% zeolite
(b) 0.1-1.5 wt% polymeric co-builder
(c) 15-25 wt% disilicate (ration 2.0)
(d) 3-8 wt% KOH (85%)
(e) 0.1-1.5 wt% HOCl (as available Cl_2)
(f) Water to 100 wt%.

6. A composition as claimed in any one of claims 1 to 4, characterised in that it further comprises from 0.1 to 10 wt % of an electrolyte.

7. A composition as claimed in any one of the preceding claims having a Thixotropic Index of from 1.5 to 0.8.

8. The use of a composition as claimed in any one of the preceding claims as a machine dishwashing cleanser.

9. A bottle containing a composition as claimed in any one of claims 1 to 6, characterised in that the bottle has a spout of from 0.5 to 1.0 cm in diameter, optionally provided with a self-draining device.