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3,140,261 DETERGENT COMPOSITION

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The present invention relates to detergent compositions containing alkyl aryl sulphonates.

According to the present invention the detergent composition comprises a major proportion by weight of a mono alkyl aryl sulphonate in which the alkyl group contains at least 8 carbon atoms or a di-alkyl aryl sulphonate in which one of the alkyl groups is methyl and the other 15 alkyl group contains at least 8 carbon atoms, and a minor proportion by weight of (i) an alkyl aryl sulphonate in which the or each alkyl group contains less than 8 carbon atoms (and preferably in which the sum of carbon atoms in the alkyl groups is less than 8) or an aryl sulphonate, (ii) a phenol-alkylene oxide condensate, an alcohol-alkylene oxide condensate or a mercaptan-alkylene oxide condensate having an average of not more than 11 alkylene oxide units per molecule, and (iii) a phenolalkylene oxide condensate, an alcohol-alkylene oxide con- 25 densate, or a mercaptan-alkylene oxide condensate having an average of more than 11 alkylene oxide units per molecule. Such a detergent composition when dissolved in water has a high foaming performance, good stability at low temperatures, and has a viscosity which is not ap- 30 preciably dependent on concentration.

The mono- or di-alkyl aryl sulphonate which constitues the major proportion by weight of the detergent composition is preferably a sulphonic acid or a salt thereof, of an alkylated benzene or toluene, although those of 35 naphthalene may equally well be used. The salts may for example be alkali metal such as sodium or potassium salts, or be ammonium or alkanolamine salts. Examples of sulphonates of this type are the alkali metal salts of sulphonic acids such as are obtained by alkylating benzene or 40 toluene, with an alkylating agent having preferably between eight and sixteen carbon atoms inclusive per molecule, for an example an olefin, an olefin polymer or alkyl halide, and converting the alkyl aromatic hydrocarbon thus formed into the corresponding mono-sulphonic acid. The sulphonic acids may then be readily neutralised by adding for example alkali metal hydroxide or alkali metal carbonate to form the corresponding salts. In this manner, mono- or di-primary alkyl aryl sulphonates, secondary alkyl aryl sulphonates, or keryl benzene sulphonates can be readily obtained. Sulphonic acids or salts thereof, in which the alkyl group contains between 8 and 16 carbon atoms inclusive are preferred. Mixtures of such sulphonates may also be used and particularly preferred is the mixture of sodium (C₈ to C₁₃) monoalkyl benzene sulphonates, especially the straight chain $(C_8 \text{ to } C_{13})$ mono-alkyl benzene sulphonates. The term "straight chain" when used in this specification with reference to alkyl benzene sulphonates refers to the sulphonates of alkyl benzenes derived from the alkylation 60 of benzene with a 1-olefin.

The alkyl aryl sulphonates in which the or each alkyl group contains less than 8 carbon atoms, and preferably in which the sum of the carbon atoms in the alkyl group or groups is less than 8 are chemically similar to and may be prepared by similar methods to those mono- or di-alkyl aryl sulphonates described above. They may of course be polyalkyl aryl sulphonates e.g. xylene sulphonates. Other suitable sulphonates include mono- and poly-propyl, butyl, amyl or heptyl benzene sulphonates, propylated naphthalene sulphonates or butylated diphenyl sulphonates. The alkyl aryl sulphonic acid salts, particularly

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alkali metal or ammonium salts are preferred e.g. the potassium xylene sulphonates or sodium toluene sulphonates.

The aryl sulphonates may be obtained by sulphonation of the aryl hydrocarbon e.g. by sulphonation of benzene or naphthalene to form a benzene or naphthalene sulphonate. The sulphonic acids thereby formed may be neutralised to form the corresponding salts, e.g. alkali metal, ammonium or alkanol-amine salts. Examples of such salts are sodium or potassium benzene sulphonates.

If desired, instead of blending together the short chain alkyl aryl sulphonate or aryl sulphonate with the longer chain mono- or di-alkyl aryl sulphonate and the other components of the detergent composition of the invention, the desired blend of sulphonates may be prepared by sulphonating directly a mixture of short chain alkylated aryl hydrocarbon or aryl hydrocarbon with the longer chain mono- or di-alkyl aryl hydrocarbon. Thus, a mixture of straight chain (C_8 to C_{13}) mono alkyl hydrocarbon and xylene or toluene may be sulphonated using for example SO_3 in a SO_3 /alkylate mole ratio about 3:1.

The alkylene oxide/phenol, alkylene oxide/alcohol or alkylene oxide/mercaptan condensates used in compositions of the present invention may be derived from any alkylene oxide, but preferably from alkylene oxides containing between two and four carbon atoms in the molecule inclusive. The preferred alkylene oxides are ethylene oxide or 1,2-propylene oxide. Other suitable alkylene oxides are 1,2- and 2,3-butylene oxides, and isobutylene oxide. Any method suitable for the preparation of these condensates can be used, and one such method is described in copending application Serial No. 779,826, filed December 12, 1958, which comprises treating inter alia a phenol or alcohol with one or more alkylene oxides in the presence of an alkali catalyst, treating with an acid and subsequently treating with a lower aliphatic alcohol or glycol and removing the suspended solid material and the alcohol or glycol from the polyoxyalkylene compound.

Alkylene oxide/phenol and alkylene oxide/alcohol condensates may also be prepared using mixtures of alkylene oxides. Thus, for example, if a mixture of ethylene oxide and 1,2-propylene oxide is employed, a polyoxyalkylene compound is formed in which the ethylene oxide and propylene oxide units are distributed randomly throughout the polyoxyalkylene compound in substantially the same proportions as the alkylene oxides are present in the mixture used. Alternatively, two different alkylene oxides may be used alternately, or several different alkylene oxides may be used successively so giving block copolymers. One method of making these block copolymers is by condensing an organic compound containing at least one hydroxyl group e.g. a phenol or an alcohol, at an elevated temperature and in the presence of a condensation catalyst, with one or more equivalents of an alkylene oxide subsequently with one or more equivalents or an alkylene oxide different from the first alkylene oxide, and then with one or more equivalents of an alkylene oxide different from the second alkylene oxide. Suitable condensation catalyst are strong bases, e.g. a quaternary ammonium base or sodium hydroxide, or compounds such as boron trifluoride, sulphuric or phosphoric acids. Similarly, alkylene oxide/mercaptan condensates of this type may be prepared by first condensing the mercaptan with one alkylene oxide, and then subsequently reacting the mercapto alcohol thus formed with another alkylene oxide.

When preparing these alkylene oxide condensates, by controlling the proportions of the reactants, the number of alkylene oxide units per unit of phenol, alcohol, or mercaptan can be controlled. Thus, the condensates containing an average of not more than 11 alkylene oxide units per molecule, and condensates containing an aver-

age of more than 11 alkylene oxide units per molecule may be readily prepared. Particularly preferred condensates are respectively, those containing an average of between 7 and 10 moles of alkylene oxide per mole of phenol, alcohol, or mercaptan e.g. an average of 8.5 5 moles of alkylene oxide per mole of phenol, alcohol or mercaptan, and those containing an average of between 11 and 18 moles of alkylene oxide per mole of phenol, alcohol or mercaptan e.g. an average of 15 moles of alkylene oxide per mole of phenol, alcohol, or mercaptan. 10

The phenols from which the alkylene oxide/phenol condensates are derived include phenol itself, the cresols, resorcinol and the alkyl and dialkyl phenols. Preferred phenols are the alkyl phenols, and these are generally prepared by alkylating phenol with an olefin containing 15 detergent composition, but preferably after dilution. the desired number of carbon atoms. Preferred alkyl phenols are those in which the alkyl group contins between 4 and 10 carbon atoms inclusive, and a particularly preferred alkyl phenol is octyl phenol. Another suitable phenol is dodecyl phenol.

The alcohols from which the alkylene oxide/alcohol condensates are derived, include monohydric primary, secondary or tertiary alcohols, preferably those having between 6 and 20 carbon atoms inclusive in the molecule and more preferably between 12 and 18 carbon atoms 25 inclusive in the molecule. Preferably aliphatic alcohols, for example, lauryl alcohol, cetyl alcohol, oleyl alcohol and 2-ethyl hexanol are used but arylalkyl alcohols, for example benzyl alcohol or the alkyl benzyl alcohols can be used.

Similarly, the mercaptan/alkylene oxide condensates may be derived from primary, secondary, or especially tertiary mercaptans. Preferably the mercaptan has between 6 and 20 carbon atoms inclusive per molecule, especially between 12 and 18 carbon atoms inclusive per molecule. The mercaptan may be an aralkyl mercaptan, but aliphatic mercaptans are preferred. Examples of suitable mercaptans are the primary, secondary or tertiary dodecyl or octadecyl mercaptans.

Phenol condensates particularly alkyl phenol condensates are preferred to alcohol or mercaptan condensates and the particularly preferred condensates are respectively a condensate of octyl phenol and ethylene oxide containing an average of 8.5 ethylene oxide units per molecule and a condensate of octyl phenol and ethylene oxide containing an average of 15 ethylene oxide units per molecule.

As with the mono- or di-alkyl aryl sulphonate constituting the major proportion of the detergent composition, mixtures of each of the three components (which together constitute the minor proportion of the detergent

composition) may be used.

The proportion by weight of mono- or di-alkylaryl sulphonate may vary provided of course it is a major proportion by weight. However, the preferred proportion 55 by weight is between 55% and 80%, especially between 60% and 70% e.g. about 65%.

Similarly the proportions of the other components may vary provided they together constitute a minor proportion of the composition of the invention. Thus, a proportion by weight of between 10% and 30%, especially between 15% and 25% e.g. about 20%, is preferred for the phenol-, alcohol- or mercaptan-alkylene oxide condensate having an average of not more than 11 alkylene oxide units per molecule. The proportion by weight of 65 each of the two other components (i.e. the alkyl aryl sulphonate in which the or each alkyl group has less than 8 carbon atoms or the aryl sulphonate and the phenol-, alcohol- or mercaptan-alkylene oxide condensate having an average of more than 11 alkylene oxide units per molecule) is preferably between 1% and 17.5%, particularly between 5% and 12.5% e.g. about 8.5%.

In order to reduce the clear point of the resultant blend, additives well-known for this purpose, e.g. urea, may be added to the blend. Usually no more than 10% 75 and the residence time was 30 minutes.

by weight e.g. about 5% by weight of the detergent active matter, need be added.

Detergent compositions of the invention are more conveniently sold in aqueous solution. Thus a suitable aqueous solution preferably contains between 20% and 60% by weight of the detergent composition, for example about 40% by weight.

Detergent compositions of the present invention may include the usual builders provided the use of such materials does not adversely affect the desired properties. These builders include for example the water soluble alkali metal phosphates, the polyphosphate salts, sodium silicate, and sodium carboxymethyl cellulose. The builders may be added either before or after dilution of the

EXAMPLE I

A detergent composition was prepared by mixing 23.8% by weight of sodium (C₈ to C₁₃) monoalkyl benzene sulphonates, 3.4% by weight of potassium xylene sulphonate, 7.1% by weight of octyl phenol-ethylene oxide condensate containing an average of 8.5 ethylene oxide units per molecule, and 3.1% by weight of octyl phenol-ethylene oxide condensate containing an average of 15 ethylene oxide units per molecule, the remainder comprising water.

This composition was found to have good foam stability as determined in a Dish-Washing Test. It also showed good viscosity/dilution characteristics, and good stability 30 when stored at low temperatures.

EXAMPLE II

Straight chain (C₈ to C₁₃) monoalkyl benzenes were oleum sulphonated using a SO₃/alkylate mole ratio of 3.5:1 and a residence time of 2 minutes. The sulphonic acids were then neutralised with aqueous sodium hydroxide, and the resulting solution of sodium sulphonates were desalted so that the final sodium alkyl benzene sulphonates had an inorganic salt content of about 2.0% by weight on active matter.

70 parts by weight of the thus prepared sodium (C8 to C₁₃) alkyl benzene sulphonates were then mixed with 9 parts by weight of octyl phenol-ethylene oxide condensate having an average of 15 ethylene oxide units per molecule and 21 parts by weight of octyl phenol-ethylene oxide condensate having an average of 8.5 ethylene oxide units per molecule.

To the three-component blend thus obtained 10 parts by weight of short chain alkyl aryl sulphonate was then added. The four-component blend was then diluted to different active matter concentrations and the viscosity and clear points determined. Using four different short chain alkyl aryl sulphonates comparative figures were obtained.

Detergent active	e Viscosity, cs. @ 20° C.				Clear point, ° C.			
matter, percent by weight	Na/T	Na/X	K/T	K/X	Na/T	Na/X	K/T	K/X
34 30 25 20 15	247 230 215 171 60	256 222 182 103 29	208 196 190 193 166	249 235 225 165 55	2 1 -3 	-4 -5 	14 12 10 7 4.5	7 3 2 -

In this and following examples Na/T=sodium toluene sulphonate, Na/X=sodium xylene sulphonate, K/T= potassium toluene sulphonate and K/X=potassium xylene sulphonate. Also, in this and the following examples the term "detergent active matter" does not include

EXAMPLE III

Exactly the same procedure as Example II was carried out except that the SO₃/alkylate mole ratio was 2.8:1, The figures for the viscosities and clear points were as follows.

Detergent active matter.	viscosity, es. @ 20° C.				Clear point, ° C.			
percent by weight	Na/T	Na/X	K/T	K/X	Na/T	Na/X	K/T	K/X
34 30 25 20 15	275 244 220 177 66	295 243 184 111 31	210 209 191 190 136	269 250 228 183 61	5 0 -2 	-4 	16 13 11 7 4	7 4 3 1 -2

EXAMPLE IV

Mixed feedstocks of straight-chain (C_8 to C_{13}) monoalkyl benzenes with toluene or xylene were prepared which would give 10% sodium toluene or sodium xylene sulphonate on the total active matter in the finished blend with the non-ionics. These mixtures were then sulphonated using a SO_3 /alkylate mole ratio of 2.9:1 and a residence time of 25 minutes. The reaction mixtures were then de-acidified, neutralised, desalted and de-oiled.

To 80 parts by weight of each of these blends 9 parts by weight of octyl phenol-ethylene oxide condensate having an average of 15 ethylene oxide units per molecule and 21 parts by weight of octyl phenol-ethylene oxide condensate having an average of 8.5 ethylene oxide units per molecule were added.

The finished blends were then diluted with water to 30 different active matter concentrations and the viscosities and clear points determined. The results were as follows

Analysis	Detergent active matter percent wt.	Blend con- taining sodium toluene sulphonate	Blend con- taining sodium xylene sulphonate	35
Viscosity, cs. at 20° C	34 30 25 20	291 229 227 232	258 241 224 184	40
Clear point, ° C	15 34 30 25 20 15	117 17. 0 9. 5 4. 0	68 2.0 -1.0	45

Comparative Test

By way of comparison, the blends of Examples II, III and IV but omitting the fourth component i.e., the Na/T, Na/X, K/T, or K/X, were diluted to equivalent active matter concentrations and the viscosities and clear points determined.

The equivalent comparative blends to those of Examples II, III and IV are denoted by A, B and C.

Blends	Detergent active matter, percent wt.	Viscosity, cs. at 20° C.	Clear point, ° C.	60
A	34 30 25 20	316 362	34 10 -1	65
В	20 15 34 30	284 52 338 337	18 7	
C	15 34 30 25 20 15 34 30 25	380 360 26. 6		70
	30 25 20 15	298 341 341 61	13.5	
			<u> </u>	75

Thus, at active matter concentrations of below 20% wt., e.g. at 15 or 17% wt. the compositions of the invention, especially those containing potassium toluene sulphonate, usually have higher viscosities than those of blends A, B or C above. In addition, the viscosities of the compositions of the invention at higher concentrations are not as high as those of blends A, B and C.

EXAMPLE V

To blends of 70 parts by weight of sodium (C_8 to C_{13}) monoalkyl benzene sulphonates with 9 parts by weight of octyl phenol-ethylene oxide condensate having an average of 15 ethylene oxide units per molecule, and 21 parts by weight of octyl phenol-ethylene oxide condensate having an average of 8.5 ethylene oxide units per molecule were added 8, 10 or 12 parts by weight of sodium toluene sulphonate.

The viscosities and clear points of the resultant blends diluted to different aqueous concentrations were as follows:

Analysis	Deter- gent active matter,	Sodium toluene sulphonate, percent wt. on detergent active matter			
	percent wt.	8	10	12	
Viscosity, es. at 20° C	34	263	256	248	
	30	238	227	217	
	25	224	208	197	
Clear point, ° C	20	215	195	179	
	34	11	8	6	
	30	7	4	3	

EXAMPLE VI

A blend of 70 parts by weight of sodium (C₈ to C₁₃) monoalkyl benzene sulphonates, 27 parts by weight of octyl phenol-ethylene oxide condensate having an average of 8.5 ethylene oxide units per molecule, 3 parts by weight of octyl phenol-ethylene oxide condensate having an average of 15 ethylene oxide units per molecule, and 10 parts by weight of potassium xylene sulphonate was prepared.

This blend was diluted with water to various concentrations and the viscosities determined. 5% and 10% by weight based on the active matter of urea was also added, the corresponding viscosities at different dilutions determined. The clear points at 35% detergent active matter dilutions were also determined.

The results were as follows:

Viscosity, cs. at 20° C.	Urea	Urea present		
,	absent		10%	
35% Detergent active matter	211 193 185 182 122 11	240 220 204 184 101 10	260 233 233 173 86 9	
	<u> </u>	<u>'</u>		

EXAMPLE VII

Detergent compositions which have good detergent properties combined with good foaming characteristics and a low critical solution temperature are made by mixing the following components in aqueous solution in the proportions indicated in the following table where the percentages are by weight of the aqueous detergent solution.

D. I	Perce	Percent by weight			
Detergent composition	A	В	С		
Higher mono alkyl aryl sulphonate: Sodium dodecyl benzene sulphonate Sodium propylene tetramer benzene sulphonate.	40.7	38. 9		5	
Cs-C ₁₃ alkyl benzene sodium sulphonate cracked wax olefin fraction Lower molecular weight sulphonate: Sodium xylene sulphonate. Potassium toluene sulphonate	3.7	5. 5	40.0	10	
Sodium cumene sulphonate Alkylene oxide condensate, average not more than 11 oxyalkylene units per molecule: Sec. butyl phenol-propylene oxide con- densate, average 7 oxyalkylene units per molecule. Nonyl phenol-ethylene oxide condensate, average 9 oxyalkylene units per mole-	18. 5		5. 0	15	
cule Lauryl alcohol-ethylene and propylene- oxide condensate, average 8 oxyalkylene units per molecule.		8.3	12. 5		
Alkylene oxide condensate, average more than 11 oxyalkylene units per molecule: Sec. butyl phenol-propylene oxide condensate, average 11 oxyalkylene units per molecule	7.4			20	
average 17 oxyalkylene units per mole- cule		. 2.8		25	
Water	29. 6	44. 4	37. 5		

A similar good detergent is obtained by substituting corresponding amounts of dodecyl mercaptan-ethylene 30 oxide condensates having an average of 8.5 and 16 oxyethylene units per molecule respectively for the condensates of composition A.

I claim as my invention:

1. A detergent composition having good detersive and 35 viscosity dilution properties consisting essentially of water and from 20 to 60% of solute, said solute consisting essentially of

(a) 60 to 70% by weight of alkali metal alkyl aryl

sulfonates selected from the group consisting of alkyl benzene sulfonate and alkyl toluene sulfonate having 8 to 13 alkyl carbon atoms,

(b) 5 to 12.5% by weight of alkali metal alkyl aryl sulfonates selected from the group consisting of

toluene sulfonate and xylene sulfonate,

(c) 15 to 25% by weight of a polyethylene oxide ether and alkyl phenol condensate having 7 to 10 ethylene oxide units per molecule and 4 to 10 alkyl carbon atoms, and

- (d) 5 to 12.5% by weight of a polyethylene oxide ether and alkyl phenol condensate having 11 to 18 ethylene oxide units per molecule and 4 to 10 alkyl carbon atoms.
- 2. A detergent composition having good detersive and viscosity dilution properties consisting essentially of water and from 20 to 60% of solute, said solute consisting essentially of
 - (a) 60 to 70% by weight of sodium alkyl aryl sulfonates selected from the group consisting of alkyl benzene sulfonate and alkyl toluene sulfonate having 8 to 13 alkyl carbon atoms,

(b) 5 to 12.5% by weight of alkali metal alkyl aryl sulfonates selected from the group consisting of toluene sulfonate and xylene sulfonate,

(c) 15 to 25% by weight of a polyethylene oxide ether and octyl phenol condensate having an average of 8.5 ethylene oxide units per molecule, and

(d) 5 to 12.5% by weight of a polyethylene oxide ether and octyl phenol condensate having an average of 15 ethylene oxide units per molecule.

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