(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 168 889**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **85201127.9**

(22) Date of filing: **09.07.85**

(51) Int. Cl.⁴: **C 11 D 3/36**, C 11 D 1/34, C 11 D 3/30, C 11 D 1/40, C 11 D 3/12

(30) Priority: **18.07.84 GB 8418320**

(43) Date of publication of application: **22.01.86 Bulletin 86/4**

(84) Designated Contracting States: **AT BE CH DE FR GB IT LI LU NL SE**

(71) Applicant: **THE PROCTER & GAMBLE COMPANY, One Procter & Gamble Plaza, Cincinnati Ohio 45202 (US)**
(84) Designated Contracting States: **CH GB LI SE AT**

(71) Applicant: **Procter & Gamble European Technical Center, Temselaan 100, B-1820 Strombeek-Bever (BE)**
(84) Designated Contracting States: **BE DE FR IT LU NL**

(72) Inventor: **Burckett St. Laurent, James Charles Théophile R., 2, H. Vandevelde Laan, B-1980 Tervuren (BE)**
Inventor: **Busch, Alfred, Luitberg 10, B-1820 Grimbergen (BE)**

(74) Representative: **Brooks, Maxim Courtney et al, Procter & Gamble European Technical Center Temselaan 100, B-1820 Strombeek-Bever (BE)**

(54) Dispersible fabric softeners.

(57) Amines and phosphate esters are combined in sub-stoichiometric amounts to provide water-insoluble, water-dispersible fiber and fabric softeners. The softeners are formulated in a variety of laundry and shampoo compositions.

EP 0 168 889 A2

0168889

DISPERSIBLE FABRIC SOFTENERS

James Charles Théophile Roger BURCKETT St. LAURENT
Alfred BUSCH

Technical Field

The present invention relates to means of treating fibers and fabrics, wherein a sub-stoichiometric complex of amines and phosphate esters is used to provide softness and anti-static benefits. Detergent compositions containing said amine-phosphate ester softeners are disclosed. The compositions herein can be used to soften fabrics.

Background

The use of softeners to treat fabrics after a washing operation is a well-known laundering practice. Fabric softeners are, in the main, water-insoluble cationic materials that are incompatible with anionic detersive surfactants used in most fabric washing compositions. For that reason, the softening operation is

generally carried out in the laundry rinse bath after the surfactant has been removed from the washing machine. This entails additional work for the user.

Formulators of fabric laundering compositions have long sought means whereby fabric washing and softening could be done concurrently. Laundering methods employing clay softeners, mixtures of clays and various amine materials and the like, are described in the following patents: German 29/64114.3, 28/57163.3, 24/39541.3, 23/34899.4 and EPO 80200570.2, 80200877.1 and 80201015.7. The use of mixtures of amines and soaps (salt of fatty acids) as through-the-wash softeners is disclosed in U.K. Patent 1.514.276.

The prior art also discribes the use of various cationic materials in sheet form. See U.S. Patent 4.220.562.

The prior art also teaches the softener use of alkyl phosphonate and quaternary ammonium compounds. EPO Application 0 006 268, filed June 11, 1979.

The prior art also teaches various mixtures of phosphate esters in detergents with fabric softening action - BE 802,679.

The present invention employs amine-phosphate ester softeners in laundry compositions to provide cleaning and softening concurrently. The softeners herein provide softening and anti-static benefits, especially when used with clay softeners. Importantly, the use of phosphate esters in sub-stoichiometric quantities with the amines in the manner disclosed herein advantageously enhances deposition of the amines on fabrics by as much as 1.5- or 2-fold, as compared with prior art amine fabric softening compositions.

Summary of the Invention

The present invention encompasses a method for softening fabrics by contacting same with sub-stoichiometric, water-insoluble, water-dispersible complexes of amine and phosphate ester (as described more fully, hereinafter) in the presence of water. The method can be carried out, for example, by tumbling damp fabrics with said complexes in a hot air clothes dryer. In another mode, said complexes can be used in an aqueous rinse bath, for example in a laundry rinse. In still another mode, the method can be carried-out concurrently with a fabric cleansing treatment, for example in a detergent-containing laundry liquor, to soften fabrics.

The invention also encompasses detergent compositions (preferably granular) which may be described succinctly as containing conventional detergent ingredients such as detersive surfactants (including anionics), detergency builders, optical brighteners, detersive enzymes, fabric bleaches, and the like, all at rather conventional levels, as well as clay fabric softeners (preferably, smectite clays), said compositions being characterized in that they contain at least 0.1% (preferably 1.0% to 15%) of the aforesaid sub-stoichiometric, water-insoluble, water-dispersible amine-phosphate ester softeners. The most preferred compositions with clay are formulated to contain not more than 5% (preferably not more than 1%-2%) of a nonionic detersive surfactant.

The invention also encompasses an article for use in a laundry bath or rinse bath, or in a laundry dryer, comprising the aforesaid sub-stoichiometric amine-phosphate ester softeners releasably affixed to a water-insoluble carrier, for example, a sheet of paper or fabric. Such compositions are optionally formulated to

contain a bleach activator and such activator-containing compositions are especially useful in laundry baths.

The ingredients and means for preparing the compositions are disclosed more fully hereinafter. All weights and proportions are by weight, unless otherwise specified.

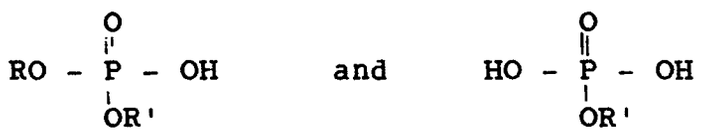
Detailed Description of the Invention

As noted hereinafter, the compositions of this invention comprise, in major part, conventional ingredients that are quite familiar to formulators of laundry compositions. One of the major advantages of the amine-phosphate softeners used herein is that they are entirely compatible with such conventional laundry ingredients, used at conventional concentrations.

Amines - The amines employed herein are of the formula $R_1R_2R_3N$ where R_1 is C_6 to C_{20}, R_2 is C_1 to C_{20} or hydrogen, and R_3 is C_1 to C_{10} or hydrogen.

Preferably, the amines have both R_1 and R_2 as C_6-C_{20} alkyl, with C_{16}-C_{18} being most preferred, and with R_3 as C_1-C_3 alkyl. Mixed amines, such as dicoconutalkyl- and ditallowalkyl-methyl amines can be used. Such materials are commercially available under Trade Marks such as "Armeen".

Phosphate Ester - The phosphate esters which are critical to the practice of this invention are commercially available materials of the general formulae:



wherein R and R' are C_1-C_{20} alkyl or (preferably)

ethoxylated alkyl groups of the general formulae: alkyl-$(OCH_2CH_2)_Y$, wherein the alkyl substituent is C_1-C_{20}, preferably C_8-C_{16} and Y is an integer of 1 to 15, preferably 2-10, most preferably 2-5. Such compounds are prepared by known methods from phosphorus pentoxide, phosphoric acid or phosphorus oxy halide and alcohols or ethoxylated alcohols.

It will be appreciated that the formulae depicted represent mono- and di-esters, and commercial phosphate esters will generally comprise mixtures of the mono- and di-esters, together with some proportion of tri-ester. Typical commercial esters are available under the Trade Marks "Phospholan" PDB3 (Diamond Shamrock) and "Servoxyl" VPAZ (Servo).

Amine-Phosphate Ester Softeners - The prior art describes various phosphate ester-amine compounds - see U.S. Patent 3.364.192 - some of which have been disclosed for use as fiber-finishing agents - see U.S. Patents 3.434.874; 3.428.481; and 3.560.382. However, the prior art compositions generally involve 1:1 (mole basis) compounds or complexes, i.e., compounds or complexes from stoichiometric mixtures. Surprisingly, such stoichiometric complexes are of no use in the present invention, apparently because they form unstable dispersions prone to aggregation. In contrast, the sub-stoichiometric mixtures herein are extremely well dispersed in water, but are not water-soluble.

While not intending to be limited by theory, it is instructive to consider the physico-chemical behaviour of the amine-phosphate ester softeners herein, inasmuch as this can be of assistance to the formulator.

It will be appreciated that the amines used herein and in art-disclosed compositions exist in aqueous solutions as fairly coarse particles, or oily globules, having a

spectrum of sizes. It appears that attachment of such particles to fabrics to provide the desired softening action can be considerably enhanced by reduction of their average size; coarser material being rinsed away by mechanical action. On the other hand, complete solubilization or micellization is to be avoided since this also leads to inadequate attachment of the amine to fabrics.

In addition to size of the dispersed amine particles, their phase structure is of importance since this will influence their effective spreading after attachment to fiber or fabric surfaces. Phase structure influences also the stability of amine dispersions.

Consideration of these factors apparently explains why, on one hand, amines untreated with phosphate ester and on the other hand, stoichiometric amine-ester complexes are of very low effectiveness relative to the sub-stoichiometric mixtures of amine-phosphate ester now disclosed.

It has now been discovered that sub-stoichiometric mixtures of amine-phosphate ester exist as aqueous dispersions whose particles readily deposit on, spread on, and soften, fibers and fabrics.

By "sub-stoichiometric" herein is meant that there is an excess of amine relative to phosphate ester. In general, there are at least about two parts amine (on a weight basis) per one part (weight) of phosphate ester, but this will, of course, vary with the molecular weights of the amine and ester, respectively. The objective is to have a readily-dispersible (in water) mixture, but not one that is water-soluble.

Useful amine-phosphate esters can easily be observed by a simple test. The amines herein, suspended in water, form a generally greasy-appearing, non-homogeneous mixture. By contrast, the sub-stoichiometric

amine-phosphate ester mixtures used in this invention form stable "milky" suspensions in water. Laboratory estimates of the particle sizes of these suspensions indicate that 60% to 80% of the particles fall within the size range of .1 to 8 micrometers; 20% to 40% within the range 8 to 20 micrometers; and essentially all the particles are below 40 micrometers in diameter.

For the preferred sub-stoichiometric amine-phosphate ester softeners herein, the weight ratio of amine:phosphate ester is above 5:1, generally 7:1 to 15:1, most preferably 10:1. Again, such softeners are selected to be water-dispersible, not water-soluble.

In general terms, the amine-phosphate ester softeners are prepared separately from the balance of the compositions, and are preferably then added to the other, conventional ingredients to provide the final formulations. This can most conveniently be done by preparing a melt of the phosphate ester and the amine and maintaining the melt stage for a few minutes. The melt can then be layered onto a sheet substrate to prepare, for example, a dryer-added fabric softener. To prepare a detergent, the melt can be solidified and comminuted to the desired particles size (e.g., in an extruder), and dry-mixed with a granular detergent composition. The melt may also be sprayed onto detergent granules. The melt may also be dispersed into a stirred, aqueous crutcher mix comprising the balance of the detersive ingredients, and spray-dried in standard fashion. This crutcher-addition is less preferred, as it leads to some decomposition of the complex. Simply adding the amine and phospate ester, individually, to a detergent crutcher mix does not secure the intended benefits of this invention.

An especially preferred softener herein is prepared by melting together ten parts by weight of di-C_{12}-C_{14} alkyl monomethyl amine and one part by weight of a mono - [C_{12}-C_{14} $(EO)_{1-5}$] ester of phosphoric acid, sold under the Trade Mark "Servoxyl VPAZ".

The amine-phosphate ester softeners will generally be used at levels of at least 0.1%, preferably 1% to 15%, in detergent compositions; at

levels of at least 1%, preferably 1% to 25% in rinse-added fabric softeners; and at levels of 2% to 60% in dryer- and wash machine- added sheets (where the balance of the composition mainly comprises the weight of the sheet substrate).

Softener Clay - The above-disclosed amine-phosphate ester softeners are preferably used in granular detergent compsitions, where they are most preferably used in combination with a detergent-compatible clay fabric softener. Such clay softeners are well-known in the detergency patent literature and are in broad commercial use, both in Europe and in the United States. Included among such clay softeners are various heat-treated kaolins and various multi-layer smectites. Preferred clay softeners are smectite softener clays that are described in German patent document 23 34 899 and in U.K. Patent 1.400.898 which can be referred to for details. Softener clays are used in the preferred compositions at levels of at least 1%, generally 1-20%, preferably 2-7%.

Detersive Surfactants - The detergent compositions of this invention will contain organic surface-active agents ("surfactants") to provide the usual cleaning benefits associated with the use of such materials.

Detersive surfactant useful herein include well-known synthetic anionic, amphoteric and zwitterionic surfactants. Typical of these are the alkyl benzene sulfonates, alkyl- and alkylether sulfates, paraffin sulfonates, olefin sulfonates, amine oxides, α -sulfonates of fatty acids and of fatty acid esters, and the like, which are well-known from the detergency art. In general, such detersive surfactants contain an alkyl group in the C_9-C_{18} range; the anionic detersive surfactants can be used in the form of their sodium, potassium or

triethanolammonium salts. U.S. Patent 4.111.855 contains detailed listings of such typical detersive surfactants. C_{11}-C_{16} alkyl benzene sulfonates, C_{12}-C_{18} paraffin-sulfonates and alkyl sulfates are especially preferred in the compositions of the present type.

Also useful herein as the surfactant are the water-soluble soaps, e.g. the common sodium and potassium coconut or tallow soaps well-known in the art.

It is to be understood that the use of typical alkoxylated nonionic surfactants (e.g. the C_9-C_{18} alkyl) alcohols and alkyl phenols with 5 to 20 ethoxyl groups) are preferably limited in the practice of this invention to levels of not more than about 5%, preferably not more than 2%, most preferably 0-1%, of the compositions when clay is present as a co-softener, since alkoxylates can interfere with the softening properties of clay. In clay-free compositions, the alkoxylated nonionics can be used at any desired level.

The surfactant component can comprise as little as 1% of the laundry detergent compositions herein, but generally the compositions will contain 5% to 40%, preferably 6% to 30%, of surfactant. Mixtures of the anionics, such as the alkyl benzene sulfonates, alkyl sulfates and paraffin sulfonates are preferred for through-the-wash cleansing of a broad spectrum of soils and stains from fabric.

Detersive Adjuncts - The compositions herein can contain other ingredients which aid in their cleaning performance. For example, it is highly preferred that through-the-wash detergent compositions contain a detergent builder and/or metal ion sequestrant. Compounds classifiable and well-known in the art as detergent builders include the nitrilotriacetates, polycarboxylates,

citrates, water-soluble phosphates such as tri-polyphosphate and sodium ortho- and pyro-phosphates, silicates, and mixtures thereof. Metal ion sequestrants include all of the above, plus materials like ethylene diaminetetraacetate, the amino-polyphosphonates and phosphates (DEQUEST) and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail here. See U.S. Patent 3.579.454 for typical examples of the use of such materials in various cleaning compositions. In general, the builder/sequestrant will comprise 0.5% to 45% of the composition. The 1-10 micrometer size zeolite (e.g. zeolite A) builders disclosed in German Patent 24 22 655 are especially preferred for use in low-phosphate compositions which contain the softeners described herein.

The laundry compositions herein also preferably contain enzymes to enhance their through-the-wash cleaning performance on a variety of soils and stains. Amylase and protease enzymes suitable for use in detergents are well-known in the art and in commercially available liquid and granular detergents. Commercial detersive enzymes (preferably a mixture of amylase and protease) are typically used at levels of 0.001% to 2%, and higher, in the present compositions.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, bleaches, optical brighteners, soil suspending agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents, bleach activators and the like.

The compositions can further contain a peroxygen bleach activator, particularly tetraacetyl ethylenediamine (TAED), typically from 0.1% to 5%, preferably from 0.5% to 2.5%. Other highly desirable detergent ingredients for use in the detergent compositions of the present invention are quaternary ammonium compounds of the form $R_4R_3R_6R_7N^+X^-$, wherein R_4 is alkyl having from 10 to 20, preferably from 12-18 carbon atoms, and R_5,R_6 and R_7 are each C_1 to C_4 alkyl preferably methyl; X^- is an anion, e.g. chloride. Examples of such quaternary ammonium compounds include monotallowalkyl trimethyl ammonium chloride and mono(cocoalkyl) trimethyl ammonium methosulfate. The quaternary ammonium compounds can be used at levels from 0.5% to 5%, preferably from 1% to 3%. Detergent compositions containing both TAED and the mono(long chain alkyl) tri(short chain alkyl) ammonium compound are highly preferred.

In a through-the-wash laundry mode, the compositions are typically used at a concentration of at least 500 ppm, preferably 0.10% to 2.5%, in an aqueous laundry bath at pH 7-11 to launder fabrics. The laundering can be carried out over the range from 5°C to the boil, with excellent results.

In an alternate mode, the amine-phosphate ester softeners herein may be releasably adsorbed or releasably coated onto a non-particulate substrate such as a non-woven or paper sheet or flexible sponge mat, or the like. Such sheet-form objects may be added to the laundry or rinse bath, or to the laundry dryer, where the softener is released to provide fabric softening. In an alternate, and highly preferred, mode the amine-phosphate ester softener is used in sheet form in combination with a bleach activator (such as tetraacetyl ethylene diamine or

a straight- or branched-chain C_6-C_{10} oxybenzene sulfonate) as a combined perborate-activator and softener in a laundry liquor. See, for example U.S. Patent 4.220.562.

Such sheet-form products will generally employ 1-20 grams of the amine-phosphate ester softener and 1-20 grams of the bleach activator.

In still another mode, the amine-phosphate ester can be formulated as a liquid fabric softener and used in a post-laundry rinse bath. Such liquid softeners can comprise, for example, a simple dispersion of the amine-phosphate ester softener in water or water-alcohol.

It is to be understood that the compositions and processes of this invention are carried out in a manner that will, typically, deposit at least a few milligrams (generally, at least 1-1000 mg) of the sub-stoichiometric amine-phosphate ester softener per square meter on the fabric being treated, as will be seen in the following examples.

INDUSTRIAL APPLICATION

The following examples are typical of the preferred compositions of this invention, but are not intended to limit the scope of the invention.

EXAMPLE I

A mix of ditallow methyl amine (total 3.8% of complete formulation after spray-drying) and monococonutalkyl(ethoxy)1-5 phosphoric acid ester (0.38% of complete formulation) are admixed, melted in a jacketed bath, and maintained as a melt for about ten minutes. Stirring assures homogeneity.

A standard aqueous crutcher mix comprising the following ingredients is prepared (percentages listed relate to percent ingredients in the complete formulation after spray-drying).

Ingredients	Percent
C_{11}-$_{12}$ alkyl benzene sulfonate	6.2
Tallow alcohol ethoxylate (EO11)	1.0
Sodium perborate	20.0
Sodium tripolyphosphate	24.0
Sodium sulfate	22.0
Sodium silicate	8.0
Smectite Clay *	2.4
Carboxymethyl cellulose	0.4
Polyacrylate (soil suspender)	1.7
Enzymes	0.5
Optical brightener	0.23
Sulphonated zinc phthalocyanine **	25 ppm
EDTA	0.2
Perfume/copper salts/minors	0.5
Moisture	to 100

* Natural smectite; ion exchange capacity above 50 meq/100g clay;
** U.S. Patent 3 927 967

The crutcher mix is handled in entirely standard fashion, and spray-dried to form a granular composition.

The amine-phosphate ester softener is added to the spray-dried granules as particles or "prills".

The composition of Example I is free-flowing and provides excellent cleaning and through-the-wash fabric softening when used at laundry concentration of 0.1% and above.

In an alternate mode, the amine-phosphate ester softener can be sprayed onto the spray-dried granules.

The composition of Example I may be modified by adding 1.0% tetraacetyl ethylenediamine (TAED) as a perborate bleach activator. It is preferred that materials such as bleach activators and enzymes be dry-mixed with the balance of the composition, after spray-drying.

The composition may be modified further by adding, in addition to TAED, 2.4% monotallowalkyl trimethyl ammonium chloride.

EXAMPLE II

A low-P spray-dried detergent formulation is as follows :

Ingredient	Percent
Zeolite A (1-10 micron)	26.0
Sodium nitrilotriacetate	5.0
Smectite clay *	3.0
Amine-phosphate Ester **	4.1
C_{11}-$_{12}$ alkyl benzene sulfonate (Na)	6.5
Tallow ethoxylate (EO 9-11)	0.5
Sodium Perborate.$4H_2O$	20.0
Sodium silicate	8.0
CMC	1.0
Sodium sulfate	20.0
Enzymes (1:1 amylase/protease) ***	1.5
Optical brightener	0.5
TAED	1.2
Water, minors	to 100

* As Gelwhite GP (TM):$CaCO_3$ ion exchange capacity 70 Meq/100g.

** As in Example I.

*** Dry-mixed with composition.

The composition of Example II is prepared by spray-drying an aqueous crutcher mix, in the manner described for Example I. In use, the composition gives excellent cleaning and through-the-wash fabric softening performance.

EXAMPLE III

A clay-free composition is prepared by removing the clay from Example I and substituting therefor an additional softener comprising monotallowalkyl trimethyl ammonium chloride as 2.4% of the total composition.

EXAMPLE IV

A laundry additive product is prepared by warming 6.5g of bis(tetradecyl)methyl amine and 0.8g of tetradecylphosphate to form a melt, and spreading the melt onto an ordinary disposable paper hand-towel (20x20 cm). 4 grams of TAED powder (1-10 microns) are sprinkled onto, and pressed into, the melt before it has the chance to solidify.

The article of Example IV is added to a laundry liquor containing a commercial perborate/clay detergent composition (DASH-3; Trade Mark) to enhance through-the-wash softening and bleaching performance.

EXAMPLE V

The article of Example IV is modified by deleting the TAED and replacing the Example IV softener with 3.5g. of the amine-phosphate ester softener of Examples I and II. The resulting article is tumbled with damp fabrics in a standard hot air clothes dryer, whereby the softener is transferred to the fabrics to impart softness.

EXAMPLE VI

A fine-fabric laundering composition with fabric softening properties is as follows :

Ingredient	Percent
C_{10-14} Alkyl Sulfate	9.0
Tallow alkyl benzene sulfonate	2.0
Coconut Soap	4.0
Glycerine	3.0
Amine-Phosphate ester complex *	6.0
Triethanolamine	to pH 7.0
Perfume	0.25
Water	to 100

* Octadecyl amine (15 parts)/bis-decylphosphate (1 part) as melt.

The composition of Example VI is in the form of a "milky" liquid.

CLAIMS

1. A method of softening fabrics which comprises contacting said fibres or fabrics with a sub-stroichiometric, water-dispersible amine-phosphate ester softener in the presence of water.

2. A method according to Claim 1 which is carried-out in an aqueous laundry liquor.

3. A method according to Claim 1 which is carried-out by tumbling damp fabrics with said amine-phosphate ester softener in a hot air clothes dryer.

4. A laundry detergent composition comprising conventional detersive ingredients, characterized in that it contains at least 0.1% of a sub-stroichiometric, water-dispersible amine-phosphate ester softener.

5. A composition according to claim 4 which contains from 1% to 15% of said amine-phosphate ester softener.

6. A composition according to Claim 5 which also contains at least 1% of a clay fabric softener.

7. A composition according to Claim 6 which contains not more than 5% of an alkoxylated nonionic detersive surfactant.

8. A composition according to any of Claims 4 through 7 which contains a detergency builder selected from phosphate, nitrilotriacetate, polycarboxylate, citrate and zeolite builders, or mixtures thereof.

9. A composition according to any of the Claims 4 through 8 which contains from 0.1% to 5% TAED and from 0.5% to 5% of a quaternary ammonium compound of the formula $R_4R_5R_6R_7N^+X^-$, wherein R_4 is alkyl having from 10 to 20 carbon atoms, R_5,R_6 and R_7 are each alkyl having from 1 to 4 carbon atoms, and X^- is an anion.

10. An article for use in a laundry or rinse bath, or in a laundry dryer, comprising a non-particulate substrate, preferably a flexible sheet, having releasably affixed thereto a fabric softener which comprises a sub-stoichiometric, water-dispersible amine-phosphate ester fabric softener.

11. An article according to Claim 10 which additionally has affixed thereto a bleach activator.

12. A composition of matter comprising a water-insoluble, water-dispersible mixture or melt of a phospate ester and an alkyl amine, at a weight ratio of amine:phosphate ester of at least 2:1.