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

(11) Publication number: **0 154 380**
**A2**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **85200301.1**

(22) Date of filing: **01.03.85**

(51) Int. Cl.⁴: **C 11 D 1/06**
C 11 D 3/12, C 11 D 3/06

(30) Priority: **05.03.84 NL 8400706**

(43) Date of publication of application:
**11.09.85 Bulletin 85/37**

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

(71) Applicant: **Chemische Fabrik, Chem-Y, GmbH**
**Kupferstrasse 1**
**D-4240 Emmerich 1(DE)**

(72) Inventor: **Van Paassen, Nicolaas Adrianus Ignatius**
**Elzenhof 11**
**Bodegraven(NL)**

(74) Representative: **Elzas, Salomon, Drs. et al,**
**Octrooibureau Polak & Charlouis Laan Copes van Cattenburch 80**
**NL-2585 GD The Hague(NL)**

(54) **Laundering agent.**

(57) A laundering agent is provided which contains active detergent, builders, a combination of polyphosphate with zeolite as sequestering agent and, if desired, further usual additives, wherein the sequestering effect of the polyphosphate-zeolite combination is enhanced by an ethercarboxylic acid of the formula $RO-(C_2H_4O)_x-CH_2COOM$ or $R-CO-NH-(C_2H_4O)_x-CH_2COOM$, wherein R is the residue of an aliphatic or alkyl aromatic hydrocarbon having at least 8 carbon atoms, x is a number having an average value of 0.5-20 and M is hydrogen or a cation permissible in laundering agents, said polyether carboxylic acid being present in an amount of 0.3-10%, preferably 0.3-5%, based on the entire composition.

EP 0 154 380 A2

Laundering agent

0154380

This invention relates to a laundering agent, containing detergent, builders, a combination of polyphosphate with zeolite and, if desired, further usual additives.

Such laundering agents have been known already for a long time and have been commercialized on a large scale. The combinations of sequestering agents formed by phosphate and zeolite have been developed in the last decade in order to alleviate the environmental pollution by phosphate. With this kind of combinations the amount of polyphosphate can be reduced to about 50%. An example of a patent publication on this matter is Dutch published application 159712. In an article in Tenside Detergents 20 (1983), number 6, pages 276-282 various systems of polyphosphate, zeolite, citrate, NTA, polyhydroxy carboxylic acids and phosphonates, both separately and in binary and ternary systems, are disclosed.

As usual additives for general purpose laundering agents can be mentioned in the first place bleaching agents, particularly perborate. Besides this often also optical brighteners are added and furthermore for example enzymes, carboxy methyl cellulose, EDTA etc.

Furthermore should be mentioned the possibility to compose a completely phosphate-free laundering agent, as for instance disclosed in Dutch patent application 7307916. Herein a buffer system is used of the perborate with certain acidic-reacting substances, among which in actual practice sodium bisulfate and citric acid are of interest in the first place sothat the 0.5% aqueous solution of the laundering agent possesses an initial pH of 5.0-8.5, preferably about 6.5-8.0, measured at room temperature. In view of the relatively low pH it appears necessary in actual practice to use an activator for the sodium perborate, because otherwise the bleaching action is insufficient. Although such a laundering agent possesses excellent properties, viz. a low incrustation of the laundry (precipitation of alkaline earth metal compounds which make the laundry hard), for which for the rest reference can be made to the text of said patent application, these laundering agents up till now have not been used on a large scale. The most important marketed products in this field are now the laundering agents, wherein the polyphosphate has been replaced for about 50% with zeolite.

In the compositions of Dutch patent application 7307916 compounds of the formula $RO-(C_2H_4O)_x-CH_2COOM$, wherein R is a hydrophobic hydrocarbon residue and x has a value of about 0.5-10, and M is a suitable monovalent cation, can be used as detergents. The same applies to US-A-3,819,538

which discloses phosphate-free laundering agents which do not contain any bleaching agent and consequently are not general purpose laundering agents.

A problem occuring with the laundering agents having a combination of phosphate with zeolite is the incrustation which is considerably higher than with phosphate only. This incrustation shows from the ash content after a number of test launderings. Also the above article from Tenside Detergents relates to this problem and it appears therefrom that for instance a combination of 30% zeolite A with 5% NTA gives a low ash content, but on the other hand does not possess a very good primary laundering power. Without further additives mixtures of polyphosphate and zeolite A lead to a higher ash content than laundering agents containing polyphosphate only. A combination which is particularly good as regards ash content is 20% polyphosphate plus 10% NTA, a system, of which also the primary laundering activity appears to be reasonably good. However, the NTA is a relatively expensive component which moreover should not be used in unlimited quantities. As appears from the above mentioned article from Tenside Detergents, relatively large amounts of NTA would be necessary to arrive at a good result. Also a ternary system of phosphate, zeolite and NTA is not ideal and complicates the system.

It has now been found that the use of a small amount of ether carboxylic acid lowers on the one hand the higher incrustation caused by the combination of phosphate and zeolite, and on the other hand in the ternary combinations of phosphate, zeolite and NTA makes it possible to considerably reduce the amount of NTA.

Consequently, this invention provides a laundering agent, containing active detergent, builders, a combination of polyphosphate with zeolite and, if desired, further usual additives, which is characterized by the fact that it also contains at least 0.3% and no more than 10% of a compound of the formula $RO-(C_2H_4O)_x-CH_2COOM$ or $R-CO-NH-(C_2H_4O)_x-CH_2COOM$, wherein R is an aliphatic or alkyl aromatic hydrocarbon residue containing at least 8 carbon atoms, x is a number having an average value of 0.5-20, and M is hydrogen or a cation acceptable in laundering agents.

The abovementioned lower limit of 0.3% is based on a replacement of the usual amount of polyphosphate (30 to 40%) with about the half amounts of polyphosphate plus zeolite (and if desired NTA). In the case of an amount of less than 0.3% of the present ether carboxylic acids the effect is then too small. The upper limit given is only a economical one. The polyether carboxylic acid itself is a detergent and in principle could also constitute entirely or partially the detergent component. However, at

present, this is not (yet) economically feasible for mass production, for the polyether carboxylic acids are considerably more expensive than for instance the so-called ABS-products (alkylbenzene sulphonates). This is the reason why an amount of more than 10% ethercarboxylic acid economically is senseless and usually and preferably no more than 5% thereof is used and even more preferably even less.

The present laundering agent is of the usual, strongly basic kind. As active detergents it may contain all usual anionic, non-ionic and zwitterionic surfactants. Usually a number of surfactants is used in combination. The total content of active detergents usually is 7-16% of a laundering powder. The combination of polyphosphate and zeolite usually constitutes 25-45% by weight of the laundering agent. Usually sodium perborate as a bleaching agent is also used in an amount of generally 15-25%. In stead of perborate of course any other bleaching agent can be used, such a trichloro cyanuric acid. Besides this often an optical brightener is used, usually in a small amount of no more than 0.5%. A further usual ingredient is carboxymethyl cellulose which is usually used in an amount of 0.5-5%. Furthermore, an enzyme, particularly a proteolytic enzyme, may be present in amounts upto 3%. Finally then alkaline builder is present, usually sodium carbonate and sodium silicate and the like. The remainder of the laundering agent can be constituted by so-called neutral builders, i.e. sodium and magnesium sulphates.Furthermore, additional EDTA as a complexing agent can be present in a small amount (upto 1%). In such a laundering agent the present ethercarboxylate is now incorporated in an amount in the abovementioned range.

The present ethercarboxylic acids, in as far as they are derived from alcohols,are commercially available many years already and they have been described in numerous publications, which also applies to their preparation. For the sake of completeness it is only mentioned here that the ethoxylation may be carried out both with a basic catalyst (NaOH), and with an acidic catalyst (e.g $SbCl_5$). In the first case ethoxylation products are formed according to a broad distribution and in the last case a much narrower distribution of ethoxylation products is formed. The ethercarboxylic acids derived therefrom of course show the same distribution pattern. For the present purpose both kinds are useful.

The ethercarboxylic acids derived from carboxylic acid amides as such also constitute a known group. For a discussion of these compounds and their preparation reference is made to Dutch patent application 8203257.

The following experiments show the effect of the invention. Herein the

sodium tripolyphosphate has been abbreviated as NaTPP.

A laundering powder intended for laundering at 90°C was composed as follows:

| | % |
|---|---|
| Linear dodecyl benzene sulphonate | 5 |
| Adduct of oleo-cetyl alcohol ($C_{16}$-$C_{18}$) and 11 moles of ethylene oxide | 3 |
| Soap | 5 |
| NaTPP or NaTPP:zeolite (1:1) | 35 |
| Sodium carbonate | 15 |
| Sodium silicate | 6 |
| Carboxymethyl cellulose | 1-2 |
| Sodium perborate | 20 |
| Magnesium sulphate | 3 |
| Sodium sulphate | 4 |
| EDTA | 0,2 |
| Optical brightener | 0,2 |
| Proteolytic enzyme | 0,8 |

In one experiment only NaTPP was used as sequestering agent, in one experiment the combination NaTPP:zeolite in the ratio 1:1 and in the remaining tests this same combination was used, but then always with addition of an agent for decreasing incrustation. In this comparative test a number of Sokalan products of BASF (complexing polycarboxylic acids) was compared with the most usual ethercarboxylic acid (commercial product (Akypo RLM-45 of Chem-Y) having the formula $RO-(C_2H_4O)_{4.5}-CH_2COONa$, wherein R is a mixture of lauryl and myristyl (derived from a commercial mixture of about 70% lauryl alcohol and 30% myristyl alcohol). The used zeolite was of the "A" type.

With each laundering powder 25 launderings were carried out in a tergotometer with the usual test swatches. The water used had a German hardness of 18°. After 25 launderings the following ash contents were measured:

| Sequestering agent | Ash, % |
|---|---|
| NaTPP | 0.9 |
| NaTPP:zeolite (1:1) | 2.7 |
| NaTPP:zeolite (1:1) + 1% Sokalan CP-2 | 2.3 |
| NaTPP:zeolite (1:1) + 1% Sokalan CP-4 | 2.2 |
| NaTPP:zeolite (1:1) + 1% Sokalan CP-5 | 1.8 |

| Sequestering agent | Ash, % |
|---|---|
| NaTPP:zeolite (1:1) + 1% Sokalan PAS | 2.1 |
| NaTPP:zeolite (1:1) + 0.5% Akypo RLM-45 | 1.3 |
| NaTPP:zeolite (1:1) + 1.0% Zkypo RLM-45 | 0.7 |

It will be clear that the polyether carboxylic acid can also be incorporated as the free acid in the alkaline laundering agent, whereby the salt is formed in situ without the relatively small added amount influencing the pH to an important degree. Also the polyether carboxylic acid may be used in the form of a crude reaction mixture, as is obtained during its preparation after treatment with a small amount of water and acid, as disclosed in Dutch patent application 8103860. The optimum nature of the ethercarboxylic acid (or salt thereof) somewhat depends on the other ingredients of the laundering agent, particularly the active detergent, and in this respect the known variations in the hydrphobic residue and the average number of oxyethylene units are possible. The product used in the above experiment will be satisfactory in a great number of cases or will even constitute the optimum product.

In accordance with the abovementioned possibility of varying the ethercarboxylic acid some further compounds were tested, using the same base recipe for the laundering powder.

These tests were carried out at an other place than the above described tests, but with water of the same hardness. The tests were carried out analogous to test method RAL 992, but with 25 launderings in stead of 50. The test tissues and the evaluation were in accordance with DIN 53919. The following experiments were carried out:

| Test | Sequestering agent |
|---|---|
| 1 | NaTPP |
| 2 | NaTPP:zeolite (1:1) |
| 3 | NaTPP:zeolite (1:1) + 1% $C_{11}H_{23}$-CO-NH-$(C_2H_4O)_x$-$CH_2COONa$ x averages 3 |
| 4 | NaTPP:zeolite (1:1) + 1% octyl-$(C_2H_4O)_x$-$CH_2COONa$ x averages 1 |
| 5 | NaTPP:zeolite (1:1) + 1.0% RO-$(C_2H_4O)_x$-$CH_2COONa$, wherein RO is derived from tallow alcohols and x averages 6 |

After 25 launderings the results were as follows:

| Test | % Ash | Reflectance on Cotton | Terry | Polyester/cotton |
|---|---|---|---|---|
| 1 | 0,8 | 84,9 | 73,2 | 74,2 |
| 2 | 2,2 | 85,0 | 72,1 | 74,2 |
| 3 | 2,8 | 85,4 | 74,1 | 75,4 |
| 4 | 1,7 | 84,6 | 72,0 | 74,7 |
| 5 | 1,6 | 84,9 | 72,2 | 74,4 |

| Test | Tear strength according to DIN 53919 | Redeposition factor, RP[1)] |
|---|---|---|
| 1 | 54,1 | 2,0 |
| 2 | 51,3 | 1,5 |
| 3 | 51,9 | 1,0 |
| 4 | 53,4 | 0,4 |
| 5 | 53,8 | 0,5 |

[1)] According to DIN 44983, part 21

All the above experiments have some correlation with the incrustration and from the entire picture of these data it appears that all the ether-carboxylic acids tested in this experiment show the desired effect.

C L A I M S:

1) Laundering agent containing active detergent, builders, a combination of polyphosphate with zeolite and, if desired, further usual additives, characterized in that it also contains 0.3-10% of an ethercarboxylic acid of the formula $RO-(C_2H_4O)_x-CH_2COOM$ or $R-CO-NH-(C_2H_4O)_x-CH_2COOM$, wherein R is the residue of an aliphatic of alkyl aromatic hydrocarbon having at least 8 carbon atoms, x is a number having an average value of 0.5-20 and M is hydrogen or a cation permissible in laundering agents.

2) Laundering agent according to claim 1, characterized in that it contains 0.3-5% of an ethercarboxylic acid as defined in claim 1.

3) Laundering agent according to claim 1 or 2, characterized in that the ethercarboxylic acid is a compound of the formula $RO-(C_2H_4O)_{4.5}CH_2COONa$, wherein R is the residue of a mixture of lauryl and myristyl alcohols.

## CLAIMS FOR AUSTRIA:

1) A process for preparing a laundering agent containing active dertergent, builders, a combination of polyphosphate with zeolite and, if desired, further usual additives, characterized in that also 0.3-10% of an ether-carboxylic acid of the formula $RO-(C_2H_4O)_x-CH_2COOM$ or $R-CO-NH-(C_2H_4O)_x-CH_2-COOM$ is incorporated in the laundering agent, wherein in the above formulae R is the residue of an aliphatic or alkyl aromatic hydrocarbon having at least 8 carbon atoms, x is a number having an average value of 0.5-20 and M is hydrogen or a cation permissible in laundering agents.

2) A process according to claim 1, characterized in that 0.3-5% of an ethercarboxylic acid as defined in claim 1 is incorporated in the laundering agents.

3) A process according to claim 1 or 2, characterized in that as ether-carboxylic acid a compound is used of the formula $RO-(C_2H_4O)_{4.5}CH_2COONa$, wherein R is the residue of a mixture of lauryl and myristyl alcohols.