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(54) **Detergent composition with fabric softening properties.**

(57) A detergent composition for treating fabrics comprising an organic precipitant builder, other than soap, and a water-soluble nonionic cellulose ether. The composition is intended to soften natural fibre wash load articles without causing redeposition problems on synthetic fibres fabrics.

EP 0 360 392 A2

DETERGENT COMPOSITION WITH FABRIC SOFTENING PROPERTIES

BACKGROUND

This invention relates to a detergent composition for treating fabrics, in particular to such compositions which are capable of softening natural fibre wash load articles without causing redeposition problems on any synthetic fibre fabrics in the load. In particular the invention is directed to alkaline compositions capable of achieving an optimum balance of softening and detergency across a mixed fibre wash load.

It is desirable to overcome the possible harshening of fabrics which may result from repeated washing by treating the fabrics with a fabric softening agent either during the fabric washing step or in a subsequent fabric rinsing operation. Amongst the materials proposed as fabric softening agents are quaternary ammonium compounds, imidazolinium derivatives, fatty amines, fatty amine oxides, soaps, clays and mixtures thereof. Harshening of fabrics is a particular problem when the fabric is formed of or contains natural fibres such as cotton and wool.

A problem associated with the deposition of organic fabric softening agents on fabrics during the wash is that to achieve a desirable degree of softening effect on fabrics, an increase in the deposition of fatty and particulate soil occurs on synthetic fabrics, leading to unsightly discolouration.

Products designed for cleaning fabrics often contain in addition to a detergent active material to remove soil from the fabric, an anti-redeposition material to reduce the redeposition of the removed soil from the wash liquor back onto the fabrics. Sodium carboxy methyl cellulose (SCMC) is one material used for this purpose. It reduces redeposition of clay and soot (or carbon) particulate soils onto hydrophilic fabrics such as cotton but not on hydrophobic fabrics.

For hydrophobic fabrics, such as polyester and acrylic fabrics, problems of redeposition are particularly extreme because the redeposition problem is one of organic fatty soil together with particulate, inorganic, soil.

The problem of redeposition on hydrophobic fabrics can be alleviated by incorporation of certain nonionic cellulose ether polymers, as described in South African Patent Specification No 71/5149 (UNILEVER).

It is proposed in United States Patent Specification No 3 920 561 (DESMARAIS assigned to THE PROCTER AND GAMBLE COMPANY) to treat fabrics with a composition comprising a fabric softener and a highly substituted methyl cellulose derivative, such as a methyl cellulose containing from 2.14 to 2.62 methyl groups per anhydroglucose ring, in order to impart superior soil release benefits, especially to polyester fabrics while simultaneously imparting fabric softness in the rinse. These specified cellulose ether derivatives however do not increase the deposition of organic fabric softening agents on natural fibre fabrics in the wash step.

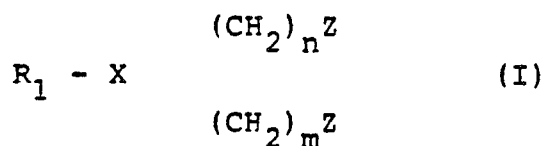
In EP213730 (Unilever C3076) there is disclosed a fabric treatment composition comprising an organic fabric softening agent and a water-soluble nonionic substituted cellulose ether derivative having a specified HLB and gel point.

DISCLOSURE OF THE INVENTION

We have now surprisingly found that such a composition is particularly effective when the organic fabric softening agent is selected from certain organic precipitant builders.

Thus, according to the invention there is provided a fabric treatment composition comprising:

i) an organic precipitant builder having the formula (I):



wherein: R₁ is C₁₀-C₂₄ alkyl or alkenyl, or an arylalkyl or alkylaryl group of equivalent chain length; X is CH, CR₂, N or CON; R₂ is C₁-C₃ alkyl; Z is COOY or SO₃Y; Y is hydrogen or a solubilising cation, preferably alkali metal and especially sodium; and n and m, which may be the same or different, are 0 or integers

from 1 to 4; and

- ii) a water-soluble nonionic cellulose ether derivative having an HLB of between 3.1 and 4.3, preferably between 3.3 and 3.8, and a gel point of less than 58 °C, preferably between 33 °C and 56 °C, provided that the derivative contains substantially no hydroxyalkyl groups containing 3 or more carbon atoms, the composition preferably yielding a pH of more than 8.0 when added to water at a concentration of 1% by weight at 25 °C.

THE CELLULOSE ETHER DERIVATIVE

The useful substituted cellulose ether derivatives are defined in part by their HLB. HLB is a well known measure of the hydrophilic-lyophilic balance of a material and can be calculated from its molecular structure.

A suitable estimation method for emulsifiers is described by J T Davies, 2nd Int Congress of Surface Activity 1957, 1 pp 426-439. This method has been adopted to derive a relative HLB ranking for cellulose ethers by summation of Davies's HLB assignments for substituent groups at the three available hydroxyl sites on the anhydroglucose ring of the polymer. The HLB assignments for substituent groups include the following:

Residual hydroxyl	1.9
Methyl	0.825
Ethyl	0.350
Hydroxy ethyl	1.63

The cellulose ether derivatives useful herein are polymers which are water-soluble at room temperature. The gel point of polymers can be measured in a number of ways. In the present context the gel point is measured on a polymer solution prepared by dispersion at 60/70 °C and cooling to 20 ° - 25 °C at 10 g/l concentration in deionised water. 50 ml of this solution placed in a beaker is heated, with stirring, at a heating rate of approximately 5 °C/minute. The temperature at which the solution clouds is the gel point of the cellulose ether being tested and is measured using a Sybron/Brinkmann colorimeter at 80% transmission/450 nm.

Provided that the HLB and gel point of the polymer fall within the required ranges, the degree of substitution (DS) of the anhydroglucose ring may be any value up to the theoretical maximum value of 3, but is preferably from about 1.9-2.9, there being a maximum of 3 hydroxyl groups on each anhydroglucose unit in cellulose. The expression 'molar substitution' (MS) is sometimes also used in connection with these polymers and refers the number of hydroxyalkyl substituents per anhydroglucose ring and may be more than 3 when the substituents themselves carry further substituents.

The most highly preferred polymers have an average number of anhydroglucose units in the cellulose polymer, or weight average degree of polymerisation, from about 50 to about 1,200. For certain product forms, eg liquids, it may be desirable to include polymers of relatively low degree of polymerisation to obtain a satisfactory product viscosity.

A number of cellulose ether derivatives suitable for use in the present invention are commercially available, as follows:

			DS/MS
Trade Name	Gel Point °C	HLB (Davies)	alkyl/hydroxyalkyl
BERMOCOLL CST035 (ex Berol Kemi)	35	3.40	) 1.4 ethyl) 0.5 hydroxyethyl
BERMOCOLL E481 (ex Berol Kemi)	56	3.77	) 0.9 ethyl) 2.0 hydroxyethyl
TYLOSE MHB 1000 (ex Hoechst)	54	3.52	) 2.0 methyl) 0.1 hydroxyethyl

A number of other cellulose ether derivatives are known from the prior art, but have been found to be unsuitable for use in the present invention. Thus, British Specification No GB 2 038 353B (COLGATE-PALMOLIVE) discloses TYLOSE MH 300 (ex Hoechst) which has a gel point of 58°C and METHOCEL XD 8861 (ex Dow Chemical Company, now coded METHOCEL HB12M) which contains about 0.1 hydroxybutyl substituents per anhydroglucose ring, while Japanese Patent Specification No 59-6293 (LION KK) discloses KLUCEL H (ex Hercules Chemical Corp) which has an HLB of about 4.4, METHOCEL K4M (ex Dow Chemical Company) which has a gel point of about 69°C, and NATROSOL 250H (ex Hercules Chemical Corp) which has an HLB of about 6.9.

The level of the cellulose ether derivative in the compositions of the invention is ideally from 0.1% to 3% by weight, preferably 0.5% to 2% by weight.

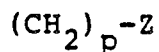
THE ORGANIC PRECIPITANT BUILDER

The organic precipitant builder is a water-soluble material that reacts with Ca^{2+} ions, and preferably also with Mg^{2+} ions, usually in a 1:1 stoichiometric ratio, to form an insoluble salt. In order to retain adequate detergency, the solubility product of the calcium salt of the organic precipitant builder is usually less than 10^{-8} , preferably less than 10^{-9} , ie. a pK of usually more than 8.0, preferably more than 9.0 where pK is the negative logarithm to base 10 of the solubility product.

One preferred group of compounds within the general formula I consists of those in which X is CH, n is zero, and m is 0 or 1. Thus, according to a first preferred embodiment of the invention, the organic precipitant builder is a compound of the formula II:



(II)



wherein R_1 , Y and Z have the meanings given above, and p is 0 or 1.

Especially preferred classes of compounds within the general formula II are the following:

i) substituted malonates of the formula III:



(III)

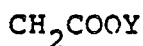


- and -

ii) substituted succinates of the formula IV:

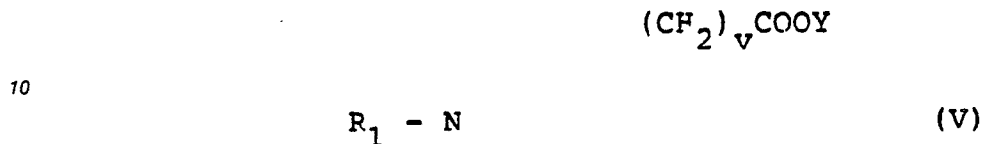


(IV)

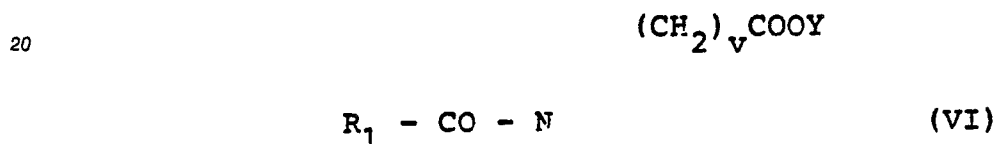


Compounds of the formulae III and IV are described, for example, in GB 1,293, 753, GB 1,342,247 and GB 1,342,340 (Unilever). Examples of such compounds include disodium dodecyl malonate (C₁₂-AKM), disodium hexadecyl succinate (C₁₆-AKS) disodium hexadecenyl succinate (C_{16:1}-AKS), and disodium mixed C₁₅-C₁₈ succinate (C₁₅₋₁₈-AKS).

5 According to a second preferred embodiment of the invention, the organic precipitant builder is a compound of the formula V:



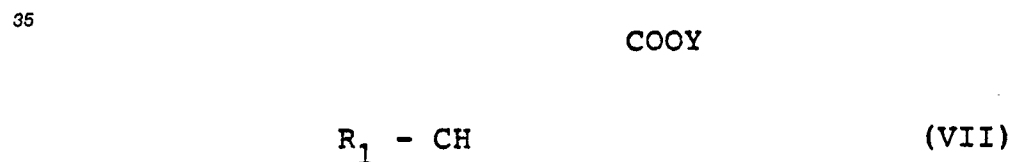
or of the formula VI:



wherein R₁ and Y have the meanings given above and v and w are each 1 to 4, preferably 1 or 2.

30 Compounds of the formula V in which v and w are both 1, the N-alkyl iminodiacetates, are of especial interest.

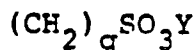
Compounds of the formula V in which v and w are both 2, the -iminodipropionates, are known amphoteric surfactants, disclosed, for example, in GB 1,296,793 (General Mills).
-sulphocarboxylic acid salts of the formula VII:



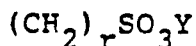
45 wherein R₁ and Y have the meanings given previously, are of interest as organic precipitant builders for use in the present invention, although the previously mentioned malonates and succinates of the formulae III and IV are preferred. Compounds of the formula VII are described, for example, in GB 1,368,736 and GB 1,380,390 (Unilever). A typical example is disodium -sulphostearate (C₁₈-SFAS). Blends of compounds of different chain lengths, for example, the -sulpho salt of coconut fatty acids (coco-SFAS), or of tallow fatty acids (tallow-SFAS), or of blended coconut and tallow fatty acids, may also advantageously be used.

50 According to a further preferred embodiment of the invention, the organic precipitant builder is a compound of the formula VIII:

55



(VIII)



where R_1 and Y have the meanings given above and q and r are each 0 to 4. Compounds of the formula VIII in which q is zero and r is zero or 1, eg. C_{18} alkane 1,2 disulphonate and the corresponding 1,2 sulphinate-sulphonate are of especial interest.

Compounds of the formula VIII are described in US 3,975,312 (Lever Brothers/Daveis et al).

The level of organic precipitant builder in the compositions of the invention is ideally from 3% to 75% by weight, preferably more than 10% by weight. To leave room in the formulation for other ingredients, it is preferred not to exceed a level of 50% by weight.

THE OPTIONAL DETERGENT ACTIVE

The compositions according to the invention optionally additionally contain one or more detergent active materials, selected from soaps, non-soap anionic, nonionic, zwitterionic and amphoteric synthetic detergent active materials. Nonionic detergent active materials are especially useful in the context of the present invention. Many suitable detergent compounds are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Anionic non-soap detergent active materials are usually water-soluble alkali metal salts of organic mono sulphates and mono sulphonates (as distinguished eg. from the disulphonates mentioned as organic precipitant builders above) having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8 - C_{18}) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl (C_9 - C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8 - C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acids and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8 - C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10} - C_{20} alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{11} - C_{15}) alkyl benzene mono sulphonates and sodium (C_{16} - C_{18}) alkyl mono sulphates.

Suitable nonionic detergent compounds which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6 - C_{22}) phenols-ethylene oxide condensates, generally up to 25 EO, ie up to 25 units of ethylene oxide per molecule, the condensation products of aliphatic (C_8 - C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally up to 40 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include alkyl polyglycosides, long tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Mixtures of anionic and nonionic compounds may be used in the detergent compositions, particularly to provide controlled low sudsing properties. This is beneficial for compositions intended for use in suds-intolerant automatic washing machines.

Amounts of amphoteric or zwitterionic detergent compounds can also be used in the compositions of the invention but this is not normally desired due to their relatively high cost. If any amphoteric or

zwitterionic detergent compounds are used it is generally in small amounts.

The term "soap", includes not only the usual alkali metal and alkaline earth metal salts of fatty acids, but also the organic salts which can be formed by complexing fatty acids with organic nitrogen-containing materials such as amines and derivatives thereof. Usually, the soap comprises salts of higher fatty acids preferably containing from 10 to 20 carbon atoms in the molecule, or mixtures thereof. Examples of suitable soaps include sodium stearate, sodium palmitate, sodium salts of tallow, coconut oil and palm oil fatty acids and complexes between stearic and/or palmitic fatty acids and/or tallow and/or coconut oil and/or palm oil fatty acids with water-soluble alkanolamines such as ethanolamine, di- or triethanolamine, N-methylethanolamine, N-ethylethanolamine, 2-methylethanolamine and 2, 2-dimethyl ethanolamine and N-containing ring compounds such as morpholine, 2'-pyrrolidone and their methyl derivatives.

Mixtures of soaps can also be employed, such as the sodium and potassium salts of the mixed fatty acids derived from coconut oil and tallow, that is sodium and potassium tallow and coconut soap.

Particularly preferred are mixtures of oleate and coconut soaps in a weight ratio of between about 3:1 and 1:1.

The effective amount of the detergent active compound or compounds used in the composition of the present invention is generally in the range of up to 50%, preferably up to 40% by weight, most preferably not more than 30% by weight of the composition.

20 OTHER OPTIONAL INGREDIENTS

The compositions of the invention may include an additional detergency builder to improve the efficiency of the detergent active, in particular to remove calcium hardness ions from the water and to provide alkalinity. The builder material may be selected from inorganic precipitating builder materials (such as alkali metal carbonates, bicarbonates, borates, orthophosphates and silicates), sequestering builder materials (such as alkali metal pyrophosphates, polyphosphates, amino polyacetates, phytates, polyphosphonates, aminopolymethylene phosphonates and polycarboxylates), ion-exchange builder materials (such as zeolites and amorphous aluminosilicates), or mixtures of any one or more of these materials. Preferred examples of builder materials include sodium tripolyphosphate, mixtures thereof with sodium orthophosphate, sodium carbonate, mixtures thereof with calcite as a seed crystal, sodium citrate, zeolite and the sodium salt of nitrilo- triacetic acid.

The level of such builder material in the compositions of the invention, including the amount of the organic precipitant builder, may be up to 80% by weight, preferably from 20% to 70% by weight and most preferably from 30% to 60% by weight.

Apart from the components already mentioned, a detergent composition of the invention can contain any of the conventional additives in the amounts in which such additives are normally employed in fabric washing detergent compositions. Examples of these additives include additional fabric softening agents. We have found particularly beneficial effects when the fabric softening agent is a mixture of organic precipitating builder and either a cationic fabric softening agent or a fatty amine. Other optional additives include the lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes including deodorant perfumes, enzymes such as cellulases, proteases and amylases, germicides and colourants.

THE COMPOSITION

The compositions may be in any convenient form such as bars, powders, pastes or liquids which may be aqueous or non-aqueous and structured or unstructured.

PREPARATION OF THE COMPOSITION

The detergent compositions may be prepared in any way appropriate to their physical form such as by dry-mixing the components, co-agglomerating them or dispersing them in a liquid carrier. However, a preferred physical form is a granule incorporating a detergency builder material and this is most convenient.

niently manufactured by spray-drying at least part of the composition. The cellulose ether derivative may be incorporated either by dry mixing (optionally with other ingredients in a post-dosed adjunct especially in the form of a cellulose ether/organic softening agent adjunct) or by being included with other ingredients in a slurry and spray-drying.

5

USE OF THE COMPOSITION

The detergent compositions may be used in any conventional manner. A dosage level of between 1 g/l and about 12 g/l is suitable. Wash temperatures from room temperature (ie about 20 °C) to the boil may be used.

The invention will now be illustrated in the following non-limiting examples.

Examples 1 to 8

In the following Examples, the cellulose ether derivative which was used was Bermocoll CST 035 (ex Berol Kemi) which is an ethyl, hydroxyethyl derivative having a gel point of 35 °C and an HLB of 3.40.

Detergent compositions were prepared having the following formulations. The compositions were prepared by dry mixing the stated ingredients.

Composition:

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Ingredients (% by weight)	
Nonionic detergent ¹	5
Sodium tripolyphosphate	15
Organic precipitant builder	15
Sodium alkaline silicate	5
Sodium sulphate	55
Cellulose ether derivative + water balance	
Notes	

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1. Dobanol 45-7EO which is a fatty alcohol ethoxylated with an average of 7 ethylene oxide groups per molecule.

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In practice, a number of other ingredients will often be present in such compositions (as described above). However in these examples, such ingredients are replaced by sodium sulphate.

The compositions were added to water at a dosage level of 5 g/l. The wash liquor so prepared was used to wash a fabric load containing terry towelling and polyester monitors in a laboratory scale apparatus using 25 ° FH water, a liquor to cloth ratio of about 20:1, a wash time of 15 minutes at 40 °C, a 2 minute flood at 50% dilution followed by three 5 minute rinses. The fabric load was then line-dried. After drying, the process was repeated. After 3 such washes, the terry towelling monitors were assessed for softness subjectively by expert judges who assess softness by comparison of pairs of monitors leading to preference scores which are then adjusted to give a score of zero for the poorest result. A positive score indicates better softness than the control. The identification of the organic precipitant builder, its solubility product, the level of cellulose ether derivative and the results are set out in the following table.

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Example No	Organic Precipitant Builder ²	Solubility Product (pK) (25°C)	% cellulose ether	softening score (3)
1*	C ₁₆ AKS)	12.8	0	0
2	C ₁₆ AKS)		1	1.25
3*	C ₁₂ AKS)	10.2	0	0.23
4	C ₁₂ AKS)		1	1.32
5*	C ₁₆ SFAS)	9.5	0	0.13
6	C ₁₆ SFAS)		1	1.91

Notes

* - comparative example.

2 - C₁₆AKS is disodium hexadecyl succinate (formula IV),
C₁₂AKS is the corresponding dodecyl compound and
C₁₆SFAS is disodium -sulphopalmitate (formula VI).

The softening score difference for 95% confidence limit 95 was 0.48. These results therefore show that in all cases the presence of 1% cellulose ether has significantly improved softening performance.

EXAMPLES 7 TO 14

The procedure of Examples 1 to 6 was followed using a number of different organic precipitants and also using soaps of similar chain lengths. In each case 3% cellulose ether was used. Details and results were as follows:

Example No.	Builder ³	Solubility product	Softening Score (3w)	95
5	7	C ₁₂ SFAS	7.4	0)
	8*	C ₁₂ Soap	12.1	1.20) 0.50
	9	C ₁₆ SFAS	9.5	1.41)
10	10*	C ₁₆ Soap	17.1	0.74)
	11	C ₁₂ AKS	10.2	2.01)
15	12*	C ₁₂ Soap	12.1	0) 0.62
	13	C ₁₆ AKS	12.8	1.10)
	14*	C ₁₆ Soap	17.1	0.61)

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Notes

* - comparative example.

3 - C₁₂SFAS is disodium -sulpholaurate (formula VII)

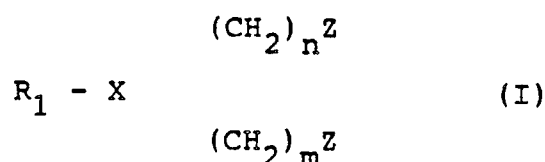
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Claims

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1. A fabric treatment composition comprising
i) an organic precipitant builder having the formula (I):

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wherein: R₁ is C₁₀-C₂₄ alkyl or alkenyl, or an arylalkyl or alkylaryl group of equivalent chain length; X is CH, CR₂, N or CON; R₂ is C₁-C₃ alkyl; Z is COOY or SO₃Y; Y is hydrogen or a solubilising cation, preferably alkali metal and especially sodium; and n and m, which may be the same or different, are 0 or integers from 1 to 4; and

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ii) a water-soluble nonionic cellulose ether derivative having an HLB of between 3.1 to 4.3, preferably between 3.3 and 3.8, and a gel point of less than 58° C, preferably between 33° C and 56° C, provided that the derivative contains substantially no hydroxyalkyl groups containing 3 or more carbon atoms.

2. A composition according to Claim 1, wherein the solubility product (pK) of the calcium salt of the organic precipitant builder is in excess of 8.0, preferably in excess of 9.0.

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3. A composition according to claim 1 or claim 2 wherein the composition comprises from 10% to 50% by weight of the organic precipitant builder and from 0.1% to 3% by weight of the cellulose ether.

4. A composition as claimed in any preceding claim wherein the organic precipitant builder is a substituted malonate preferably disodium dodecyl malonate.

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5. A composition as claimed in any preceding claim wherein the organic precipitant builder is a substituted succinate preferably disodium hexadecenyl succinate.