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(54) **Laundry detergent formulation**

(57) A laundry detergent formulation comprises at least one surfactant, a clay having fabric softening properties, and an activated bleaching system which includes at least one bleach activator which is an ester of

a polyhydric alcohol having at least 5 carbon atoms and at least 3 hydroxyl groups esterified with C₂₋₅ acyl groups. The polyhydric alcohol residue of the activator not having any substituents with six or more carbon atoms.

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Description

The present invention relates to a laundry detergent formulation incorporating an activated bleaching system.

Laundry detergent formulations containing an activated bleaching system are well known. The bleaching system generally comprises a compound (referred to herein for convenience as a hydrogen peroxide precursor compound) which provides, releases or generates hydrogen peroxide under the aqueous conditions of the wash and a bleach activator reacts with the hydrogen peroxide to generate a peracid which is a more effective bleach (particularly for low temperature washing operations) than hydrogen peroxide. Specific examples of hydrogen peroxide precursor compounds which are known for use in the art include inorganic persalts and specific examples of bleach activator include tetraacetylene diamine (TAED) and acetylated sugars such as acetylated sorbitol and acetylated mannitol. All of these specific bleach activators are capable of reacting with hydrogen peroxide to generate peracetic acid which is an active bleaching species for low temperature washes.

The bleaching properties of a laundry detergent need to meet two requirements which may be considered to be in conflict with each other. On the one hand, the bleaching system must be sufficiently active to "bleach out" a range of different types of stain with which garments being washed may be soiled. Secondly, the bleaching system should not be so "powerful" that it causes a significant degree of damage to dye present in the garments being laundered.

Prior art laundry detergent formulations incorporating a bleaching agent and a bleach activator do however suffer from the disadvantage that a relatively large amount of damage may be caused to dyes (particularly to the widely used dye Immedial Black) by the action of the bleaching system. As such, the use of activated bleaching systems is inadvisable for washing some coloured garments.

It is an object of the present invention to obviate or mitigate the abovementioned disadvantage.

According to the present invention there is provided a laundry detergent formulation comprising at least one surfactant, a clay having fabric softening properties, and an activated bleaching system which includes at least one bleach activator which is an ester of a polyhydric alcohol having at least 5 carbon atoms and at least 3 hydroxyl groups esterified with C₂₋₅ acyl groups, the polyhydric alcohol residue of said activator not having any substituents with six or more carbon atoms.

We have found in accordance with the invention that the combined use, in a laundry detergent formulation, of a clay having fabric softening properties and bleaching system whereof the activator is an ester as defined above gives rise to a formulation having good bleaching activity with reduced damage to dyes, e.g. Immedial Black, as compared to prior art activated bleach systems particularly those incorporating TAED as the activator. Performance of the detergent formulation for bleaching of hydrophobic stains may be improved by incorporation in the formulation of an enzyme of the type frequently used in laundry detergent formulations, e.g. a protease and/or an amylase. We have found that the activity of enzymes in the wash is inhibited to a lower degree (than in the case where TAED is the activator) for a similar level of bleachable stain removal.

The activator used in the invention will generally have an HLB value of at least 16.

As used herein, the HLB ("Hydrophobic Lipophilic Balance") of a molecule is calculated according to the formula:

$$HLB = 20 \times \frac{(\text{Molecular weight of hydrophilic part})}{(\text{Molecular weight of molecule})}$$

The hydrophilic part of the molecule is that which is not hydrophobic. For the purposes of the present application, the hydrophobic part of the molecule is the hydrocarbon portion consisting of CH₃, CH₂, and C groups (the latter being carbon atoms attached to four other carbon atoms) in alkyl and alkenyl chains. The molecular weights of the hydrophilic part and of the hydrophobic part of the molecular may be calculated accordingly. On this basis, hexa acetyl sorbitol which is a preferred activator for use in the invention has a HLB value of 11.8.

Preferably the activator has an HLB value of at least 7, more preferably at least 9, and even more preferably at least 11. The HLB value may be as high as 14 or 15.

The laundry detergent formulation in accordance with the present invention is preferably a powdered or granular formulation but may also be a liquid.

The alcohol residue of the activator preferably has a maximum of 12 carbon atoms and a minimum of five hydroxyl groups esterified with C₂₋₅ acyl groups. Examples of suitable alcohols are sugar and sugar derived alcohols such as sorbitol, glucitol, mannitol, glucose and sucrose.

For preference, the acyl groups in the activator are aliphatic acyl groups. It is preferred that the acyl group has two or three carbon atoms and is most preferably the acetyl group.

Specific examples of bleach activator which may be used in the detergent formulations of the invention include hexa acetyl sorbitol, hexa acetyl mannitol, penta acetyl glucose and octa acetyl sucrose. Particularly preferred are hexa acetyl sorbitol and hexa acetyl mannitol which may be used in admixture, e.g. as disclosed in EP-A-0 525 239. Further examples are compounds having nitrogen atoms in the basic carbohydrate skeleton, e.g. the peracetylated

forms of N-methyl glucosylamide, N-methyl glucamine and glucopyranosyl amine.

The amount of bleach activator incorporated in the detergent formulation of the invention will generally be in the range of 0.5% to 10% by weight of the total formulation, more preferably 1% to 8% and even more preferably 2% to 4% on the same basis.

The preferred bleaching system for use in the invention comprises a hydrogen peroxide precursor compound and the bleach activator as defined above which is capable of reacting with the hydrogen peroxide to generate a peracid. The hydrogen peroxide precursor compound may, for example, be an inorganic persalt e.g. a perborate (in the monohydrate and/or tetrahydrate form), a percarbonate or a persulphate. The alkali metal salts of these compounds are preferred, particularly sodium and potassium salts. Alternatively in the case where the detergent formulation is in solid form, the bleaching agent may be a urea-hydrogen peroxide complex. In the case of a liquid formulation the hydrogen peroxide precursor compound may be hydrogen peroxide *per se*.

The amount of hydrogen peroxide precursor compound present in the formulation of the invention is preferably such as to provide 0.5% to 3% by weight active oxygen.

The clay which is used in the formulation of the invention may be any one of the fabric softening clays having fabric softening properties used in laundry detergent formulations. Such clays are generally of the "lamellar type" and are such that the layers "separate" to become deposited on the garments being washed. The clay may for example be a smectite such as a Laponite, Bentonite, Montmorillonite, Hectorite or Saponite. For example, the clay may be a Sodium Montmorillonite, a Sodium Hectorite, a Sodium Saponite, a Calcium Montmorillonite or a Lithium Hectorite.

Generally the amount of clay in the detergent formulation of the invention will be 5% to 20% by weight.

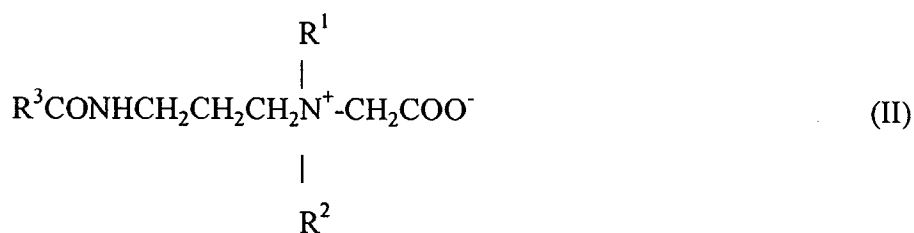
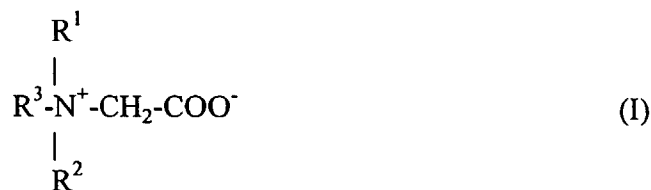
The clay may be used in conjunction with a cationic and/or amide surfactant to help delamination of the clay and absorption thereof onto the garments being laundered. The cationic surfactant may for example be a quaternary ammonium salt having one long chain (e.g. C₈₋₂₂) alkyl group and three short chain (e.g. C₁₋₄) alkyl groups. A suitable cationic surfactant is coco trimethyl ammonium chloride. The amide surfactant may contain at least one long chain (e.g. C₈₋₂₂) alkyl group and may for example be stearyl stearamide. A suitable clay formulation may contain 20-30% by weight of the formulation (i.e. clay plus surfactants) of amide surfactant and 1-2% cationic surfactant.

As indicated above, it is preferred to incorporate an enzyme in the formulations of the invention. The enzyme may, for example, be a protease, amylase, lipase or cellulase (or mixtures thereof) such as commonly used in detergent formulations. Examples of suitable enzymes are available under the names Opticlean, Savinase, Esperase; Termamyl, Maxamyl, Lipomax, Lipolase; Celluzyne and Carezyme. The amount of enzyme incorporated in the formulation will depend on activity but will typically be 0.1 to 3%. This level is particularly suitable for Savinase 6.0T, Termamyl 60T, Celluzyne 0.7T and Lipomax. We have found that the activity of enzymes is inhibited to a lower degree, for a similar level of bleachable stain removal, using the activators employed in the invention as compared to TAED.

The detergent formulation in accordance with the invention will include at least one surface active agent which may, for example, be an anionic, cationic, non-anionic or amphoteric surface active agent. Any of the surface active agents widely used in detergent formulations may be employed in the present invention.

If an amphoteric surface active agent is used it may be present in the formulation in an amount of 0.1 to 10% by weight, more preferably 0.5 to 5%, even more preferably 1 to 4% on the same basis.

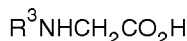
The amphoteric surface active agent may be betaine surface active agent. Preferred betaines may be either of the formula (I) or (II).



In the above formula, R^1 and R^2 may be the same or different C_{1-4} alkyl groups whereas R^3 is an alkyl group having 8-22 carbon atoms, more preferably 12 to 18 carbon atoms e.g. mixed C_{10} to C_{14} .

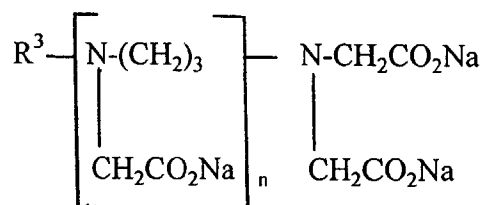
The preferred betaine for use in the formulation of the invention is cocoamidopropyl betaine (also known as cocodimethyl acetic acid betaine (CAS Registry No. 66455-29-6). Further betaines which may be used are lauryl dimethyl betaine (CAS Registry No. 683-10-3), cocoa dimethyl amidopropyl betaine (CAS Registry No. 61789-40-0) and the products identified as CAS Registry Nos. 70851-07-09 and 4292-10-8.

An alternative amphoteric surface active agent for use in the formulation of the invention is a glycinate of the formula



where R^3 is as defined above.

A further glycinate which may be used is of the formula



In which R^3 is as defined above and n is 1 to 3.

Other suitable materials are as given in chapter 1 of "Amphoteric Surfactants", e.g. Lomax Ed, Marcel Decker, New York 1996.

It is highly preferred that a cationic surface active agent is employed in conjunction with the amphoteric surface active agent. The cationic surface active agent is preferably used in an amount of up to 2% by weight of the formulation and is conveniently added in conjunction with the clay. Examples of suitable cationic surface active agents include quaternary ammonium salts having three lower (C_{1-4}) alkyl groups (preferably methyl groups) and a long chain (C_{8-20}) alkyl group, e.g. coco trimethyl ammonium chloride. Further examples include alkyl pyridinium salts and other compounds in which the nitrogen atom of the pyridine assumes a quaternary form, e.g. as in an alkyl pyridinium bromide.

Further examples of cationic surface active agents which may be used include amine and imidazoline salts.

If an anionic surface active agent is used then it is preferably present in the formulation in an amount of up to 20%, more preferably up to 10%, even more preferably up to 5% by weight of the formulation. Examples of anionic surface active agents which may be employed include alkylaryl sulphonates, alkyl sulphates, ether sulphates and ether carboxylates all as conventionally employed in laundry detergent formulations.

If a non-ionic surface active agent is used then it is preferably present in an amount of up to 20% by weight of the formulation, more preferably 2 to 10% on the same basis. Examples of non-ionic surface active agent which may be used include alkoxyates, ethylene oxide/propylene oxide block copolymers, alkanolamides (e.g. monoethanolamides and diethanolamides), esters and amine oxides.

The formulation may include at least one builder salt in a total amount of 10% to 50% by weight of the formulation. The builder may be for example be an alkali metal phosphate or alkali metal carbonate. A particularly preferred builder is sodium triphosphate.

It will be appreciated that the formulation may incorporate additional components as conventionally included in laundry detergent formulation. One example of such an additional component is a soap which may be used in an amount up to 5% by weight as a processing aid. Further examples include anti-foam agents, sequestrants (e.g. of the phosphonate type), whiteness maintenance agents (e.g. CMC, polyoxyethylene terephthalate, polyethylene terephthalate), colourants (e.g. dyestuffs), perfume, flow control agents (e.g. a sulphate) flow enhancer (e.g. a zeodite), pH regulators (e.g. a carbonate or bicarbonate), anti-corrosion agents, dye transfer inhibitors (e.g. PVP) and optical brighteners (e.g. Tinopal CBS-X and Tinopal DMS-X). These components may, for example, each be present in amounts up to 1% by weight of the formulation.

The invention will be further described with reference to the following nonlimiting Examples.

Example 1

The following laundry detergent formulation A (see Table 1) in accordance with the invention was produced using standard procedures

Table 1

	% by weight
Sodium Triphosphate	29.23
Granular Sodium Carbonate	9.81
Sodium Perborate Tetrahydrate	9.00
Sodium Perborate Monohydrate	9.00
Hexaacetyl Sorbitol	3.10
WA Powder (clay incl cationic and amide surfactants)	11.5
Ampholak X07/SD80 (Betaine Surfactant)	3.00
Synperonic 87k	4.50
Synperonic A3	1.50
Trepalbe Veg. Soap	4.92
Opticlean M375 Plus (Proteolytic Enzyme)	1.14
Maxamyl 2900 (Amylolytic Enzyme)	0.80
CMC	2.06
C-Sol (disilicate)	4.47
Wessalith P (zeolite)	3.43
Dequest 20160 (Diphosphonate Sequestrant)	0.69
Colour	0.75
Optical Brightners	0.30
Antifoam	0.41
Perfume	0.40

The surfactants included in the WA powder are stearyl stearamide and cocotrimethyl ammonium chloride.

A comparative formulation B was prepared exactly as for A save that the hexaacetyl sorbitol was replaced by tetraacetyl ethylene diamine (TAED).

Formulations A and B were used to launder standard pre-stained Red Wine, Tea, Blackcurrant, Enzyme Sensitive, Cocoa) or pre-dyed (Immedial Black) cotton swatches so as to test the bleaching activity of the formulations and the extent to which they caused dye damage. These laundering operations were carried out using a Hoover Ecologic Autowasher 100 de Luxe set on its "Main Wash" wash cycle. Laundering was carried out at 40°C and 60°C using 75 g of the formulations. Water hardness was 290 ppm calcium.

Reflectance measurements were made on the swatches both before (r_1) and after (r_2) laundering using a Harrison Reflectometer. The effect of the formulation as the swatch was calculated as ($r_2 - r_1$) which represents the extent to which the fabric had been bleached by the laundering procedure.

The results are shown in Table 2.

Table 2

Stain Type and Temperature		A	B
Red Wine Stain	40°C	21.5	21.5
	60°C	31.4	29.3
Tea Stain	40°C	10.5	10.5
	60°C	16.5	14.6
Blackcurrant Stain	40°C	23.5	23.3

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Table 2 (continued)

Stain Type and Temperature		A	B
	60°C	35.1	33.1
Enzyme Sensitive Stain	40°C	43.4	35.7
	60°C	52.4	44.6
Cocoa Stain	40°C	36.9	36.3
	60°C	45.8	38.2
TOTAL		316.9	287.0
Immedial Black Dye Damage	40°C	3.1	3.2
	60°C	6.7	7.6
TOTAL		9.8	10.8

It can be seen from Table 2 that, with regard to stain removal, formulation A was more effective (i.e. higher value of r_2-r_1) than formulation B save for Red Wine and tea stains using the 40°C wash for which A and B gave the same stain removal properties.

With regard to dye damage, formulation A was superior (lower value of r_2-r_1) to B at both 40°C and 60°C.

Example 2

Formulation C in accordance with the invention was formulated as shown in Table 3.

Table 3

Raw Material	C %
STP L16	16.5
Light Sodium Carbonate	21
Perborate Tetrahydrate	11.5
Sodium Sulphate	20.3
Al Powder (Pyramid P10)	1
CMC	1.5
Tinopal DMS-X	0.125
Tinopal CBS	0.03
Esperase/Savinase	0.5
Maxamyl 2900 CXT	0.5
Antifoam Rhodorsil 20471LV	0.2
STP L16	1.645
C Sol (Pyramid P40)	2.5
Armosoft WA Powder	10
Blue Beads	1
Green Beads	1
Synperonic A7	1.5
Nansa SS Acid	3.4

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Table 3 (continued)

Raw Material	C %
Waterglass C100	4.5
Perfume White Blossom 2951	0.2
Hexaacetyl Sorbitol	1.5
Less Evaporation	-0.4
TOTAL	100

Comparative formulation D was prepared by replacing the Hexaacetyl Sorbitol (HAS) with the same amount (1.5%) of TAED. A further comparative formulation E was prepared by omission of HAS and increasing the sodium sulphate content to 21.8% by weight.

Formulations C-E were tested as described in Example 1 save that the washing machine used was a Creda 1150 Supaspeed and 150 g of each formulation was used. The results are shown in Table 4.

Table 4

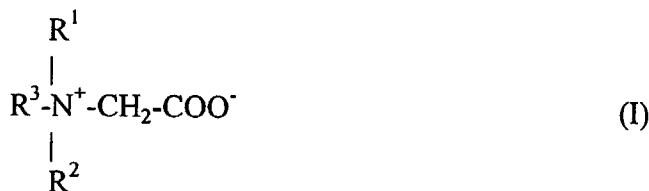
Stain Type and Temperature		C %	D %	E %
Removal of Coffee from Cotton	40°C	39.5	34.0	34.8
	60°C	48.2	47.2	43.0
Removal of Blackcurrant from Cotton	40°C	24.9	23.1	28.0
	60°C	45.5	43.7	33.2
Red Wine Stain removal	40°C	21.4	15.6	14.4
	60°C	12.4	11.9	19.8
Tea Stain Removal	40°C	11.2	9.8	8.3
	60°C	37.5	37.1	13.4
Immedial Black Dye Damage	40°C	2.5	3.1	2.0
	60°C	4.9	6.0	4.3
Enzyme Sensitive Stain Removal	40°C	34.0	33.3	36.9
	60°C	42.0	36.5	46.8
Cocoa Stain Removal	40°C	31.1	28.8	32.8
	60°C	42.1	37.4	39.5
OXIDSABLE TOTALS		247.9	231.4	201.1
ENZYME TOTALS		149.2	135.9	155.9
SUM TOTAL		397.06	367.3	357.02

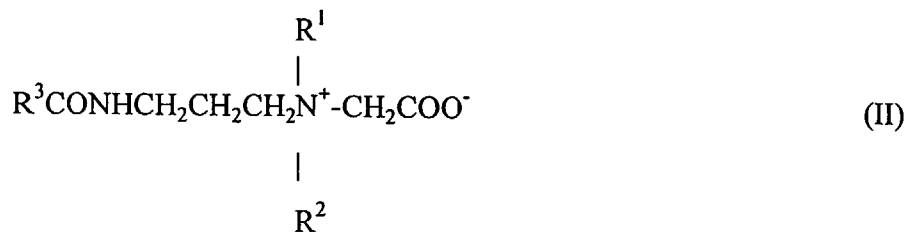
Once again it can be seen that the formulation in accordance with the invention (i.e. C) gave improved removal of stains (higher value of r_2-r_1) than comparative formulation D but gave reduced dye damage (i.e. lower value of r_2-r_1 in the case of the swatch dyed with Immedial Black).

Claims

1. A laundry detergent formulation comprising at least one surfactant, a clay having fabric softening properties, and an activated bleaching system which includes at least one bleach activator which is an ester of a polyhydric alcohol having at least 5 carbon atoms and at least 3 hydroxyl groups esterified with C_{2-5} acyl groups, the polyhydric alcohol residue of said activator not having any substituents with six or more carbon atoms.

2. A formulation as claimed in claim 1 wherein the activator has an HLB value of at least 7, more preferably at least 9 and even more preferably at least 11.
3. A formulation as claimed in claim 1 or 2 wherein the alcohol residue of the activator has a maximum of 12 carbon atoms.
4. A formulation as claimed in any one of claims 1 to 3 wherein the alcohol has at least 5 hydroxyl groups esterified with C₂₋₅ acyl groups.
5. A formulation as claimed in any one of claims 1 to 4 wherein said acyl groups have two or three carbon atoms and are preferably acetyl groups.
6. A formulation as claimed in any one of claims 1 to 5 wherein said alcohol is a sugar or sugar derived alcohol, preferably sorbitol, glucitol, mannitol, glucose or sucrose.
7. A formulation as claimed in claim 6 wherein the bleach activator is hexa acetyl sorbitol, hexa acetyl mannitol, penta acetyl glucose or octa acetyl sucrose.
8. A formulation as claimed in any one of claims 1 to 7 wherein the amount of bleach activator incorporated in the formulation is in the range 0.5% to 10% by weight.
9. A formulation as claimed in any one of claims 1 to 8 wherein the bleaching system includes a hydrogen peroxide precursor compound, for example an organic persalt such as a perborate, percarbonate or persulfate.
10. A formulation as claimed in claim 9 wherein the amount of hydrogen peroxide precursor compound present in the formulation is such as to provide 0.5% to 3% by weight active oxygen.
11. A formulation as claimed in any one of claims 1 to 10 wherein the clay is Laponite, Bentonite, Montmorillonite, Hectorite and mixtures thereof.
12. A formulation as claimed in any one of claims 1 to 11 wherein the amount of clay in the formulation is 5% to 20% by weight.
13. A formulation as claimed in any one of claims 1 to 12 wherein the surface active agent is an amphoteric surface active agent.
14. A formulation as claimed in claim 13 wherein the amphoteric surface active agent is present in an amount of 0.1 to 10%, preferably 0.5 to 5% and more preferably 1 to 4% by weight based on the total weight of the formulation.
15. A formulation as claimed in claim 13 or 14 wherein the amphoteric surface active agent is a betaine surface active agent.
16. A formulation as claimed in claim 15 wherein the betaine surface active agent is of the formula (I) or (II):





wherein R¹ and R² may be the same or different C₁₋₄ alkyl groups and R³ is an alkyl group having 8-22 carbon atoms.

17. A formulation as claimed in claim 16 wherein the betaine surface active agent is cocoamidopropyl betaine.

18. A formulation as claimed in any one of claims 13 to 17 additionally incorporating a cationic surface active agent, present for example in an amount up to 2% by weight of the formulation.

19. A formulation as claimed in claim 18 wherein the cationic surface active agent is incorporated in the clay.

20. A formulation as claimed in any one of claims 1 to 12 wherein the surface active agent is an anionic surface active agent present for example in an amount up to 20% by weight of the formulation.

21. A formulation as claimed in claim 20 wherein the anionic surface active agent is an alkylaryl sulphonate, alkyl sulphate, ether sulphate or ether carboxylate.

22. A formulation as claimed in any one of claims 1 to 12 wherein the surface active agent is a non-ionic surface active agent present for example in an amount up to 20% by weight of the formulation.

23. A formulation as claimed in claim 22 wherein the non-ionic surface active agent is an alkoxylate, ethylene oxide/propylene oxide block copolymer, alkanolamide, ester and amine oxide.

24. A formulation as claimed in any one of claims 1 to 23 including a total amount of 10% to 50% by weight of the formulation of at least one builder salt, for example an alkali metal phosphate such as sodium triphosphate or an alkali metal carbonate.

25. A laundry detergent formulation comprising at least one surfactant, a clay having fabric softening properties, and an activated bleaching system which includes at least one bleach activator having an HLB value of at least 7, more preferably at least 9 and even more preferably at least 11.