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European Patent Office  
Office européen des brevets



(11) Publication number:

**0 425 149 A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **90311210.0**

(51) Int. Cl.<sup>5</sup>: **C11D 3/12, C11D 3/37,  
C11D 3/20**

(22) Date of filing: **12.10.90**

(30) Priority: **23.10.89 GB 8923819**  
**19.12.89 GB 8928662**

(43) Date of publication of application:  
**02.05.91 Bulletin 91/18**

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

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(54) **Detergent compositions and processes of making them.**

(57) Zeolite detergent builders which are substantially free from water and which comprise a polyether or polyalcohol enable improved non aqueous detergent compositions to be made. They may be produced by contacting a corresponding zeolite which contains water with the polyether or polyalcohol and evaporating the water.

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## DETERGENT COMPOSITIONS AND PROCESSES OF MAKING THEM

THIS INVENTION relates to detergent compositions and processes of making them.

Detergent compositions which contain builders suspended in a non-aqueous medium are known. Typically, the builder is a condensed phosphate. There is however an increasing demand for low and even for non-phosphate containing detergent compositions on environmental grounds and zeolite builders have  
5 been used in some detergent compositions as substitutes.

However, it is difficult to produce acceptable detergent compositions which comprise a zeolite builder suspended in a non aqueous medium. Commercial zeolite builders in powder form usually contain at least 20% by weight of water and if they are dried by heating high temperatures of as much as 800 °C may be needed which degrade the zeolite which is then less effective as a builder. Furthermore the zeolite may  
10 readsorb water when it is cooled. Compositions containing water are undesirable for packing in water soluble containers, for example individual sachets comprising detergent enclosed in water soluble films. We have also found that if a bleach is present in such a composition, the water content of the zeolite is detrimental to the stability of the bleach.

This invention comprises a zeolite builder, for example zeolite A, which is substantially free from water  
15 and comprises a polyether or polyalcohol, the zeolite preferably being zeolite A.

The invention also comprises a process of producing a detergent builder in which water is removed from a zeolite detergent builder containing water by evaporating water from it (suitably by heating it) in the presence of the polyether or polyalcohol.

According to this invention a process of producing a substantially non-aqueous detergent composition  
20 which comprises a zeolite builder suspended in an organic phase which comprises the step of evaporating water from the zeolite in the presence of a polyether or polyalcohol.

The polyalcohol may comprise 2, 3 or 4 -OH groups and preferably has only two -OH groups. It may be an alkane diol having two to four carbon atoms, for example, propane 1,2 or 1,3 diol or preferably ethylene glycol, and is suitably a polyglycol.

The polyether may be alkoxylate of an alcohol suitably having 3 to 20 carbon atoms or of an alkyl phenol for example having 4 to 12 carbon atoms in its alkyl group or groups, but is preferably a polyalkylene glycol in which preferably substantially all of the alkylene groups have two or three carbon atoms and is more preferably a polyethylene glycol. The alkoxylates are suitably ethoxylates and/or propoxylates. The average molecular weight of the polyether or polyalcohol is suitably at most 2000 and  
30 preferably at most 500.

The removal of water is suitably carried out under vacuum, the pressure preferably being at most 0.1 bar absolute and more preferably at most 0.05 bars absolute. The temperatures of 100 to 200 °C are suitably employed.

Without wishing to be bound by this explanation, we believe that the polyether or polyalcohol serves to  
35 displace water from the zeolite.

It is preferred that the aforesaid step of removal of water should take place before the addition of any bleach which is likely to be affected adversely by the temperature and the evolution of water. Any other components of the composition which require to be dried may be present during the said step of evaporating water as they are in general sufficiently stable, especially if the water is removed under  
40 vacuum, for example of at most 0.1 bars absolute. As an alternative, they may be mixed with a polyether component of the composition in the absence of zeolite and the water evaporated preferably at a pressure of at most 0.1 bars absolute before being mixed with zeolite which has been treated in the said water evaporation step or being subsequently treated in such a step after the addition of zeolite. It is also preferred that the polyether or polyalcohol used should be a component of the final detergent composition  
45 or should not be detrimental to it so that it is not necessary to separate it from the zeolite. Further quantities of polyether or other polyethers which may be surfactants may be added after the water removal step of desired.

Although the suspension of the zeolite in the polyglycol or polyalcohol may have a tendency to gel before the water is removed, because the mixture is heated this effect has not been found troublesome at  
50 the temperatures at which water is removed. Nonetheless, it is preferred that a polyglycol which has a low tendency to form gels, for example polyethylene glycol may suitably be used during water removal if it is to be present in the final composition. Ethylene glycol is also very suitable as a polyalcohol as it is very effective in the removal of water and the zeolite containing it is very effective when exposed to water. The presence of the small quantities of ethylene glycol involved in a wash appears to be acceptable.

After water removal further components of the composition may be added and the composition may be

milled at any desired stage to reduce the particle sizes of solid components, for example bleaches in order to minimise sedimentation of solid materials.

Suitably the liquid detergent composition comprises 25 to 60% by weight of the composition of solids suspended in a non-aqueous liquid phase, the solids comprising the zeolite which preferably constitutes at least 15% and may constitute 25% to 60% by weight of the compositions, optionally a bleach which may be 1 to 20% and more preferably 2 to 15% by weight of the composition and optionally a filler; in which the liquid phase suitably comprises at least 20% by weight and preferably 25 to 90% and more preferably 50 to 85% by weight of the polyether which suitably comprises a condensation product of ethylene oxide with a mono-di- or tri- hydroxy alkane having 1 to 4 carbon atoms which is preferably polyethylene glycol and which has an average molecular weight in the range 150 to 600 and preferably 200 to 300 and/or preferably at least to 15% for example 15 to 50% by weight of one or more surfactants.

It is preferred that the solids suspended in the composition should have average particle diameters of less than 10 microns and preferably less than 5 microns. This may be assessed by considering each particle as a sphere of the same volume and dividing the total diameters of the spheres by the number of particles. In order to provide an effective dispersion of the solids in the liquid phase it is desirable that at least 80% of the particles of the solid have particle sizes less than 10 microns in diameter.

It is preferred that the pour point should be below 10° C and it is more preferably below 5° C. The pour point may be measured by ASTM Test method designation D97-66 re-approved in 1971.

Any builder which is known for use in detergent compositions may be used in compositions according to the present invention in addition to the zeolite. Generally such builders are inorganic in nature but some organic products in particular sodium carboxymethylcellulose polyacrylates and/or copolymers of acrylic, methacrylic and/or maleic acids may be used. Suitable inorganic builders include condensed phosphate builders eg trisodium phosphate, tetrasodium pyrophosphate, sodium hexametaphosphate and, preferably, sodium tripolyphosphate, carbonates eg sodium carbonate, sodium bicarbonate and sodium sesquicarbonate, clays eg kaolin, montmorillonites and sodium bentonite, and miscellaneous salts eg sodium metasilicate and sodium citrate and sodium nitrilotriacetate. The potassium analogues of the sodium compounds may also be used.

The surfactant component is preferably a non ionic surfactant for example an alkylene oxide derivative for example of an amide, alkyl phenol or an alcohol. The alkyl group in the alkyl phenol may be straight chain or branched chain and may contain from 6 to 20 carbon atoms, eg para-nonyl phenol or para-dodecylphenol. The alcohol may contain 6 to 20 carbon atoms, particularly 10 to 16 carbon atoms. The alcohol is preferably a primary or secondary alcohol having a linear or mono branched alkyl group.

In general alkylene oxide of an alkyl phenol or alcohol derivative may comprise 2 to 20 alkylene oxide units which are preferably ethylene oxide units although a lesser number of propylene oxide or a smaller number still of butylene oxide units may also be present. The amide is suitably a mono- or di-alkanol amide eg a mono- or di- ethanolamide preferably of a C<sub>6</sub> to C<sub>30</sub> more preferably C<sub>10</sub> to C<sub>20</sub> alkanolic acid, eg coconut acids, tallow acids or stearic acid or an ethoxylated derivative thereof.

A further surfactant of the anionic or cationic type may be included if desired. Such anionic or cationic surfactants may be of known type for example the anionic detergents may be soaps, alkylbenzene or olefine sulphonates, alcohol sulphates or alcohol alkoxylate sulphates; the cationic surfactants are suitably di- C<sub>10</sub>-22 and preferably di-C<sub>16</sub>-18 alkyl, di-lower alkyl ammonium salts or hydroxides for example chlorides or sulphates or for example fabric softeners for example the C<sub>10</sub>-16 alkyl, di lower alkyl (for example methyl), substituted ethyl ammonium salts. The substituent on the ethyl group may be an -OOCR group where R is a C<sub>13</sub>-22 alkyl group, and the anion of the salt may be a RSO<sub>4</sub><sup>-</sup> group where R is lower alkyl for example methyl. The lower alkyl groups are suitably methyl groups.

Suitable bleaches which may be present are alkali metal, for example sodium or potassium, perborates or percarbonates. These may be used with suitable bleach promoters for example tetra acetyl ethylene diamine salts for example Na or K salts.

In compositions according to the invention the dispersion of the solids in the non-ionic surfactant is remarkably stable especially if the average particle size of the solids is as aforesaid. If the solids separate at all then the resulting phase is usually loosely flocculated and is readily redispersible while if the relative amounts of the solids, polyethylene glycol and non-ionic surfactant in the composition are correctly chosen there is little phase separation as the liquid fills the space between the loosely packed solid particles. The composition may also contain additives conventionally found in detergent compositions eg optical brighteners, ethylene diamine tetra acetic acid, dyes, perfumes or enzymes. If an inert filler is included it may suitably be sodium or potassium sulphate. Compositions according to the invention may suitably be made by a process which comprises milling ingredients together. If desired separately milled dispersions of solids, for example bleaches in components of the composition, for example polyethylene glycol, may be

prepared and added to a zeolite suspension of the invention.

The total H<sub>2</sub>O content of the detergent compositions produced by this invention is suitably less and preferably substantially less than the quantity of water which can be absorbed into the zeolite any present as water of crystallisation in solids being ignored. The zeolite is then believed to dehydrate the organic  
5 phase or to maintain the organic phase in a substantially anhydrous state.

#### Example 1

10 213.72g of a commercial zeolite sold under the trade name WESSOLITH P made by Degussa AG was added gradually to 222.4g of polyethylene glycol of average molecular weight 200 (PEG 200) whilst using a high shear mixer to produce a dispersion of the zeolite in the PEG 200. 425.51g of the dispersion was dehydrated as follows.

The temperature was raised from 20° C to 140° C over a period of 15 minutes under a vacuum of 35 to  
15 58 mm Hg whilst bubbling nitrogen through the dispersion. It was then held for a further 45 mins at that temperature during which time the pressure fell from 58 mm Hg to 48 mm Hg. Liquid evolved was condensed using a water condenser and an ice trap, some of the liquid being lost as vapour to the vacuum pump. 35.97g of weight was lost by the dispersion and 25.17g of liquid was collected, of which 97% was water. It is estimated that at least 10.5 g of water was lost to the vacuum pump.

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#### Example 2

The above procedure was repeated using polyethylene glycol of average molecular weight 600 (PEG  
25 600). 422.86 g of the dispersion was dehydrated.

28.92g weight was lost and 17.2g of liquid was collected of which 99% was water. An estimated 11.5g minimum of water was lost to the vacuum pump.

#### Example 3

The above procedure was repeated using polyethylene glycol of average molecular weight 1000 (PEG  
30 1000). 412.55g of the dispersion was dehydrated. 27.3 g weight was lost from the dispersion. 16.93g of liquid (97.8 water) was collected. Over 10g of water was estimated to have been lost to the vacuum pump.

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#### Example 4

Example 1 was repeated except that a commercially available surfactant sold under the trade name  
40 "Synperonic" A3 which is a condensation product of average 3 moles of ethylene oxide to one mole of a primary alcohol (67% C<sub>13</sub> and 33% C<sub>15</sub>) was used instead of PEG 200.

420.87g of the dispersion was dehydrated. 33.95g of weight was lost and 19.88 g of liquid was collected of composition 89.3% water, an estimated 12.5g of water being lost to the vacuum pump.

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#### Example 5

Example 4 was repeated except that a commercially available surfactant solid under the trade name  
50 "Synperonic" A7 which is a condensation product of average 7 moles of ethylene oxide with the above said mentioned in Example 4 alcohol was used.

425.32g of the dispersion was dehydrated, 32.52g of weight was lost and 19.68 g of liquid (95.3% water) was collected. An estimated 12g of water was lost to the vacuum pump.

#### Example 6

Two detergent compositions were prepared of the same composition except that in composition A the dried dispersion of Example 1 was used in its preparation and in composition B a dispersion without drying

was used.

The compositions were prepared as follows. The dispersion, "Synperonic" A7 and "Synperonic" A3 surfactants and the polyacrylate were mixed using a high shear mixer and the remaining components except the perborate and the enzyme were then added and mixed using the high shear mixer. The perborate and enzyme were then mixed in by hand. The compositions contained the following components, differing only in that in composition A the zeolite was dried and in composition B it was undried; on a dry basis more zeolite is present in composition A therefore.

|   |      |
|---|------|
| Zeolite ("WESSALITH" P)                           | 32%  |
| Sodium carboxymethyl cellulose                    | 2%   |
| Sodium salt of ethylene diamine tetra acetic acid | 1%   |
| Sodium disilicate (spray dried)                   | 2%   |
| "Synperonic" A7                                   | 7.5% |
| "Synperonic" A3                                   | 2.5% |
| Polyethylene glycol (molecular weight 200)        | 40%  |
| Optical brightener                                | 0.2% |
| Polyacrylic acid (25%) in water                   | 2.5% |
| Sodium Perborate monohydrate                      | 7%   |
| Tetra acetyl ethylenediamine                      | 3%   |
| Enzymes   | 0.3% |
| The above percentages are by weight.              |      |

In the case of composition B, after 1 hour storage at 38° C 85.9% of the initial activity of the perborate remained 66.7% after 27 hours remained, after six days 48.7% remained after 1 month 20.5% remained and after 3 months 7.7% remained. In the case of composition A after 1 hour 100% remained after 27 hours 92.3% remained, after 6 days 87.2% remained and after 3 months 51.2% remained. Thus, despite the introduction of some water with the polyacrylic acid the bleach stability was still acceptable.

Composition A (60g/litre) was used in a Miele 451 washing machine at 60° C over a 30 minute cycle using water of 36° French hardness, 20 litres of water in the wash with 2 kg of clean cotton ballast. A comparative test was carried out using 180 grams of a commercial laundry detergent composition.

The increase in brightness (as % reflectance using a "Photovolt" 670 reflectance metre using a 3 Green filter) was measured on the following standard commercially available test cloths.

|               | Composition A | Commercial Material |
|---------------|---------------|---------------------|
| "Krefeld" 10C | 57.4%         | 64.9                |
| "EMPA" 101    | 18.2%         | 22.2                |
| "Krefeld" 20C | 40.2%         | 36.4                |
| "EMPA" 104    | 18.2%         | 22.2                |
| "EMPA" 112    | 42.3%         | 38.8                |
| "EMPA" 111    | 72.2%         | 78.7                |
| "EMPA" 116    | 55.7%         | 53.2                |
| "EMPA" 114    | 49.2%         | 48.0                |
| "Krefeld" 10K | 59.8          | 61.0                |

Composition A thus performed comparably for many purposes to the commercial material used at three times the quantity by weight.

#### Example 7

A 25% by weight solution of polyacrylic acid in water sold under the trade name NEOCRYL HX-39 (155.34g) mixed with polyethylene glycol of average molecular weight 200 (116.5g) was distilled as follows.

The mixture was heated to 60 °C under nitrogen and the pressure reduced to 150 mm Hg for about 3 hours whilst bleeding nitrogen through it. Water was evolved and condensed, and the pressure eventually fell to 30 mm Hg over a further period of about 1 hour.

The distillate collected was 102.5g, 91.49% w/w water and the residue was 154.6 g, 3.06% w/w water.

5 The largely water free mixture left could be added to a suspension of zeolite dried in accordance with the invention as a component of a detergent composition.

#### Example 8

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A mixture of zeolite (288.57g), polyethylene glycol of average molecular weight 200 (281.73g) and a 25% solution of polyacrylic acid in water (36g) was warmed to 60-70 °C and then subjected to a vacuum 30 mm Hg with nitrogen bleed and the temperature slowly raised to 140 °C with stirring. Distillate was collected for about 1 hour and when no more distillate appeared, the mixture was cooled under nitrogen. 519.1g of residue was left and 42.4g of distillate was recovered. The residue contained a total of 0.6% by weight of water, and the distillate contained 89.3% water by weight.

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#### Example 9

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250g of monoethylene glycol was mixed with 305.5 g of a commercial zeolite detergent builder sold under the trade name "Wessolith" P by stirring at 60 °C. The mixture was then exposed to a vacuum (11.25 mm Hg) for 1 hour whilst continuing stirring. 16.2g of distillate was evolved and collected in a vapour trap.

The mixture was then heated from 44 °C to 74 °C over a period of about 2 hours at a vacuum declining from 9 mm Hg to 6.3 mm Hg. A further total of 22g of distillate was recovered. A further loss of weight of 26.3g was unaccounted for, but was considered to be represented largely by loss of uncondensed water vapour to the vacuum pump.

25 The product contained a total of 0.95% by weight of water, and the distillate contained 91.66% by weight of water. The product was a readily pourable dispersion of zeolite in ethylene glycol which separated into a layer of solids and a substantially clear upper layer.

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#### Example 10

35 A mixture of glycerol (2199 g) and "Wessolith" P zeolite (2036g) was stirred and distilled under vacuum similarly to the procedure of example 7. 368g of distillate was collected, comprising 94% by weight of water. The product weighed 3795g, 33g of material being unaccounted for, and believed to represent uncondensed water evacuated by the vacuum pump. The product was a thick liquid which was stirrable at 60 °C.

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#### Claims

1. A zeolite detergent builder which is substantially free from water and comprises a polyether or polyalcohol.
2. A detergent builder as claimed in claim 1 in which the zeolite is zeolite A.
3. A process of producing a detergent builder as claimed in claim 1 or 2 by evaporating water from a zeolite detergent builder containing water in the presence of the polyether or polyalcohol.
4. A process as claimed in claim 3 in which a polyalcohol is used which contains 2 hydroxyl groups.
5. A process as claimed in claim 3 or 4 in which the polyalcohol is an alkylene or polyalkylene glycol in which substantially all of the alkylene groups have two or three carbon atoms.
6. A process as claimed in claim 3, 4 or 5 in which the polyalcohol is ethylene glycol or polyethylene glycol.
7. A process as claimed any of claims 3 to 6 in which a polyether is present.
8. A substantially non-aqueous detergent composition which comprises a builder suspended in an organic phase in which the builder comprises a zeolite detergent builder as claimed in claim 1 or 2 or produced by a process as claimed in any of claims 3 to 7.
9. A composition as claimed in claim 8 which comprises a bleach.

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10. A process of producing a composition as claimed in claim 8 or 9 which comprises a step of reducing the particle sizes of solid components by milling at least one solid component in the presence of at least one liquid component of the composition.

5 11. A detergent composition as claimed in claim 8 or produced by a process as claimed in claim 9 or 10 in which the total H<sub>2</sub>O content is substantially less than the quantity of water which can be absorbed into the zeolite, any water of crystallisation of any solids present being ignored.

12. A process of washing fabrics by contacting them with water in which a composition as claimed in claim 8, 9 or 11 is introduced into the water.

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