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(54) Machine dishwashing composition.

(57) An aqueous thixotropic liquid cleaning composition comprising an alkali-metal builder and an alkali-metal silicate can be stabilised against phase separation during storage by the addition of an alkyl phosphate, phosphonate, sulphate or sulphonate.

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MACHINE DISHWASHING COMPOSITION

The present invention relates to machine dishwashing liquid detergent compositions suitable for use in cleansing food soils from cooking utensils, dishes and glasses. More particularly, the present invention relates to an aqueous thixotropic structured system comprising an alkaline source and builder salts.

The use of liquid forms of detergent for machine dishwashing offers several advantages over powdered or granular forms. These advantages include greater ease of handling in dispensing and dosing, the elimination of lump formation, "caking" and dust, and improved solubility.

However, liquid detergents must meet certain requirements. Firstly, the liquid detergent must be a uniform mixture of ingredients to deliver the optimum combination of active components to the wash with each dose. In most current formulations, this requires that the liquid be shaken before each use to remix the components. A preferred product should be stable against physical separation and segregation of its active components. High viscosity at low shear rate contributes to physical stability of the liquid and protects against separation of the active components.

Physical stability can be achieved through the use of suspending or viscosifying systems to enhance the liquid rheological properties. These agents must maintain viscosity at low shear rate under the high ionic strength conditions present in a well-built liquid detergent, and must be chemically compatible with the other components of the formula, especially the chlorine bleach used to assist stain removal.

The liquid dishwashing 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 not designed to contain low viscosity liquids. Consequently, liquids for use as machine dishwashing detergents must possess high 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.

Although high viscosity is desirable under storage conditions or while the material is in the detergent cup, the liquid must readily and conveniently dispense from its container. Therefore, a liquid that undergoes a viscosity decrease under the influence of applied shear such that the decrease is reversible with time after the removal of shear is preferable for this application. This behaviour is termed "shear-thinning" and is desirable for liquid dishwashing detergents. Agitation of the liquid in the container, such as squeezing or shaking, will supply sufficient shear strain to initiate shear-thinning behaviour and increased liquid flow. Optimum flow properties would allow for easily pourable fluids which maintain sufficient viscosity at higher shear rates to prevent or minimise excessive spillage. The liquid should quickly regain its structure after dispensing. This liquid characteristic is termed "thixotropy".

There is now disclosed a thixotropic liquid detergent composition suitable for use in a machine dishwasher which is structured by interaction between the components, giving a positive effect on the rheology of the components, without the need to include a conventional thickening agent. This effect is shown in viscosity increases and in yield point enhancement.

The prior art has disclosed a number of systems for thickening of machine dishwashing compositions. 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 at levels used for structuring 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.

Micellar structured liquids are known in other areas, eg in thickened bleach systems (GB 1 466 560), usually containing over 90 wt% hypochlorite solution and no builder. Systems thickened by synergistic action with urea (eg GB 1 579 668) are also known. GB 2 185 037 describes aqueous, thixotropic machine dishwashing detergents which are structured by fatty mono- or polycarboxylic acid.

According to the present invention there is provided an aqueous, thixotropic liquid cleaning composition comprising an alkali-metal builder and an alkali metal silicate and a stabiliser comprising from 0.05 to 5% by weight of an alkyl phosphate, phosphonate, sulphate or sulphonate, said composition optionally comprising a detergent active.

The present invention is based upon the discovery that the alkyl derivatives named may be used as

liquid stabilisers. Alkyl phosphates have previously been described for use in machine dishwashing compositions as foam depressors, but we do not believe that their use as liquid stabilisers has previously been described. Structuring occurs independently of the presence of active detergent.

The compositions according to the present invention may also preferably incorporate a bleach, eg. a hypochlorite. The system is stable when these bleaches are included in comparison to some systems of the prior art, wherein the presence of hypochlorite destroys system stability.

The composition according to the present invention has improved rheology and stability and can deliver a high and uniform dosage of active ingredients to the machine wash cycle. An improvement of the structuring also results in easier dispensing from the product container to the dispenser and from the dispenser to the machine wash at the appropriate time.

The system of the present invention has good stability against physical separation upon storage, providing a more uniform product. Poor physical stability can lead to development of a stratified liquid through separation of a fluid layer and a solids layer. This requires remixing by the end user through vigorous shaking of the container.

The structuring system of the invention may also be adjusted to develop optimum fluid rheology in terms of low shear rate attributes, giving physical stability, cup retention and moderate shear rate flow behaviour during dispensing into the wash cycle.

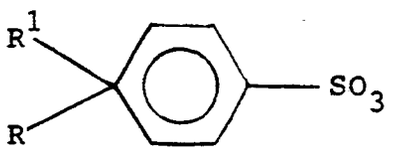
The product according to the present invention is a thixotropic machine dishwashing detergent in the form of a slurry-like paste. The product possesses a yield point of between 5-50 Pa and a viscosity between 500-5000mPas at 20^{-1}s (Haake RV2 at 20 ° C, MV2 rotor).

The stabilisers according to the present invention are long chain alkyl, ie C_{10}-C_{22}, sulphates, sulphonates, phosphates, phosphites or phosphonates. Preferred are phosphorous based compounds. Particularly preferred are compounds selected from those listed in Table 1 below, or mixtures thereof:

Table 1

Formula	Recommended Name
$R O P (OH)_2$	Alkyl phosphite
$(RO)_2 POH$	Dialkyl phosphite
$R P (OH)_2$	Alkyl phosphorous acid
$R_2 P OH$	Dialkyl phosphorous acid
$R O P(O) (OH)_2$	Alkyl dihydrogen phosphate
$(RO_2) P(O) OH$	Dialkyl hydrogen phosphate
$R P(O) (OH)_2$	Alkyl phosphonic acid
$R P(O) (OH) H$	Alkyl phosphonic acid
$R_2 P(O) (OH)$	Dialkyl phosphonic acid
$R O S (O) (OH)_2$	Alkyl sulphate
$(RO) (R^1O) S (O) (OH)$	Dialkyl sulphate
$R S (O) (OH) H$	Alkyl sulphonate
$R (R^1) S (O) (OH)$	Dialkyl sulphonate

and



Alkylbenzene sulphonates

wherein R/R^1 represent C_{10}-C_{22} alkyl chains which may be the same or different.

Most preferred is the mixture of C_{16}/C_{18} alkyl dihydrogen phosphate and dialkyl hydrogen phosphate, referred to hereafter as ALF-5 (Lancro Chemicals Limited).

The higher alkyl phosphates and phosphonic acids are also preferred due to their tendency to reduce corrosion of metals and erosion of vitreous enamel surfaces.

If sulphates or sulphonates are to be used, such as alkyl benzene sulphonates, it is preferred to additionally use a phosphate or phosphonate.

An alkali-metal condensed phosphate may be present in the formula as a water hardness sequestering agent or builder. Tripolyphosphate is the preferred sequestrant although pyrophosphate, hexametaphosphate, or other condensed phosphates may be used. The sequestrant should be present in the formula from 0.1 to 35 wt% with 15 to 30 wt% preferred. Use of the sequestrant, such as sodium tripolyphosphate, in excess of its solubility limit within the formula requires that the solid be present as fine particles which are suspended by the structuring system. The presence of solids will affect the viscosity of the liquid and may modify the range of the structurants needed to deliver the proper rheology. Zeolites may also be used as builders.

The sources of alkalinity are used in combination in the more preferred embodiments of this invention. An alkali-metal carbonate may be used as an alkaline buffering agent and may be present from 0 to 30 wt%, or more preferably from 2 to 10 wt%.

Pure alkali-metal metasilicates or alkali-metal silicates with a molar ratio of SiO_2/Na_2O and/or K_2O of from 1.0 to 3.25 (or mixtures of 2 or more metasilicate and/or silicates) may be used as alkaline sources

and as anti-corrosion agents to protect metal and china surfaces against the harshly alkaline environments present in the wash. The silicate may be used in the form of an aqueous liquor or a solid and may be present in the formula from 0.1 to 30 wt%, more preferably from 2 to 20 wt%.

An alkali-metal hydroxide may be used as an alkaline source and as a means to boost the pH of the liquid detergent concentrate to stabilise the hypochlorite. Sodium or potassium hydroxide in the form of an aqueous liquor or as a solid may be used in the formula at from 0.1 to 25 wt%, preferably from 0.5 to 15 wt%.

Polymers may be added to the system to provide a further building effect. The polymer used should be of a synthetic type and be water-soluble. Examples of applicable polymers are polyacrylic acid and its alkali-metal salts, polymethacrylic acid and its alkali-metal salts, and copolymers of these with alkyl acrylates and alkyl methacrylates, copolymers of these with maleic anhydrides, polyacrylamide and partially hydrolysed polyacrylamide, polyacrylonitrile and its partially hydrolysed forms, polymethacrylonitrile and its partially hydrolysed forms, polystyrenesulphonic acid and its alkali-metal salts, polymaleic anhydride and its alkali-metal salts, poly n-vinyl lactams (poly-vinyl pyrrolidone, poly(N-vinyl caprolactam, etc), and polymers of N-substituted acrylamides or mixtures thereof. These polymers have a weight average molecular weight of from 1,000 to 15,000,000 with a molecular weight of from 10,000 to 400,000 preferred, and 100,000 to 250,000 most preferred. These polymers may be used in the acid or the neutralised form. The polymers should be of a hypochlorite-stable type with polyacrylate and polymethacrylate being most preferred. The polymer should be of a purity such that it contains a minimum of unsaturated monomers, chemically reactive initiators, terminators, or surfactants present which will hasten the rate of hypochlorite decomposition. The polymer may be present in the formula from 0.05 to 10 wt%, preferably 0.1-0.5 wt%.

Clays such as hectorites and mortmorillonites may be included in the compositions of the invention. These assist in reduction of spot formation on glassware, and may be present at from 0.5 to 20 wt%. It has also been found that the presence of the structuring agents characterising the present invention assists in the production of low-viscosity, stable, clay-structured products described in the art without the need to incorporate known structuring agents, such as polymers, actives, etc. Particularly preferred is the addition of laponite clay at 0.5-2 wt%. An increase in solds level implies a need for lower levels of stabiliser to achieve stability.

The system may incorporate a bleach generating system, such as a hypochlorite, at from 0.5 to 5 wt% active chlrine. Actives may optionally be included within the system. Preferred are nonionic actives. However, low levels of anionic actives such as secondary alkyl sulphates may be included.

Conventional additives such as colourants and perfumes may be present in the composition in amounts not exceeding 5 wt%. Other foam depressors may be included.

The product according to the invention may be prepared by initial formulation of a premix comprising the stabilising component and water, the addition of this premix to a silicate and alkali-metal hydroxide mixture, and the subsequent addition of builder and hypochlorite. The process is preferably carried out at above 40 ° C.

The product according to the invention has been shown to possess a high degree of stability at room temperature, whilst also demonstrating a suitably low viscosity to assist dispensing. The pH of the composition may range from 10-14, preferably 12-13.5. It also demonstrates an improved washing performance in comparison to other thickened machine dishwashing systems.

The invention will now be further illustrated by means of the following non-limiting Examples.

EXAMPLES

Example 1

A basic machine dishwashing liquid system was formulated, and viscosity and stability investigated at different levels of ALF-5 addition.

		wt%
Base system:	STP	20.0
	Na-disilicate	19.0
	Na-carbonate	6.0
	Na-OH	2.5
	Hypochlorite (Av.Cl_2)	1.0
	Water	to 100.0

ALF-5	Viscosity (20 sec^{-1})	Separation (%)					
(wt%)	(mPas)	1 week	37°C	RT	8 week	37°C	RT
0	993		1	1		6	5
0.16	1300		0	0		0	0
0.50	990		0	0		0	0
1.00	1273		0	0		0	0

Example 2

The incorporation of different levels of ALF-5 into a clay-structured system was carried out in order to examine any increased stability.

		wt%
Base system:	STP (anhydrous)	20.5
	Na-disilicate	11.0
	Na-carbonate	6.0
	Na-OH	1.2
	Hypochlorite (Av.Cl_2)	1.0
	Clay	2.0
	Water	to 100.0

ALF-5	Viscosity (20 sec^{-1})	Separation (%)					
(wt%)	(mPas)	4 week	37°C	RT	12 week	37°C	RT
0	1645		12	6		17	15
0.1	1805		3	5		7	6
0.5	2375		3	0		7	3
At a clay level of 3.5 wt%, after 8 weeks:							
			37°C				RT
0	1715		6				11
0.16	1835		0				0

Example 3

The following compositions were prepared and found to be stable for 8 weeks at RT and 37° C:

	wt%	
STP (anhydrous)	20	25
Na Disilicate	19	16
Na Carbonate	6	2
Na OH	2.5	2.5
Ti O_2	0.2	-
SAS	-	0.2
HOCl (as Av.Cl_2)	1.0	1.0
ALF-5	0.16	0.16
Water	to 100	

Claims

1. An aqueous thixotropic liquid cleaning composition comprising an alkali-metal builder, an alkali-metal silicate and a stabiliser comprising from 0.5 to 5 wt % of an alkyl phosphate, phosphite, phosphonate, sulphate or sulphonate, the composition being substantially free from clay.

2. The composition according to claim 1 further comprising 0-5 wt % chlorine bleach-stable organic detergent active material.

3. The composition according to claim 1 further comprising a bleaching agent providing 0.5-5 wt % available chlorine.

4. The composition according to claim 2 consisting essentially of:

(a) 0.1-35% wt % alkali-metal phosphate;

(b) 0.1-30 wt % alkali-metal silicate;

(c) 0-15 wt % NaOH;

(d) 0-30 wt % alkali-metal carbonate;

(e) 0.05-5 wt % alkyl phosphate, phosphite, phosphonate, sulphate or sulphonate;

(f) 0.50-5 wt % available chlorine; and

(g) balance water.

5. An aqueous thixotropic liquid cleaning composition comprising an alkali-metal builder, an alkali-metal silicate and a stabiliser of 0.5 to 5 wt % of an alkyl phosphate, phosphite, phosphonate, sulphate, or sulphonate, the composition being substantially free from organic detergent active material.

6. The composition according to claim 5 further comprising 0.5-20 wt % clay.

7. A process of thickening an aqueous liquid thixotropic cleaning composition containing alkali-metal builder, alkali-metal silicate and water, the process comprising:

(a) forming a mixture of water and at least some of the builder or silicate; and

(b) adding 0.5-5 wt % of the final composition of alkyl phosphate, phosphite, phosphonate, sulphate or sulphonate to the mixture and adding any remaining builder or silicate to the mixture.

8. The process according to claim 7 further comprising adding up to 5 wt % of the final composition of secondary alkyl sulphate to the mixture.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 31 0546

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	FR-A-2 193 871 (COLGATE-PALMOLIVE) * Page 5, line 5 - page 6, line 19; claims *	1	C 11 D 3/08 C 11 D 1/34 C 11 D 1/12 C 11 D 3/395 C 11 D 17/00
X	US-A-4 431 559 (R.J. ULRICH) * Claims *	1-3	
X	FR-A-2 520 004 (COLGATE-PALMOLIVE) * Examples; claims *	2-6	
D,X	GB-A-2 140 450 (COLGATE-PALMOLIVE) * Examples; claims *	2-6	
X	GB-A-2 163 448 (COLGATE-PALMOLIVE) * Examples; claims *	2-6	
A	EP-A-0 142 197 (PROCTER & CAMBLE) * Claims *	2	
A	FR-A-2 330 763 (UNILEVER) * Claims *	8	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 11 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03-02-1989	GOLLER P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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