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⑤④ **Detergent composition.**

⑤⑦ A liquid detergent composition for use in automatic dishwashers comprises detergent builder, bleach, silicate, an inorganic base and a copolymer of ethyl acrylic and methyl acrylic acids. The composition is free from clay thixotropic thickeners.

This invention relates to detergent compositions and especially, but not exclusively to liquid detergent compositions for use in an automatic dishwasher.

Recently a number of liquid automatic dishwasher detergent compositions have become available. These liquid products have a number of advantages when compared with the more traditional powdered products in that they have improved solubility, are easier to handle, dose and dispense, they are dust free and they do not cake in the machine dispenser.

However, these liquid compositions pose a number of formulation problems which must be overcome if a viable, stable product is to be obtained. Liquid products contain high levels of solid ingredients which must be suspended in the composition so as to prevent physical separation. This may be achieved by producing a highly viscous composition. This also has the advantage in that it enables the liquid to be effectively retained within the detergent dispenser of the machine. However, ease of dispensing the composition is also important. It is therefore advisable to provide a composition with a high viscosity when not subjected to shear and a reduced viscosity when subjected to shear. Thixotropic dishwasher liquids have in the past comprised clays to modify their viscosity. However, the use of clay thickeners in these compositions has a number of disadvantages as indicated in EP 0323209.

The present invention aims to provide a dishwasher detergent composition which avoids the use of clay thickeners.

According to a first aspect of the present invention there is provided a detergent composition comprising detergent builder, bleach, silicate and a polymeric thickener comprising a copolymer of ethyl acrylic and methyl acrylic acids and at least one inorganic base, the said composition being free or substantially free of clay thixotropic thickeners.

In a preferred embodiment of the invention the inorganic base comprises a salt of an alkaline metal such as sodium hydroxide. The thickener comprises ACRY SOL ASE-108 (ACRY SOL ASE is a registered trade mark). The composition preferably comprises from 1% to 5% of ACRY SOL ASE-108 by weight of the total composition, more preferably from 1.5% to 3%. In the most preferred embodiment of the invention the composition comprises from substantially 2% of ACRY SOL ASE-108 by weight of the total composition.

ACRY SOL ASE-108 is a copolymer emulsion containing a cross linked copolymer of ethyl acrylic and methyl acrylic acids with a mean molecular weight in the order of 500,000.

The ACRY SOL ASE-108 polymer comprises a number of polymer chains which are tightly wound to one another. Neutralisation with a suitable inorganic base such as sodium hydroxide causes the polymer chains to unwind. This produces an interwoven structure of polymer chains leading to viscosity increases and stabilisation of suspended solids with the system.

The silicate provides the composition with alkalinity for cleaning efficiency as well as acting as a corrosion inhibitor and providing protection for glazed surfaces of china ware.

Preferred silicates include silicate solutions of suitable alkali or metals and especially sodium or potassium silicate. The incorporation of the silicate in a solution enhances ease of manufacture.

Sodium silicate solution exists in a number of different grades with varying ratios of alkalinity to silicate content, varying total solid content and varying viscosities. Theoretically the high alkalinity, high active grades of this material should be preferred such as with $\text{SiO}_2:\text{Na}_2\text{O}$ ratios of 2:1 or less. However, we have found that these produce undesirably high viscosities within the composition leading to dispensing difficulties. Work conducted on neutral grades of silicate with $\text{SiO}_2:\text{Na}_2\text{O}$ ratios at 3.3:1 or more has shown improvement in product viscosity but at the expense of alkalinity. The effect of blend of the two types of material have been studied and the preferred chemical and physical characteristics of the optimum blend established.

According to a second aspect of the present invention there is provided a detergent composition comprising a detergent builder, a bleach, a thickener, an inorganic base and sodium silicate characterised in that the sodium silicate has a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio within the range from substantially 2.3 to 2.6:1 and an active solid content within the range from 42% to 44% of the total composition.

It is considered that the use of this grade of sodium silicate helps to provide the desired rheology of the composition.

In a preferred embodiment of the second aspect of the invention the preferred thickener is an ACRY SOL ASE polymer thickener and preferably ACRY SOL ASE-108 in combination with an inorganic base. The preferred sodium silicate grade has a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of substantially 2.5:1 and an active solids content of substantially 43.6%.

The amount of silicate used is preferably in the range from 2.5% to 22% by weight of the total composition, more preferably from 15% to 22% and still more preferably from 18% to 20%.

According to a third aspect of the invention there is provided a detergent composition comprising water, the copolymer emulsion of ethyl acrylic and methyl acrylic acids known as ACRY SOL ASE-108 and at least one inorganic base, wherein the ratio by weight of the ACRY SOL ASE-108 to the water to the base is in the

range from 1:3.5:1.5 to 1:5:1.5

In a preferred embodiment of the invention the ratio of ACRY SOL ASE-108 to water to base is substantially 1:4:1.5

A suitable builder may be used such as an alkali metal tripolyphosphate, sodium tripolyphosphate being particularly preferred. The amount of builder used is preferably in the range from 5% to 35% by weight of the total composition, more preferably from 20% to 33% by weight of the total composition and especially in the range from 25% to 27% by weight of the total composition.

The main purpose of the builder is to soften hard water and to emulsify and/or to peptise soils. The preferred grade is partially moisturised having approximately 3% water content corresponding to a degree of hydration in the order of 1, and having fine granular particle size distribution. By using this grade of material the formation of agglomerates during the addition of the material to the reaction mixture during manufacture is substantially eliminated.

Although any chlorine bleach may be used in the compositions of the invention preferred bleaches include hypochlorites such as alkali metal hypochlorites preferably sodium hypochlorite. This bleach is the source of the available chlorine within the formulation. The compound should provide at least 0.2% available chlorine in the final product although substantially 0.7% to 1.5% available chlorine is preferred.

The composition may optionally include further constituents such as alkali metal carbonates, perfumes or anti foaming agents.

The hydroxide such as sodium hydroxide is preferably included in the range from 2% to 4% and preferably substantially 3% by weight of the total composition.

The carbonate such as sodium carbonate is preferably included in the range from 0% to 9% and more preferably substantially 2% by weight of the composition.

The composition preferably comprises from 8.0% to 10% by weight of water (excluding water content of raw materials) and more preferably in the order of 8% water.

It is noted that these compositions generally do not comprise clay thickeners.

The compositions of the invention are aqueous thixotropic detergent compositions with particular application as automatic dishwasher detergent compositions.

In order that the present invention may be more readily understood a specific embodiment thereof will now be described by way of example only.

EXAMPLE 1

	<u>COMPONENT</u>	<u>%</u>
	Water	8.57
	Polycarboxylate polymer emulsion	2.00
	Sodium Hydroxide solution	6.50
	Sodium silicate solution (43%)	46.03
	Sodium Hypochlorite solution	8.00
	Sodium Tripolyphosphate	26.80
	Sodium Carbonate	2.00
	Fragrance	0.10

This example was successfully provided both at laboratory scale (up to 10kg) and on a pilot plant (up to 120 kg).

The following table illustrates the maximum temperature attained in the manufacture of the formulation of Example 1.

MAX TEMP ATTAINED/°C

	<u>MATERIAL</u>	<u>%</u>	<u>LAB</u>	<u>PILOT PLANT</u>
5	1. WATER	8.57	19	14
10	2. ACRY SOL ASE 108	2.00	19	14.5
	3. SODIUM HYDROXIDE 46%	6.50	38	38
	4. SODIUM SILICATE 100S	46.03	32	30
15	5. SODIUM HYPOCHLORITE (15%)	8.00	29	26
	6. SODIUM TRIPOLYPHOSPHATE (STP/1L)	26.80	38	37
20	7. SODIUM CARBONATE	2.00	37	36
	8. PERFUME	0.10		
25		100.00		

In order to formulate the composition of example 1 on a laboratory scale the ACRY SOL ASE 108 was added to water and this was slowly stirred. Sodium hydroxide was subsequently added carefully with slow stirring in order to neutralise the ACRY SOL. This mixture was then added to a main mixing vessel after which the sodium silicate was added with fast stirring. Addition and mixing time (A.M.T.) was approximately 5 minutes here. The stirring speed was reduced and the sodium hypochlorite was added (A.M.T.) 5 minutes. The stirring speed was increased and the tripolyphosphate (A.M.T.) 10 minutes and sodium carbonate (A.M.T.) 5 minutes were added in order. Care was needed here to ensure that no agglomeration of the phosphate or carbonate occurred. The mixture was allowed to cool prior to the addition of the perfume. It is noted that mixing time may vary when producing the composition on a larger scale.

It is highly preferable that the additions take place in this order and especially that the addition of the sodium hypochlorite precedes the addition of the sodium tripolyphosphate.

For example, in one instance when sodium tripolyphosphate was added prior to the sodium hypochlorite solution, a gradual viscosity increase was noted during the addition, eventually reaching approximately 120,000 cP (Brookfield RV 8, Viscometer Spindle 6, 5 rpm) thus rendering effective mixing of further quantities of sodium tripolyphosphate impossible.

According to a further aspect of the invention there is provided a method of making a detergent composition comprising the addition of a polymeric thickener to water followed by the addition in order of the following components to the mixture: inorganic base, silicate solution, bleach and builder.

In a preferred embodiment of the invention the inorganic base comprises sodium hydroxide, the silicate solution comprises sodium silicate, the bleach comprises sodium hypochlorite and the builder comprises sodium tripolyphosphate.

Other components may be included in the composition.

The formulation of example 1 was subjected to various tests to ensure that the physical properties of the composition were acceptable to the consumer.

STABILITY

Unstable compositions will separate into a clear liquor and high solids content lower phase. This is undesirable to the consumer and also adversely affects the performance of the composition.

The inclusion of the polycarboxylate polymer ACRY SOL ASE-108 enhances the stability of the composition whilst also improving the rheology of the composition.

The stability modifying effect of the polymer can be measured in a number of ways for example as follows:-

CENTRIFUGE TESTS

- 5 By centrifuging a fixed mass of product, under specific conditions (i.e. fixed time, speed) the number of millimetres of supernatant liquid formed (if any) by phase separation can be measured and compared with other formulations. Typical results are listed below

<u>PRODUCT</u>	<u>No of MMS SUPERNATANT LIQUOR</u>		
	<u>ON PRODUCTION</u>	<u>AFTER 6 DAYS</u>	<u>1 MONTH</u>
1. Example 1 with 0% Acrysol ASE 108	23	18	13
2. Example 1 + 1% Acrysol ASE 108	19	10	9
3. Example 1 + 2% Acrysol ASE 108	12	5	6
4. Example 1 + 3% Acrysol ASE 108	6	5	4
5. Pilot Plant Batch (equivalent to 3)	0	0	2

NOTE: Formulations 1 to 4 have been laboratory produced.

COMPARATIVE TESTS

Comparative tests were conducted on commercially available products which were most likely at least 6 weeks old.

The standard test conditions were as follows: -

Centrifuges used: - M.S.E. Centaur 2 Model.

4 samples filled to 100g

Rotated at 3,500 r.p.m. for 150 minutes.

The viscosity of the composition of the example were measured with a brookfield RV8 Viscometer at the quoted speeds using a spindle 6 at 20°C. The results of the tests were as follows: -

No of MMS SUPERNATANT LIQUOR

5	V	40
	W	43
	X	9
10	Y	4
	Z	29

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ON PURCHASEONE MONTH

		5rpm	20rpm		5rpm	20rpm
20	X	24,300	9,700		24,000	9,400
	Y	37,300	18,800		27,500	14,900

25 NORMAL STABILITY TESTING

Products are placed on test under a variety of conditions in both final packaging (when appropriate) and glass bottles, for at least a 3 month period. Typical conditions for testing are refrigerated (5°C), ambient temperature (20°C), elevated temperature (37 to 40°C) and when appropriate light exposure testing and testing under conditions of high humidity. A series of physical and chemical parameters are checked on a monthly basis, these are

(a) Physical tests

35 Tests for indications of phase separation, tests for sedimentation, viscosity and physical appearance.

(b) Chemical tests (generally more frequently)

pH, available chlorine content.

40 The initial data on viscosity, in particular, is as follows: -

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PRODUCT	VISCOSITY c.p.s.					
	ON PRODUCTION		AFTER 6 DAYS		24 DAYS	
	5RPM	20RPM	5RPM	20RPM	5RPM	20RPM
1. Example 1 with 0% Acrysol ASE 108	8,500	3,900	20,500	8,600	35,000	13,500
2. Example 1 with 1% Acrysol ASE 108	13,600	6,200	25,900	10,800	29,200	11,300
3. Example 1 with 2% Acrysol ASE 108	26,000	11,200	31,000	13,300	35,000	14,200
4. Example 1 with 3% Acrysol ASE 108	24,000	12,500	35,800	16,900	37,000	15,800
5. Pilot Plant Batch (Equivalent to 3)	26,100	11,400	31,500	14,100	40,000	17,300

Viscosity was measured with a Brookfield RV8 Viscometer at quoted speeds using spindle 6 at 20°C.

EXAMPLE 2

	<u>g</u>
Water	8.57
Acrysol ASE-108	2.00
Sodium Hydroxide Solution	6.50
* Sodium Silicate Solution	46.03
Sodium Hypochlorite Solution	8.00
STP/ 1L	26.80
Sodium Carbonate	2.00

The composition of Example 2 was prepared by the method previously described. Three formulations were prepared each with a different grade of sodium silicate solution. Formulation 2A comprises a neutral grade (crystal 79), formulation 2B comprises an intermediate grade (crystal 100S) and formulation 2C comprises an alkaline grade of sodium silicate solution (Crystal 120A) supplied by Crosfield Chemicals.

The details of the grades of silicate are as follows: -

Grade	Mean Density at 20°C/20°C	Mean Wt Ratio SiO ₂ :Na ₂ O	Mean Mol Ratio SiO ₂ :Na ₂ O	Mean Na ₂ O %	Mean SiO ₂ %	Mean Total Solids %	Viscosity at 20°C cP. (mPas)	Litres per Tonne	Gallons per Tonne
	Tw	Be	SG						
Crystal 120A	120.0	54.4	1.60	2.00	2.06	16.07 32.15	48.2 2000	623	137
Crystal 100S	100.0	48.3	1.50	2.50	2.58	12.45 31.10	43.6 400	664	146
Crystal 79	79.5	41.2	1.40	3.30	3.41	8.85 29.25	38.1 250-500	714	157

All viscosity measurements were carried out on a Brookfield RV 8 Viscometer, Spindle 6 at 5rpm at 25°C.

5	Spindle Speed	Viscosity/CP		
		A	B	C
	5 rpm	19000	41000	90000
10	50 rpm	5200	13800	48700
	T.I.	3.7	3.0	1.8

15 T.I. is the Thixotropic Index and is defined as the ratio of the viscosity of the composition at 5 rpm to the viscosity at 50 rpm.

The products final viscosity and the thixotropic index are seen to vary with the grade of silicate used. The most preferred grade of silicate has been found to be 2.5:1 SiO₂:Na₂O.

20 It is to be understood that the above described embodiments are by way of illustration only. Many modifications and variations are possible.

Claims

- 25 1. A detergent composition comprising detergent builder, bleach, silicate and a polymeric thickener comprising a copolymer of ethyl acrylic and methyl acrylic acids, and at least one inorganic base, the said composition being free or substantially free of clay thixotropic thickeners.
- 30 2. A detergent composition as claimed in claim 1, wherein the inorganic base comprises a salt of an alkaline metal.
- 35 3. A detergent composition as claimed in claim 1 or claim 2, wherein the inorganic base comprises at least one hydroxide salt.
- 40 4. A detergent composition as claimed in claim 1, claim 2 or claim 3, wherein the polymeric thickener comprises a copolymer emulsion containing a cross linked copolymer of ethyl acrylic acid and methyl acrylic acids with a mean molecular weight of substantially 500,000.
- 45 5. A detergent composition as claimed in any of claims 1 to 4, wherein the polymeric thickener comprises ACRY SOL ASE-108.
- 50 6. A detergent composition as claimed in any preceding claim, wherein the silicate comprises at least one alkali metal silicate solution.
- 55 7. A detergent composition as claimed in claim 6, wherein the silicate comprises at least one of sodium silicate solution or potassium silicate solution.
8. A detergent composition as claimed in claim 7, wherein the sodium silicate solution has a SiO₂:Na₂O ratio within the range from substantially 2.3 to 2.6:1 and an active solid content within the range from 42% to 44% of the total composition.
9. A detergent composition comprising a detergent builder, a bleach, a thickener, an inorganic base and sodium silicate solution, characterised in that the sodium silicate solution comprises a SiO₂:Na₂O ratio within the range from substantially 2.3 to 2.6:1 and an active solid content within the range from 42% to 44% of the total composition.
10. A detergent composition as claimed in claim 9, wherein the sodium silicate solution comprises a SiO₂:Na₂O ratio of substantially 2.5:1 and an active solids content of substantially 43.6%

11. A detergent composition as claimed in claim 9 or claim 10, wherein the thickener comprises a copolymer emulsion of ethyl acrylic acid and methyl acrylic acid.
- 5 12. A detergent composition as claimed in any preceding claim, wherein the amount of silicate is in the range from 2.5% to 22% by weight of the total composition.
13. A detergent composition as claimed in claim 12, wherein the amount of silicate is in the range from 15% to 22% by weight of the total composition.
- 10 14. A detergent composition as claimed in claim 12 or claim 13, wherein the amount of silicate is in the range from 18% to 20%.
- 15 15. A detergent composition comprising water, a copolymer emulsion of ethyl acrylic acid and methyl acrylic acids known as ACRY SOL ASE-108 and at least one inorganic base wherein the ratio of weight of the ACRY SOL ASE-108 to the water to the base is in the range from 1:3.5:1.5 to 1:5:1.5.
16. A detergent composition as claimed in claim 15, wherein the ratio of ACRY SOL ASE-108 to water to inorganic base is substantially 1:4:1.5.
- 20 17. A detergent composition as claimed in claim 15 or in claim 16, wherein the detergent composition further comprises a detergent builder.
18. A detergent composition as claimed in claim 15, claim 16 or claim 17, wherein the detergent composition further comprises bleach.
- 25 19. A detergent composition as claimed in any of claims 1 to 14 or claim 17, wherein the builder comprises an alkali metal tripolyphosphate.
20. A detergent composition as claimed in claim 19, wherein the builder comprises sodium tripolyphosphate.
- 30 21. A detergent composition as claimed in any of claims 1 to 14 or 17, wherein the amount of builder is in the range from 5% to 35% by weight of the total composition.
- 35 22. A detergent composition as claimed in claim 21, wherein the amount of builder is in the range from 20% to 33% by weight of the total composition.
23. A detergent composition as claimed in claim 21, wherein the amount of builder is in the range from 25% to 27% by weight of the total composition.
- 40 24. A detergent composition as claimed in any of claims 1 to 14 or 17, wherein the builder comprises substantially 3% by weight of water corresponding to a degree of hydration in the order of 1.
25. A detergent composition as claimed in any of claims 1 to 14 or 18, wherein the bleach comprises at least one hypochlorite.
- 45 26. A detergent composition as claimed in claim 25, wherein the bleach comprises at least one alkali metal hypochlorite.
27. A detergent composition as claimed in claim 26, wherein the detergent composition comprises sodium hypochlorite.
- 50 28. A detergent composition as claimed in any of claims 1 to 14, 18 or 25 to 27, wherein the composition provides at least 0.2% available chlorine.
- 55 29. A detergent composition as claimed in claim 28, wherein the composition provides from substantially 0.7% to 1.5% available chlorine.
30. A detergent composition as claimed in any preceding claim, wherein the composition further comprises

at least one perfume.

- 5 31. A detergent composition as claimed in any preceding claim, wherein the composition further comprises at least one alkali metal carbonate.
32. A detergent composition as claimed in claim 31, wherein the composition comprises from 0% to 9% of sodium carbonate.
- 10 33. A detergent composition as claimed in claim 32, wherein the composition comprises substantially 2% of sodium carbonate.
34. A detergent composition as claimed in any of claims 9 to 33, wherein the composition further comprises at least one hydroxide salt.
- 15 35. A detergent composition as claimed in claim 3 or claim 34, wherein the hydroxide salt is present in an amount in the range from 2% to 4% by weight of the composition.
- 20 36. A detergent composition as claimed in claim 35, wherein approximately 3% by weight of the composition comprises hydroxide.
37. A detergent composition as claimed in any preceding claim, which comprises from 8.0% to 10% by weight of water not including the water contained within the other raw materials.
- 25 38. An automatic dishwasher detergent composition as claimed in any preceding claim.
39. A method of making a detergent composition comprising adding a polymeric thickener to water and subsequently adding the following components in order to the mixture: inorganic base, silicate solution, bleach and builder.
- 30 40. A detergent composition as substantially hereinbefore defined with reference to example 1.

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