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

(11) Publication number: **0 612 842 A2**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **94200398.9**

(51) Int. Cl.[5]: **C11D 3/37**

(22) Date of filing: **15.02.94**

(30) Priority: **24.02.93 IT MI930350**

(43) Date of publication of application:
31.08.94 Bulletin 94/35

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL PT SE

(71) Applicant: **ENICHEM S.p.A.**
Piazza della Repubblica, 16
I-20124 Milano (IT)

(72) Inventor: **Du Vosel, Annick**
Cascina Molinaccio, 2
I-28010 Caltignaga (Novara) (IT)
Inventor: **Muratori, Giuseppe**
Via Bazzoni, 2/C
I-28100 Novara (IT)
Inventor: **Colombo, Paolo**
Via A. Avogadro, 12
I-21047 Saronno (Varese) (IT)
Inventor: **Faccetti, Edoardo**
Via Chopin, 45
I-20141 Milan (IT)
Inventor: **Verzellino, Santina**
Via Adria, 54
I-20030 Bovisio Masciago (Milan) (IT)

(74) Representative: **Fusina, Gerolamo et al**
Ing. Barzanò & Zanardo Milano S.p.A,
Via Borgonuovo, 10
I-20121 Milano (IT)

(54) **Compositions for textile material washing.**

(57) Compositions for washing textile materials in automatic washing cycles characterized in that they contain, as builder additives, one or more polyamino acid(s) at a level of less than 5% by weight.

EP 0 612 842 A2

The present invention relates to compositions for washing textile materials in automatic cycles characterized in that the builder additives contained in said compositions are constituted by, or comprise, in mixture with conventional builders, one or more polyaminoacid(s) at a level of less than 5% by weight.

By the term "textile materials", within the context of the instant invention, woven materials or textile fibres either of natural origin or man-made, are meant.

By the terms "composition", "formulation" or "formulate", those products are meant within the context of the present invention, which are designed for use in textile materials washing.

It is widely known that the detergency products are among the causes of the presence of phosphorus in waters: among all of them, the effect of sodium tripolyphosphate (STPP), used as a detergency builder, was evidenced.

Also known are the efforts aiming at searching for alternatives to polyphosphates, but the solutions tried from time to time not always supplied satisfactory results because, when STPP is either removed or its content in formulates is reduced, the negative effect on the washing process is greater than as expected from the simple decrease in sequestering capabilities of the detergent matrix.

This unsatisfactory situation results from the impossibility of locating a product which displays the same characteristics as of SPTT, i.e., besides controlling water hardness, acting as a buffer, and acting as a soil release and soil suspending agent, as well as performing soil anti-redeposition actions.

The most widely used compound in order to replace STPP in such formulates, is Zeolite A (sodium alumino silicate).

At present, Zeolite A is used both in powder and in liquid compositions.

As regards the negative effects on the environment, this product is acceptable: it does not constitute a risk for water bodies and, by being inorganic and insoluble, it does not increase the BOD load to waste waters treating facilities.

From the view point of detergency, Zeolite A displays good adsorption capabilities for dyes and pigments released by fabrics and its ion-exchange capability increases with increasing temperature. Drawbacks are its slow exchange kinetics, in particular as regards magnesium, its absence of buffering action, and its having to be dispersed.

Therefore, Zeolite A is always used in association with other components (referred to as "builder additives" or "co-builders").

The presently used products for such a purpose, in association with Zeolite A, are sodium salts of polymeric polycarboxy acids.

Among those polymeric polycarboxy acids which were evaluated for that purpose, acrylic acid-maleic anhydride copolymers are those which proved to be the most efficient ones.

These products are good complexing agents, display good soil dispersing and anti-redeposition capabilities, improve the texture of laundry detergents, preventing clumps from getting formed.

Owing to the fact that, as well known, the polymeric polycarboxy acids, by being provided with a -C-C- backbone, are rather slowly biodegraded, intense efforts were carried out aiming at developing alternative compounds displaying similar performance characteristics, additionally with improved biodegradability.

The improvement in biodegradability was the starting point for the definition of builders which might prove to be a valuable replacement for those builders which are used at present. Thus, copolymers of maleic anhydride and/or acrylic acid with natural substances, as starch or dextrins, copolymers of maleic anhydride and substances capable of contributing allyl and vinyl moieties, maleic anhydride/ethylene oxide copolymers, glyoxylic acid/formaldehyde copolymers, and so forth, were studied, unfortunately with results which are far from the desired outcomes.

At present, most laundry detergents contain from 2 to 4% of polymers, usually acrylic-maleic copolymers, also combined with other builders.

It is known as well (British patent No. 1,404,814) that functionalized polyaminoacids can be used as surfactants, by being obtained by reacting polyimidic derivatives with long-chain aliphatic amines; from the control of the type of chain of the latter, or from the polymerization degree of the polyimide, the possibilities of selecting the end characteristics of the interesting polyaminoacid arise.

However, the products disclosed in said British patent do not seem to possess, at the highest level, that desired balance of properties which could allow them to be more generally used in other applications than as suggested, i.e., just to briefly list them, such characteristics as biodegradability, lack of toxicity, lack of irritant effects, high water solubility, which -- besides detergent properties --determine the applicability and use versatility in consequent formulations.

From European Patent Application Public. No. 454 126 it is known as well that polyaminoacids, or their derivatives, can be used as builders or co-builders in detergent formulations, because they display extremely good calcium complexing capabilities and inhibit the formation of $CaCO_3$ crystal germs, provided

that they are used at concentrations of not less than 5%.

The products set forth in the above said application display good effectiveness as complexing agents, high heat and pH stability, are not toxic, not irritating and are totally biodegradable, which would enable them to be used without causing environmental problems to arise.

However, the use of such concentrations as disclosed in the above said patent application might lead to problems of excessive organic loadings in the waste waters.

The present Applicant has found now, what is the object of the present invention, that the above said drawback can be completely eliminated if detergent formulations are used which comprise, as builders or co-builders, polyaminoacids at concentrations comprised within the range of from 0.5 to 5% by weight; particular advantages were attained when polyaspartates were used.

This result is all the more so surprising, because it is known that although they display good transition metal complexing capabilities, such amino acids as L-aspartic acid and L-glutamic acid are unable to form stable complexes with alkaline or alkali-earth metals [Angew. Chem. Ind. English Ed., 29 (1990) 1090-1103].

Therefore, in its widest form, the present invention relates to suitable compositions for textile material washing, characterized in that they contain surfactants and other salts.

As anionic surfactants, we may remind here, for exemplifying purposes, sodium, potassium or ammonium salts of linear-chain C_{10}-C_{20} fatty acids, alkyl sulfates, alkylbenzene sulfonates, alkane sulfonates, hydroxyalkane sulfonates, alkene sulfonates and alkyl ethoxy sulfates; we furthermore wish to cite various sulfonates, such as alkyl sulfosuccinates and alkali-metal and/or ammonium N-acyl-N-methyl taurinates, and so forth, or mixtures thereof.

As nonionic surfactants we would mention, for exemplifying purposes, the products of condensation of ethylene oxide with substances containing active hydrogen atoms, such as C_{10}-C_{20} fatty acids; as well as amides, fatty alcohols and amines, sucrose esters and alkyl phenols with C_6-C_{12} alkyl chains; as nonionic surfactants, also amino oxides may be cited.

As ampholytic surfactants, may we cite in general those compounds which derive from aliphatic amines, characterized by the presence of at least one C_8-C_{18} chain and at least one chain containing a hydrophylic anionic moiety, e.g., a carboxy or sulfonic acid group.

Those agents which complex alkali-earth cations according to the present invention, are commonly defined as "builders" and, as already said, perform several positive actions for the purposes of good textile washing results. One of most important among these actions, consists in sequestering metal ions, in particular alkali-earth metal ions, which constitute the water hardness (Ca^{++}, Mg^{++}). For use as "builders", the prior art suggests several inorganic compounds such as, e.g., water-soluble alkaline salts, such as carbonates, silicates, etc., or water insoluble compounds, such as alumino silicates, e.g., natural or synthetic zeolites; furthermore, water soluble organic compounds such as alkali-metal or ammonium salts of polycarboxy acids (citric acid, carboxy-methyloxy succinic acid, oxydisuccinic acid, and so on), are suggested.

Among most suitable optical brighteners for simultaneous textile washing and brightening, the optical brighteners from DAA (aminostilbene-disulfonic derivatives), DP (pyrazolinic) and AC (aminocoumarinic) series may be mentioned here.

Whenever so required, said formulations may contain, as bleaching agents, oxidixing or reducing compounds, such as, e.g., hydrogen peroxide, alkali-metal perborate, preferably sodium perborate, sodium percarbonate, hypochlorites, chlorites, phosphites, hydrosulfites.

In the event of use of persalts or hydrogen peroxide in formulations for low-temperature textile washing, the use is suggested of bleach activators, such as, e.g., tetraacetylenediamine, TAGU, pentaacetyl glucose, nonanoyl phenol sulfonate (sodium salt), and so forth.

As an alternative, for low-temperature wash requirements, the use is possible of organic peroxides, such as peracetic acid, dodecanediperdioic acid, phthalimino caproic acid, and so forth.

Besides the already mentioned ingredients, the formulates according to the present invention may obviously contain other common ingredients, such as, e.g., perfumes, antifoaming agents, stabilizers, anticaking agents, buffering agents, through-the-wash colour protecting agents, and, finally, extenders, such as, e.g., sodium sulfate.

Furthermore, the formulates according to the present invention also contain at least one poly-amino acid, which can also be in partially solidified form, at a concentration comprised within the range of from 0.5 to 5% by weight and, possibly, a conventional co-builder selected from the copolymers of maleic anhydride and/or acrylic acid with such natural substances as starch or dextrins or glucose, copolymers of maleic anhydride and compounds bearing allyl or vinyl moieties, maleic anhydride/ ethylene oxide copolymers, glyoxylic acid/formaldehyde copolymer, and still other polyelectrolytes.

The molecular weight of useable polyaminoacids can be comprised within the range of from 1,000 to 300,000, preferably of from 10,000 to 100,000, with a salification degree preferably comprised within the range of from 70 to 85%.

In the formulations according to the present invention, all those aminoacids can be used which are disclosed in above cited European Patent Application Public. No. 454 126, including polyaspartic acid and its salts.

An exemplifying, however non-limitative, composition for the detergent formulations according to the present invention, can be as follows:

* Surfactants	5-40% by weight
* 4A Zeolite	5-50% by weight
* Polymer	0.5-5% by weight
* Sodium perborate tetrahydrate	0-30% by weight
* Tetraacetyl ethylene diamine	0-5% by weight
* Sodium disilicate	0-10% by weight
* Sodium carbonate	5-25% by weight
* CMC	0-2% by weight
* Enzymes	0-1%
* Perfume, antifoamers, etc.	0-2%
* Sodium sulfate + H_2O	q.s. to 100%

The following example is supplied in order to further illustrate the invention. The effectiveness of the present products is also evidenced.

Example

Wash tests were carried out by using formulations which contained either sodium salts of polyaminoacids as co-builders, or, as reference, 85%-salified 1:2 maleic-acrylic copolymers with an average molecular weight of 75,000, as well as mixtures thereof.

The test conditions were as follows:

* Tested fabrics	EMPA 103 (combined strips) White WfK cloth
* Wash temperature	90 °C
* Water hardness	40 °fH
* Washing liquor pH	10.5
* Detergent concentration	10 g/l

The composition (values as % by weight) of the detergent used was the following:

* C_{11}-C_{13} alkylbenzene sulfonate	7.0
* C_{12}-C_{22} soap	2.0
* Lialet-145.7 EO (oxo C_{14-15} alcohol + 7.0 mol of EO)	5.0
* Polymer	0 - 4
* 4A Zeolite	27.0
* Sodium perborate tetrahydrate	20.0
* Tetraacetyl ethylenediamine	4.0
* Sodium disilicate	3.0
* Sodium carbonate	10.0
* Enzyme	0.4
* Sodium sulfate + H_2O	q.s. to 100

No carboxymethylcellulose (CMC) was added in order to better evidence the performance of the polymers; furthermore, optical brighteners were also excluded.

The tests were carried out without polymer; in the presence of acrylic/maleic copolymer; in the presence of two different samples of polyaspartic acid; and in the presence of a blend of acrylic/maleic

copolymers and polyaspartic acid.

The results are summarized in following Tables 1 and 2.

Table 1

(Detergent capabilities)					
	1	2	3	4	5
Oily soil	23.7	25.1	26.6	26.1	26.3
Proteinic soil	55.2	57.2	57.7	55.5	56.8
Oxidizable soil	48.2	53.5	52.1	52.4	52.8
Average value	42.4	45.3	45.5	44.7	45.3

Remarks

1 = No polymers

2 = Sodium salt (85%) of acrylic-maleic copolymer (molecular weight [mw] = 75,000) (4%)

3 = Sodium salt (80%) of polyaspartic acid (mw = 12,000) (4%)

4 = Sodium salt (80%) of polyaspartic acid (mw = 70,000) (4%)

5 = Sodium salt of acrylic-maleic copolymer (2%) + sodium salt of polyaspartic acid (mw = 70,000) (2%).

From the data reported in Table 1, one may infer that polyaspartate supplies detergency performances which are at least comparable to those offered by the commercial copolymers.

In Table 2, the data are reported which relate to the values of residual incrustations on cotton after different numbers of wash cycles, which were obtained with the above cited formulates.

Table 2

(Ash content)					
	1	2	3	4	5
5 cycles	0.5	0.5	0.5	0.4	0.5
10 cycles	1.1	0.6	1.0	0.7	0.7
15 cycles	1.4	0.7	1.1	0.8	0.8

The data reported in Table 2 confirm that polyaspartic acid displays primary and secondary detergency performances which are perfectly acceptable and anyway are equivalent to those as offered by the commercially available copolymers.

Claims

1. Powder and liquid compositions suitable for textile material washing, comprising from 5 to 40% by weight of one or more surfactant(s), from 5 to 50% by weight of Zeolite A, from 0.5 to 70% by weight of one or more additive(s) selected from bleaches, bleach activators, builders, enzymes, stabilizers, antifoaming agents, perfumes and from 0.5 to 5% by weight of at least one polyaminoacid, either as such or partially salified, and possibly from 0.2% to 2.5% of a conventional co-builder selected from the copolymers of maleic anhydride and/or acrylic acid with such natural substances as starch of dextrins or glucose, maleic anhydride/acrylic acid copolymers, maleic anhydride copolymers with compounds bearing allyl or vinyl groups, maleic anhydride/ethylene oxide copolymers, glyoxylic acid/formaldehyde copolymer.

2. Detergent compositions according to the preceding claim, in which said polyaminoacid is polyaspartic acid.

3. Detergent compositions according to claim 1, in which said polyaminoacid is present in salt form, which a salification degree ranging from 0 to 100%.

4. Detergent compositions according to the preceding claim, in which said polyaminoacid is present as sodium, potassium or ammonium salt.

5. Detergent compositions according to claims 2 and 3, in which said polyaminoacid is present at concentrations of 4%.