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(71) Applicant (for AE, AG, AU, BB, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, KN, LC, LK, LS, MN, MW, NA, NG, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London Greater London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KM, KP, KR, KZ, LR, LT, LU, LV, LY, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RS, RU, SE, SI, SK, SM, SN, SY, TD, TG, TJ, TM, TN, TR, UA, UZ, VN only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BATCHELOR,**

Stephen, Norman [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **TYNAN, Matthew** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB).

(74) Agents: **ELLIOTT, Peter, William** et al.; Unilever Patent Group, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

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(54) Title: STAIN REMOVAL

(57) Abstract: The present invention provides a laundry detergent composition comprising an efficient sequestrant.



WO 2007/042140 A2

- 1 -

STAIN REMOVAL**FIELD OF INVENTION**

The present invention concerns the use of particularly
5 efficacious sequestrants for the removal of stains from
fabrics.

BACKGROUND OF INVENTION

Tea and red wine are the source of many textile stains that
10 are difficult to remove. There is a need for effective stain
removal agents for laundry products that function at low
temperature. Sequestrants can provide stain removal benefits
at low temperatures, however many of these are not weight
effective or contain phosphorous which is not desirable on
15 environmental grounds.

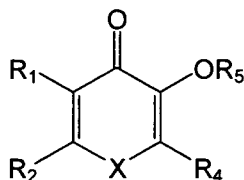
SUMMARY OF THE INVENTION

Some of the non-phosphorous sequestrants used in the present
invention have been disclosed in WO2002051961 and
20 WO2005001016 as having utility in semiconductor cleaning
solutions. We have found that the non-phosphorous
sequestrants, primary sequestrant, are surprisingly weight
and molar effective when compared to conventional
sequestrants used in laundry applications. The non-
25 phosphorous sequestrants have particular utility in removing
stains from cotton textiles. The non-phosphorous
sequestrants provide a better stain removal profile when
used in combination with other sequestrants, particularly
in combination with phosphorous based sequestrants.

30

- 2 -

In one aspect the present invention provides use of a composition, for cleaning a textile stain, in an aqueous medium, the composition comprising between 2 and 60 wt% of a surfactant and between 0.001 to 5 wt %, preferably 0.05 to 1 wt %, of a sequestrant, the non-phosphonate sequestrant having a molecular weight of less than 400 and of the following structure:



10

wherein X = N-R3;

R₁, R₂, and R₄ are independently selected from: a sulphonic acid group, an organic group and hydrogen; and,

R₃ and R₅ are independently selected from: an organic group and hydrogen. The aforementioned composition preferably comprises a phosphonate sequestrant in the range 0.05 to 1 wt % and the present invention extends to such composition per se.

20 In another aspect the present invention provides use of the composition comprising the non-phosphonate sequestrant, wherein the use comprises the following steps:

(i) treating a stained textile in an aqueous medium, the aqueous medium comprising composition comprising:
25 from 0.005 to 0.2 g/L of the non-phosphonate sequestrant, a surfactant at a level in the range from

- 3 -

0.1 g/L to 4g/L, the aqueous medium having a pH in the range from 7 to 12;

- (ii) rinsing the textile in an aqueous medium; and
- (iii) drying the textile.

5

The use of the composition is preferably conducted in the presense of a phosphonate sequestrant that is present in the aqueous medium in the range from 0.005 to 0.2 g/L.

10 **DETAILED DESCRIPTION OF THE INVENTION**

The pendant groups R_1 to R_5 may be optionally substituted without detracting from efficacy of the non-phosphonate sequestrant. In particular R_1 to R_5 may be optionally by amines or carboxylic acids, for example $R_3 = \text{CH}_2\text{C}(\text{NH}_2)\text{CO}_2\text{H}$.

15

It is preferred that R_5 is selected from the group consisting of: H, a keto group, a C1 to C10-alkyl group, phenyl, and naphthyl. It is preferred that R_1 , R_2 and R_4 are independently selected from: methyl, ethyl, propyl, butyl, 20 phenyl, naphthyl, methoxy, ethoxy, hydrogen, sulphonic acid, carboxylic acid or salts thereof, ketone group, ester group and an acid amide group;

R_3 is independently selected from: methyl, ethyl, propyl, phenyl, naphthyl, and hydrogen.

25

Preferably $R_1 = R_2 = R_5 = \text{H}$ and R_4 is CH_3 or C_2H_5 , R_3 is selected from the group consisting of selected from CH_3 , C_2H_5 , C_3H_7 , and $\text{C}_2\text{H}_4\text{COOM}$, wherein M is H, an alkali metal or alkaline earth metal. It is most preferred that R_3 is 30 preferably CH_3 .

- 4 -

A preferred non-phosphonate sequesterent (X =N) is 3-hydroxy-1,2-dimethyl-4-pyridone.

Particularly good results may be obtained when the
5 hereinbefore defined sequestrants, primary sequesterant, are
used in conjunction with an additional sequestrants in the
range 0.001 to 5 wt %, preferably 0.05 to 1 wt %, the
additional sequesterant other than the primary sequesterant.
Phosphonate sequestrants are preferred as the additional
10 sequesterant, particularly those sold under the Dequest trade
name, most preferably 2060-2069, 2010-2019, 2040-2049.

Preferably the primary sequesterant is stored in an acidic
granule in high pH powders. In this regard, the granule
15 containing the primary sequesterant possesses a component
selected from the group consisting of: a cogranulent, a
binder and a coating, wherein the component is an acidic
component.

20 **BALANCE CARRIERS AND ADJUNCT INGREDIENTS**

The composition in addition to the non-phosphonate
sequesterant and surfactant comprises the balance carriers
and adjunct ingredients to 100 wt % of the composition.

25 These may be, for example, builders, foam agents, shading
dyes, anti-foam agents, solvents, fluorescers, bleaching
agents, and enzymes. Preferably the composition comprises
from 0.0001 to 0.1 wt % of a shading dye, from 0.01 to 1 wt
% enzyme and from 0.1 to 1 wt % perfume. The use and amounts
30 of these components are such that the composition performs

- 5 -

depending upon economics, environmental factors and use of the composition.

The composition comprises a surfactant and optionally other
5 conventional detergent ingredients. The composition may also
comprise an enzymatic detergent composition which comprises
from 0.1 to 50 wt %, based on the total detergent
composition, of one or more surfactants. This surfactant
system may in turn comprise 0 to 95 wt % of one or more
10 anionic surfactants and 5 to 100 wt % of one or more
nonionic surfactants. The surfactant system may additionally
contain amphoteric or zwitterionic detergent compounds, but
this is not normally desired owing to their relatively high
cost. The enzymatic detergent composition according to the
15 invention will generally be used as a dilution in water of
about 0.05 to 2 wt%.

The composition comprises between 2 to 60 wt % of a
surfactant, most preferably 10 to 30 wt %. In general, the
20 nonionic and anionic surfactants of the surfactant system
may be chosen from the surfactants described "Surface Active
Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol.
2 by Schwartz, Perry & Berch, Interscience 1958, in the
current edition of "McCutcheon's Emulsifiers and Detergents"
25 published by Manufacturing Confectioners Company or in
"Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser
Verlag, 1981.

Suitable nonionic detergent compounds which may be used
30 include, in particular, the reaction products of compounds
having a hydrophobic group and a reactive hydrogen atom, for

- 6 -

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 C₆ to C₂₂ alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C₈ to C₁₈ primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

10 Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates 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.

15 Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₈ to C₁₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₉ to C₂₀ benzene sulphonates, particularly sodium

20 linear secondary alkyl C₁₀ to C₁₅ benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C₁₁ to C₁₅

25 alkyl benzene sulphonates and sodium C₁₂ to C₁₈ alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

30

- 7 -

Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C₁₆ to C₁₈ primary alcohol sulphate together with a C₁₂ to C₁₅ primary alcohol 3 to 7 EO ethoxylate.

The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25 to 90 wt % of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 5% to about 40 wt % of the surfactant system.

15 CATIONIC COMPOUND

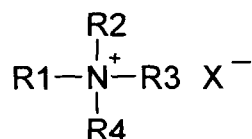
When the present invention is used as a fabric conditioner it needs to contain a cationic compound. The preferred pH when for a fabric conditioner is in the range from 3 to 5.

20 Most preferred are quaternary ammonium compounds.

It is advantageous if the quaternary ammonium compound is a quaternary ammonium compound having at least one C₁₂ to C₂₂ alkyl chain.

25

It is preferred if the quaternary ammonium compound has the following formula:



- 8 -

in which R¹ is a C₁₂ to C₂₂ alkyl or alkenyl chain; R², R³ and R⁴ are independently selected from C₁ to C₄ alkyl chains and X⁻ is a compatible anion. A preferred compound of this type is the quaternary ammonium compound cetyl trimethyl
5 quaternary ammonium bromide.

A second class of materials for use with the present invention are the quaternary ammonium of the above structure in which R¹ and R² are independently selected from C₁₂ to C₂₂
10 alkyl or alkenyl chain; R³ and R⁴ are independently selected from C₁ to C₄ alkyl chains and X⁻ is a compatible anion.

A detergent composition according to claim 1 in which the ratio of (ii) cationic material to (iv) anionic surfactant
15 is at least 2:1.

Other suitable quaternary ammonium compounds are disclosed in EP 0 239 910 (Proctor and Gamble).

20 It is preferred if the ratio of cationic to nonionic surfactant is from 1:100 to 50:50, more preferably 1:50 to 20:50.

The cationic compound may be present from 0.02 wt % to 20 wt
25 % of the total weight of the composition.

Preferably the cationic compound may be present from 0.05 wt % to 15 wt %, a more preferred composition range is from 0.2 wt % to 5 wt %, and most preferably the composition range is
30 from 0.4 wt % to 2.5 wt % of the total weight of the composition.

- 9 -

If the product is a liquid it is preferred if the level of cationic surfactant is from 0.05 wt % to 10 wt % of the total weight of the composition. Preferably the cationic compound may be present from 0.2 wt % to 5 wt %, and most preferably from 0.4 wt % to 2.5 wt % of the total weight of the composition.

If the product is a solid it is preferred if the level of cationic surfactant is 0.05 wt % to 15 wt % of the total weight of the composition. A more preferred composition range is from 0.2 wt % to 10 wt %, and the most preferred composition range is from 0.9 wt % to 3.0 wt % of the total weight of the composition.

15 BLEACHING SPECIES

The laundry treatment composition may comprise bleaching species. The bleaching species, for example, may selected from perborate and percarbonate. These peroxy species may be further enhanced by the use of an activator, for example, TAED or SNOBS. Alternatively or in addition to, a transition metal catalyst may used with the peroxy species. A transition metal catalyst may also be used in the absence of peroxy species where the bleaching is termed to be via atmospheric oxygen, see, for example WO02/48301. Photobleaches, including singlet oxygen photobleaches, may be used with the laundry treatment composition. A preferred photobleach is vitamin K3.

FLUORESCENT AGENT

30 The composition most preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known

- 10 -

and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or
5 agents used in laundry treatment composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.1 wt %. Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure
10 Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN. Preferred fluoescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]trazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate,
15 disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfoslyryl)biphenyl.

Examples

20

Example 1

Black tea beverage was created by placing 1 PG Tips pyramid tea bag in 400ml of boiled ultrapure water for 5 minutes. The tea bag was then removed and the beverage allowed to
25 cool to room temperature. Desized non-mercerised non-fluorescent white cotton sheeting was dipped in the cold tea and removed. The cloth was left to dry for 1 day in the dark, then used for experiments.

30 The tea stained cotton cloths were washed in pH 8.5 buffer containing 0.1g/L of the compounds listed in the table

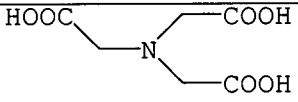
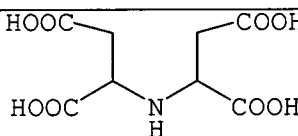
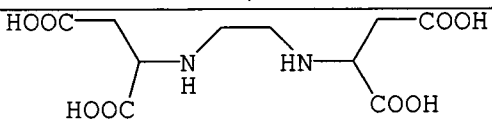
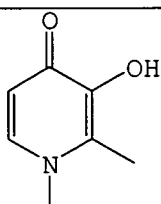
- 11 -

below, for 30 minutes. Compounds were selected to provide a comparison of the pyridone compounds to current non-P containing sequesterants. The liquor to cloth ratio was 50:1. The cloth was removed rinsed and dried and the DeltaE values measured relative to a clean cloth. Whether the compound gave a benefit or a negative in terms of stain removal was quantified using the equation

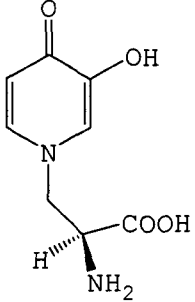
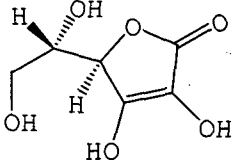
$$\text{deltaE}(\text{benefit}) = \text{deltaE}(\text{control}) - \text{deltaE}(\text{compound})$$

The 2 pyridones provided the highest benefit

10

Compound	RMM	deltaE(benefit)
 Nitrilo triacetate	191	1.5
 Imino Disuccinic acid	249	0.0
 N,N' - Ethylenediaminedisuccinic acid	292	-0.1
 3-hydroxy-1,2-dimethyl-4- pyridone	139	4.9

- 12 -

 <p>L-Mimosine</p>	198	2.8
 <p>Ascorbic acid</p>	176	0.1

Example 2

Tea stained cloth was created as per example 1. The tea stained cloth was washed in the following commercial laundry products: Persil Performance (ex UK), OMO MA (ex Brasil) and Persil Liquid concentrate (ex UK). Persil Performance is a zeolite based product with anionic and non-ionic surfactants which contain the TAED/percarbonate bleaching system. OMO MA is a sodium tri-polyphosphate based product with anionic surfactant and does not contain bleach. Persil liquid concentrate contains surfactants, it does not contain bleach and operates at a lower pH than the powders. The washes were conducted at 30°C for 30 minutes using 2.5g/L product and a liquor to cloth ration of 35:1. All cloth was stained.

Following the wash the clothes were rinsed, dried and the clothes measured using a reflectometer and the staining of the cloth expressed as deltaE relative to unwashed clean white cloth. Experiments were repeated with addition of varying levels of 3-hydroxy-1,2-dimethyl-4-pyridone (CAS No 30652-11-0).

- 13 -

The deltaE results are shown in the table below:

Product	[3-hydroxy-1,2-dimethyl-4-pyridone] in g/L			
	0	0.01	0.05	0.1
Persil Performance	15.8	14.5	13.6	11.8
OMO MA	16.4	15.2	13.6	12.9
Persil Liquid	17.9	16.3	13.4	12.7

Addition of 3-hydroxy-1,2-dimethyl-4-pyridone increases the
5 tea stain removal seen with all products, as shown by a
decrease in the deltaE value.

Example 4

3-hydroxy-1,2-dimethyl-4-pyridone increased the stain
10 removal of the tea and wine stains when washed in pH buffer
solution at 8.5 and 10.

Example 5

Tea stains were created as per example 1. Red wine stains
15 were created in an analogous manner, except here the cloth
was dipped into red wine (Australian, Shiraz Cabinet 2003).
The stains were washed at 30°C for 30 minutes using 4g/L of
ECE reference detergent with a liquor to cloth ratio of
50:1. 6°FH (Ca:Mg 2:1) water was used in the experiment.
20 After washing, rinsing and drying the colour of the cloth
was measured and expressed as the DeltaE relative to clean
white cloth. The experiment was then repeated with the
addition of 0.05 g/L of the sequesterants listed below.

- 14 -

ECE reference detergents contains 0.80% of the phosphorous based sequesterant Dequest 2066. Dequest 2016 and Dequest 2060 are also phosphorous based sequestrant. Dequest 2060 and 2066 are analagous except 2060 is the phosphonic acid, and
5 2066 is Na salt.

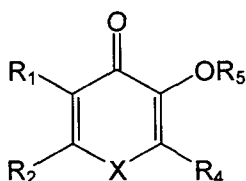
Wash system	deltaE tea stain	deltaE red wine stain
ECE	10.6	11.3
ECE + 3-hydroxy-1,2-dimethyl-4-pyridone	8.5	8.7
ECE + Dequest 2016	10.4	10.4
ECE + Dequest 2060	10.4	10.8
ECE + Na Ascorbate	10.5	11.0

From the results 3-hydroxy-1,2-dimethyl-4-pyridone increases the stain removal by the largest amount. For example for tea
10 and additional stain removal of 2.1 units is observed compared to a maximum of 0.2 units for the other sequestrants.

- 15 -

We Claim:

1. Use of a composition, for cleaning a textile stain, in an aqueous medium, the composition comprising between 2 and 60 wt% of a surfactant and between 0.001 to 5 wt % of a sequestrant, the non-phosphonate sequestrant having a molecular weight of less than 400 and of the following structure:



10

wherein X = N-R3;

R₁, R₂, and R₄ are independently selected from: a sulphonic acid group, an organic group and hydrogen;

15

and,
R₃ and R₅ are independently selected from: an organic group and hydrogen.

2. Use according to claim 1, wherein R₅ is selected from the group consisting of: H, a keto group, a C1 to C10-alkyl group, phenyl, and naphthyl.
3. Use according to claim 1 or 2, wherein R₁, R₂ and R₄ are independently selected from: methyl, ethyl, propyl, butyl, phenyl, naphthyl, methoxy, ethoxy, hydrogen, sulphonic acid or carboxylic acid or salts thereof, ketone group, ester group and an acid amide group;

25

- 16 -

R₃ is independently selected from: methyl, ethyl, propyl, phenyl, naphthyl, and hydrogen.

4. Use according to claim 3, wherein R₃ is CH₃ or C₂H₅.

5

5. Use according to claim 3 or 4, wherein R₁ = R₂ = R₅ = H and R₄ is CH₃ or C₂H₅, R₃ is selected from the group consisting of selected from CH₃, C₂H₅, C₃H₇, and C₂H₄COOM, wherein M is H, an alkali metal or alkaline earth metal.

10

6. Use according to claim 1, wherein the non-phosphonate sequestrant is 3-hydroxy-1,2-dimethyl-4-pyridone.

7. Use according to any preceding claim, wherein the composition comprises an additional sequestrant in the range range 0.001 to 5 wt %, the additional sequestrant other than that defined in claim 1.

15

8. Use according to any claim 7, wherein the additional sequestrant is a phosphonate sequesterant.

20

9. Use according to claim 8, wherein the additional sequestrant is selected from the group Dequest 2060 to 2069, 2010 to 2019, 2040 to 2049.

25

10. Use of the composition comprising a non-phosphonate sequestrant, the non-phosphonate sequestrant as defined in any one of claims 1 to 6, wherein the use comprises the following steps:

30

(i) treating a stained textile in an aqueous medium, the aqueous medium comprising composition

- 17 -

comprising: from 0.005 to 0.2 g/L of the non-phosphonate sequestrant, a surfactant at a level in the range from 0.1 g/L to 4g/L, the aqueous medium having a pH in the range from 7 to 12;

- 5 (ii) rinsing the textile in an aqueous medium; and
(iii) drying the textile.

11. Use according to claim 10, wherein an additional
sequestrant is present in the aqueous medium in the range
10 from 0.005 to 0.2 g/L, the additional sequestrant being a
phosphonate.