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(54) Use of C1-oxidised starch hydrolysates

(57) The invention relates to the use of a chelating agent containing a starch hydrolysate that has been selectively oxidised at the C1 location as enzyme-stabilizing agent in a detergent composition. The invention further relates to an enzyme-containing detergent composition, containing a starch hydrolysate that has been selectively oxidised at the C1 location, and at most 1 wt.% of further chelating agents and/or further enzyme-stabilizing agents.

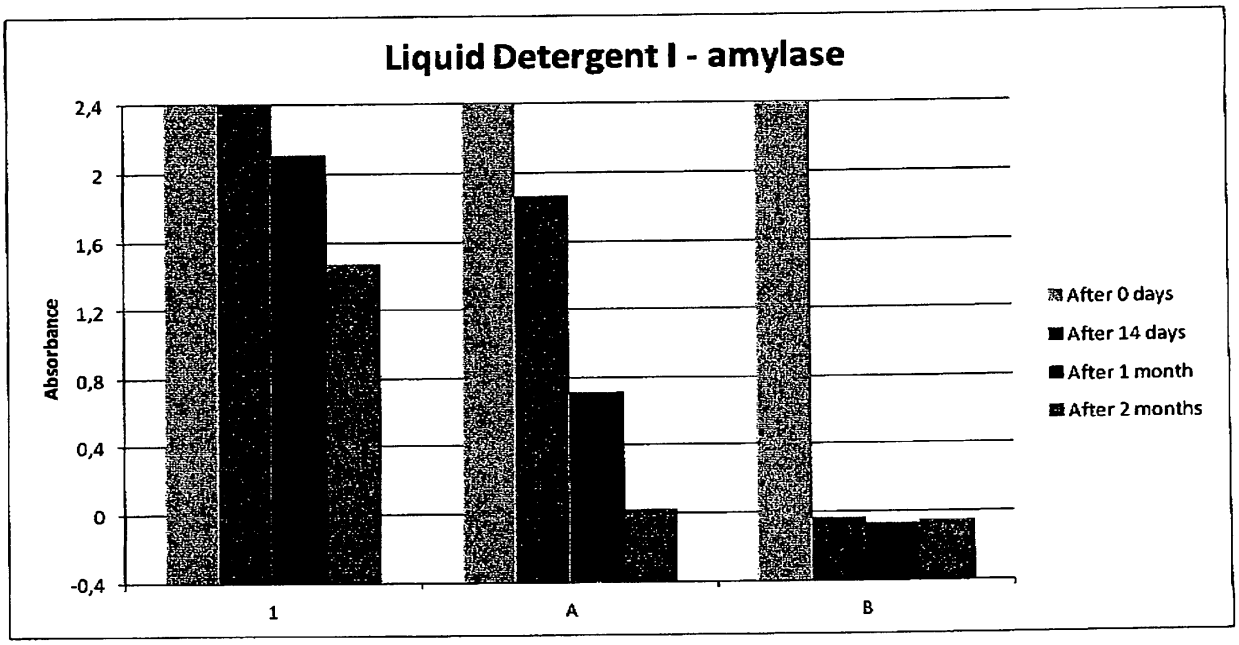


Fig. 1

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Description

[0001] The invention relates to a use of a chelating agent containing a starch hydrolysate that has been selectively oxidised at the C1 location in a detergent composition.

[0002] WO-A-2010/046070 discloses that starch hydrolysates that contain compounds with a degree of polymerisation (DP) of 2 to 4, whereby the said starch hydrolysates have been selectively oxidized at the C1 location of the carbohydrate moieties, can be used as chelating agents. A starch hydrolysate that has been selectively oxidized at the C1 location of the carbohydrate moieties is herein also referred to as a 'C1-oxidised starch hydrolysate'.

[0003] It is the objective of the invention to provide a further use of the C1-oxidised starch hydrolysate.

[0004] The said objective is achieved in that the C1-oxidised starch hydrolysate is used as enzyme stabilising agent in a detergent composition.

[0005] It is an advantage of the present invention that one component of a detergent composition can fulfil at least two functions at the same time in a detergent composition; namely, a function as chelating agent, i.e. a solubilising agent for sparingly soluble metal ions, and a function as stabiliser of enzymes. The present invention can thus advantageously allow a reduction of the amount of enzyme-stabilising agents other than C1-oxidised starch hydrolysates in a detergent composition.

[0006] The present invention relates to a further use of a chelating agent. As meant herein, the term chelating agent has its usual meaning of a compound that can form a soluble complex with certain metal ions, thereby preventing the metal ions to form precipitates or scale. When used in detergent compositions, chelating agents are normally used for the purpose of forming soluble complexes with calcium ions and/or transition metal ions.

[0007] The chelating agent of the present invention contains a starch hydrolysate that has been selectively oxidised at the C1 location. As meant herein, the term starch hydrolysate has the usual meaning of a starch that has been subjected to a hydrolysis treatment in order to reduce the degree of polymerisation (DP) of the carbohydrate moieties in the starch. Known examples of such treatments are acid hydrolysis and enzymatic hydrolysis. In a main embodiment of the invention, the hydrolysis treatment on the starch is done such that the resulting starch hydrolysate contains at least 5 wt.%, calculated on the total dry matter of the starch hydrolysate, of compounds having a DP of 2, 3, or 4. More preferably, the starch hydrolysate contains at least 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, or even at least 85 or 90 wt.%, calculated on the total dry matter of the starch hydrolysate, of compounds having a DP of 2, 3, or 4.

[0008] According to the invention, a starch hydrolysate is used that has been selectively oxidised at the C1 location of the carbohydrate moieties. Such a selective oxidation is as such known from for example WO-A-2004/099114. It is preferred that the selective oxidation is done such that at least 75, 80, 85, 90, or 95%, or even essentially all of the available target groups are oxidised.

[0009] In a preferred embodiment, the C1-oxidised starch hydrolysate contains at least 5 wt.% of maltobionic acid; more preferably, the C1-oxidised starch hydrolysate contains at least 10, 15, 20, 25, 30, or even at least 35 or 40 wt.%, calculated on the total dry matter of the C1-oxidised starch hydrolysate, of maltobionic acid. As used herein, the term maltobionic acid refers to the compound itself, as well as to salts thereof such as sodium maltobionate.

[0010] It is furthermore preferred that the chelating agent of the invention consists essentially of a starch hydrolysate that has been selectively oxidised at the C1 location.

[0011] As used herein, the terms 'essentially', 'consist(ing) essentially of, 'essentially all' and equivalents have, unless noted otherwise, in relation to a composition or a process step the usual meaning that deviations in the composition or process step may occur, but only to such an extent that the essential characteristics and effects of the composition or process step are not materially affected by such deviations.

[0012] The chelating agent of the present invention is used as a component in a detergent composition. In principle, according to the invention any type of detergent composition is suitable; it should however be a detergent composition that has, besides having one or more surfactants as components in order to generate the basic detergent functionality, at least one enzyme as a component. Typical examples of enzymes are proteases, amylases, lipases, cellulases, and mannases. Such detergent compositions are widely known, a.o. for the cleaning of textiles. The detergent composition may be in the form of for example a powder, a tablet, a gel capsule, or in liquid form; preferably, the detergent composition is in liquid form or in the form of a gel capsule.

[0013] According to the invention, the chelating agent containing or consisting essentially of a C1-oxidised starch hydrolysate is not only used in its chelating function, but also as enzyme-stabilising agent. It is known that the functionality of enzymes in detergents can reduce over time. It has therefore already in the past been an object of investigation to find ways to stabilise the enzymes. One popular method of stabilising enzymes involves the use of boron-containing compounds such as boric acid or disodiumtetraborate ('borax'). However, there is a desire in industry to avoid the use of boron-containing compounds. The use according to the present invention, therefore, achieves the objective of finding alternatives to boron-containing compounds. Advantageously, the objective is achieved by using a component which can at the same time exercise a chelating function. This combination is surprising because it is known that most of the currently used enzymes in detergent compositions require the presence of calcium ions in order to function and be

stable; thus, a chelating agent may not be of such a nature that too many calcium ions are bound by it under the conditions prevailing in a detergent composition - either as such or when in use. According to the invention, the use of the C1-oxidised starch hydrolysate strikes an advantageous balance between chelating properties and enzyme-stabilizing properties. As the person skilled in the art knows, it may be favourable in this respect to consciously add some amount of calcium in ionic form to the detergent composition.

[0014] The amount of the chelating agent containing the C1-oxidised starch hydrolysate in the detergent composition may vary within wide limits.

[0015] Preferably, the detergent composition contains at least 0.25 wt% of the chelating agent containing the C1-oxidised starch hydrolysate, as calculated on the total of the detergent composition, including any water present. In this way, the functionality of the C1-oxidised starch hydrolysate can take noticeable effect. More preferably, the detergent composition contains at least 0.50, 0.75, or 1.00 wt.% of the chelating agent containing the C1-oxidised starch hydrolysate. It is preferred that the detergent composition contains at most 6 wt.% of the chelating agent containing the C1-oxidised starch hydrolysate, more preferably at most 5.50, 5.00, 4.50, 4.00, or even at most 3.50 wt.% of the chelating agent containing C1-oxidised starch hydrolysate. In a related preferred embodiment, the weight ratio between the chelating agent containing the C1-oxidised starch hydrolysate and the sum of the enzymes in the detergent composition varies between 0.25:1 and 4:1, preferably between 0.50:1 and 2:1.

[0016] In the embodiments indicating the amount of chelating agent in the detergent composition, it is preferred that the chelating agent consists essentially of the C1-oxidised starch hydrolysate. It is furthermore preferred that the C1-oxidised starch hydrolysate contains compounds having DP of 2, 3, and 4 in amounts as indicated above; more preferably, that the C1-oxidised starch hydrolysate contains maltobionic acid in the amounts as indicated above. The maltobionic acid may be present as such, or in a corresponding ionic form such as for example sodium maltobionate.

[0017] The present invention furthermore relates to an enzyme-containing detergent composition, containing a starch hydrolysate that has been selectively oxidised at the C1 location, and at most 5 wt.% of further chelating agents and/or enzyme-stabilizing agents, calculated on the detergent composition as a whole. Due to the chelating action of the C1-oxidised starch hydrolysate, the need to use any further chelating agents can be reduced. Similarly, due to the enzyme-stabilising action of the C1-oxidised starch hydrolysate, the need to use any further enzyme-stabilising agents can be reduced. Preferably, the detergent composition contains at most 4.0, 3.0, 2.0, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or even at most 0.1 wt. % of further chelating agents and/or enzyme-stabilising agents. In one preferred embodiment, the detergent composition according to the invention contains essentially no further chelating agents or enzyme-stabilising agents. The amount and preferred embodiments of the C1-oxidised starch hydrolysate in the detergent composition according to the invention are as indicated above for the method of the present invention.

[0018] In a main preferred embodiment, the detergent composition according to the invention is in liquid form or in the form of gel capsules.

[0019] The invention will be illustrated by means of the following Example and Comparative Experiments, without being limited thereto.

[0020] In the Figures:

- Figure 1 shows the evaluation of amylase stability in a first liquid detergent;
- Figure 2 shows the evaluation of protease stability in a first liquid detergent;
- Figure 3 shows the evaluation of amylase stability in a second liquid detergent;
- Figure 2 shows the evaluation of protease stability in a second liquid detergent.

Examples and Comparative Experiments

[0021] The effect of a C1-oxidised starch hydrolysate on the stability of enzymes in a liquid detergent composition was evaluated. Two liquid detergent formulations were used, named liquid detergent I and liquid detergent II.

Liquid Detergent I

[0022] The composition of liquid detergent I, a typical formulation for a concentrated eco-style laundry liquid detergent, is given in Table 1.

Table 1

Ingredient	*Wt.%*
Demin water	19.30
Chelating agent	1.50

(continued)

Ingredient	*Wt.%*
Ethanol	3.33
Sodium n-Octyl Sulphate (Texapon 842)	2.85
Sodium Lauryl Sulphate (Standapol WAQ-LCK)	45.07
Lauryl/Myristyl Glucoside	17.12
Oleic acid (Emersol 622)	3.33
Potassium hydroxide	1.60
Sodium bicarbonate	1.90
Protease (Savinase 16L Ultra)	1.00
Amylase (Stainzyme 12L)	1.00

[0023] Liquid detergent I was prepared by first heating the water to 40°C; then, all ingredients except the protease and the amylase were added to the aqueous phase and mixed; this was done in the order of their appearance in Table 1. The so-prepared detergent was cooled down to room temperature, after which the enzymes were added. The pH was adjusted to 8.5 with citric acid/sodium hydroxide; this completed the preparation of liquid detergent I.

[0024] The type of chelating agent added can be found in Table 3 below.

Liquid Detergent II

[0025] The composition of liquid detergent II, a typical formulation for a regular heavy duty laundry liquid detergent, is given in Table 2.

Table 2

Phase	*Ingredient*	*Wt.%*
1	Demin water	45.44
1	Sodium hydroxide	3.23
1	Palm kernel fatty acid (Endenor K1218)	8.54
1	Propylene glycol	4.74
2	Sodium Laureth Sulphate 2EO (Texapon N 70)	13.57
2	Lauryl/Myristyl Glucoside (Glucopon 600 CSUP)	7.59
2	Fatty alcohol 7EO (Dehydol LT 7)	5.69
3	Chelating agent	1.50
3	Citric acid	2.85
3	Ethanol	2.85
4	Protease (Savinase 16L Ultra)	1.00
4	Amylase (Stainzyme 12L)	1.00

[0026] Liquid detergent II was prepared by first combining the Phase 1 ingredients, followed by heating to 70°C, mixing during 15 minutes, and cooling to 40°C. The Phase 2 ingredients were then added, followed by mixing. Subsequently, the Phase 3 ingredients were mixed in, followed by cooling down to room temperature and the adding of the Phase 4 ingredients (i.e. the enzymes). The pH was adjusted to 8.5 with citric acid/sodium hydroxide; this completed the preparation of liquid detergent II.

[0027] The type of chelating agent added can be found in Table 3 below.

Table 3

Chelating agent	*Liquid Detergent*	*Example*	*Comparative Experiment*
C1-oxidised starch hydrolysate	I	1	
MGDA	I		A
EDTA	I		B
C1-oxidised starch hydrolysate	II	2	
MGDA	II		C
EDTA	II		D

[0028] The C1-oxidised starch hydrolysate as used in Examples 1 and 2 was prepared from a starch hydrolysate having a high maltose content (75 wt.% on total dry matter), according to the method of WO-A-2004/099114. The starch hydrolysate was essentially fully converted, and it then contained about 85 wt.% (on total dry matter) of C1-oxidised compounds having a DP of 2, 3, or 4, of which the large majority (75 wt.% on total dry matter) was maltobionic acid - as such and/or in the corresponding sodium maltobionate form.

Sample evaluation

[0029] The stability of the enzymes was determined by utilising the known test procedure for detergency enzymes as made available by Megazyme as 'Measurement of endo-Protease and α-Amylase in Biological Washing Powders & Liquids using Azo-Casein and Amylazyme Tablets' - document code BWPL 11/03, a document freely available for download from www.megazyme.com in at least August 2012.

[0030] Samples of the liquid detergent compositions of the Examples 1 - 2 and the Comparative Experiments A - D were measured at four moments in time: upon preparation, after 14 days, after 1 month, and after 2 months.

[0031] The results of the stability evaluation is shown in Figures 1 - 4. In the Figures, an absorbance factor is given that was calculated from optical transmission measurements done as prescribed in the Megazyme method. The higher the factor, the higher the stability of the enzyme is.

[0032] The figures clearly show that in Examples 1 and 2 the enzymes are significantly more stable over time as compared to the enzymes in Comparative Examples A - D, which contained chelating agents not according to the invention that were evaluated, namely MGDA (methylglycine diacetate) and EDTA (ethylene diamino tetraacetate).

Claims

1. Use of a chelating agent containing a starch hydrolysate that has been selectively oxidised at the C1 location as enzyme-stabilizing agent in a detergent composition.

2. Use according to claim 1, wherein the starch hydrolysate that has been selectively oxidised at the C1 location contains at least 5 wt.%, calculated on the total dry matter of the starch hydrolysate, of compounds having a DP of 2, 3, or 4.

3. Use according to claim 2, wherein the starch hydrolysate that has been selectively oxidised at the C1 location contains at least 5 wt.%, calculated on the total dry matter of the starch hydrolysate, of maltobionic acid.

4. Enzyme-containing detergent composition, containing a starch hydrolysate that has been selectively oxidised at the C1 location, and at most 1 wt.% of further chelating agents and/or further enzyme-stabilizing agents.

5. Detergent composition according to claim 4, wherein the detergent composition is in liquid form or in the form of a gel capsule.

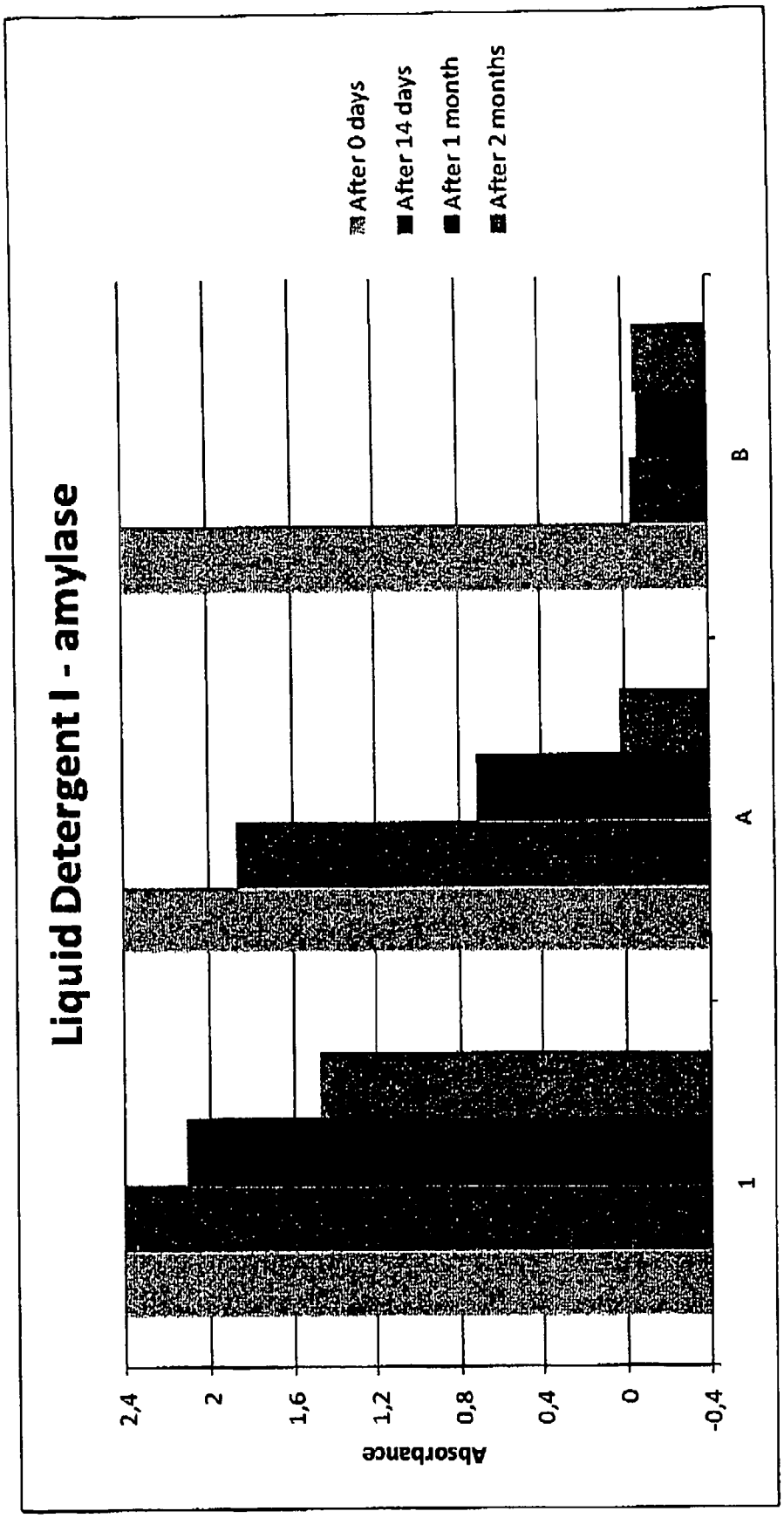

Liquid Detergent I - amylase
After 0 days
After 14 days
After 1 month
After 2 months
Absorbance
2,4
2
1,6
1,2
0,8
0,4
0
-0,4
1
A
B

Fig. 1

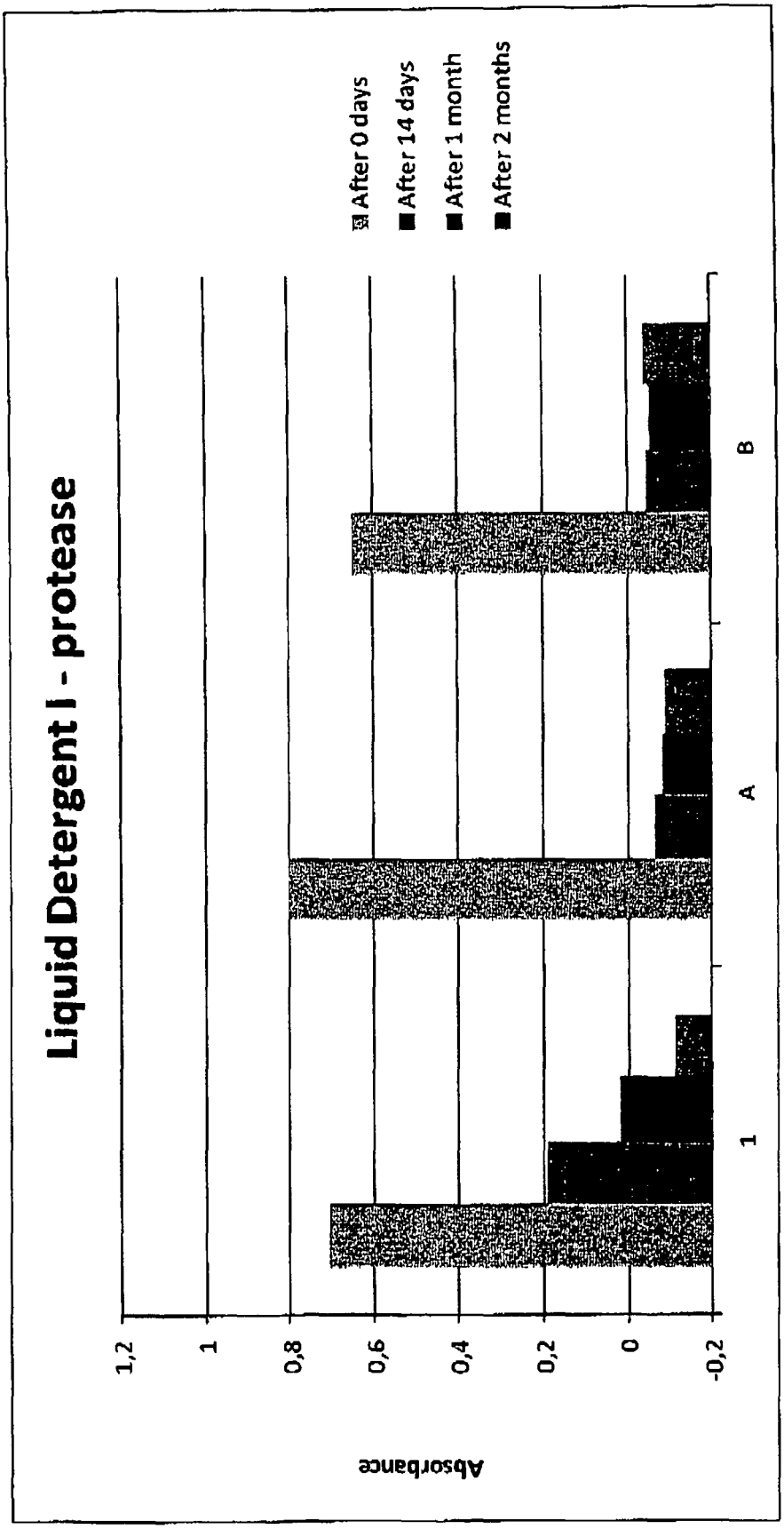

Liquid Detergent I - protease
After 0 days
After 14 days
After 1 month
After 2 months
Absorbance
1,2
1
0,8
0,6
0,4
0,2
0
-0,2
1
A
B

Fig. 2

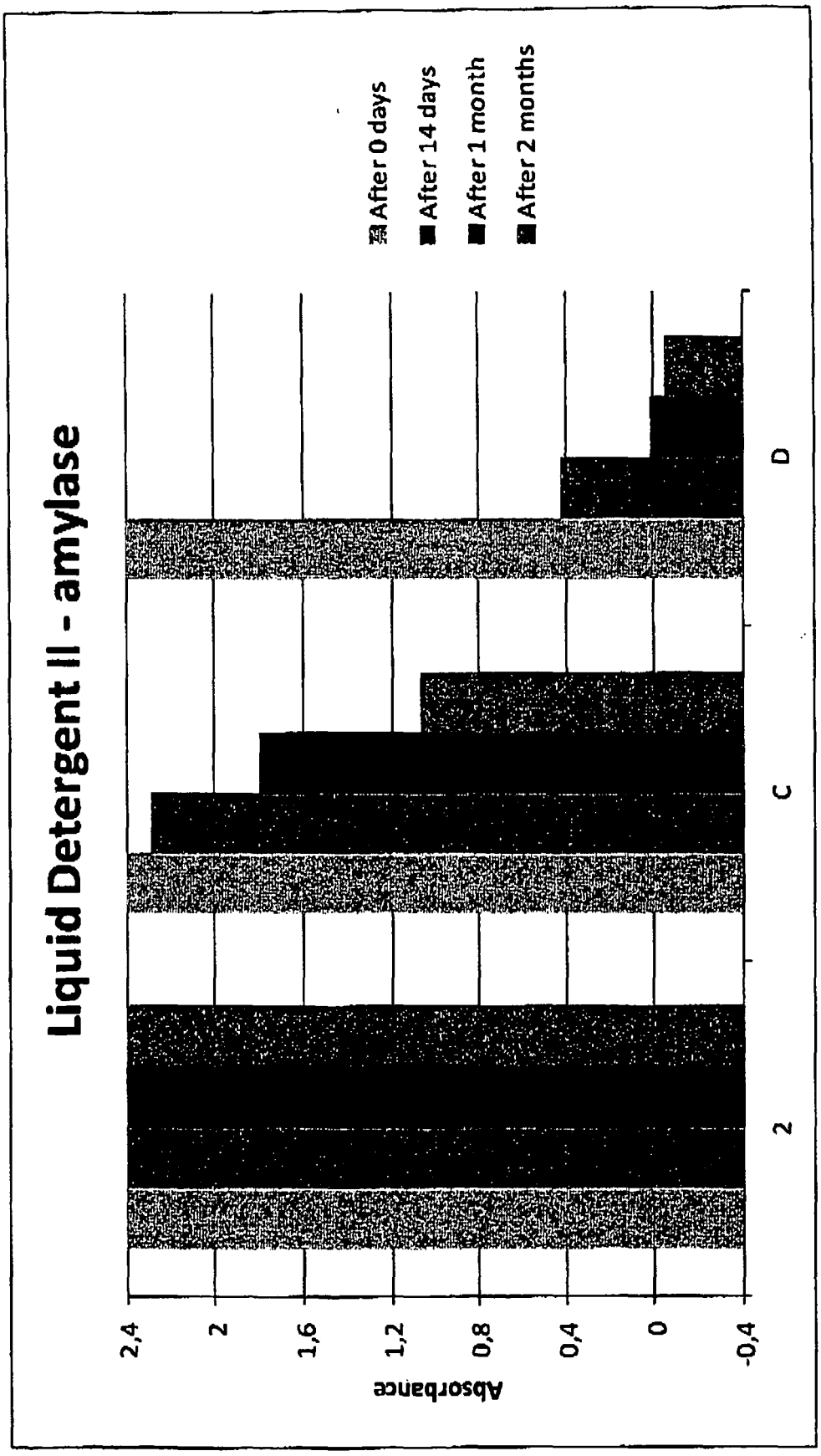

Liquid Detergent II - amylase
After 0 days
After 14 days
After 1 month
After 2 months
Absorbance
2,4
2
1,6
1,2
0,8
0,4
0
-0,4
2
C
D

Fig. 3

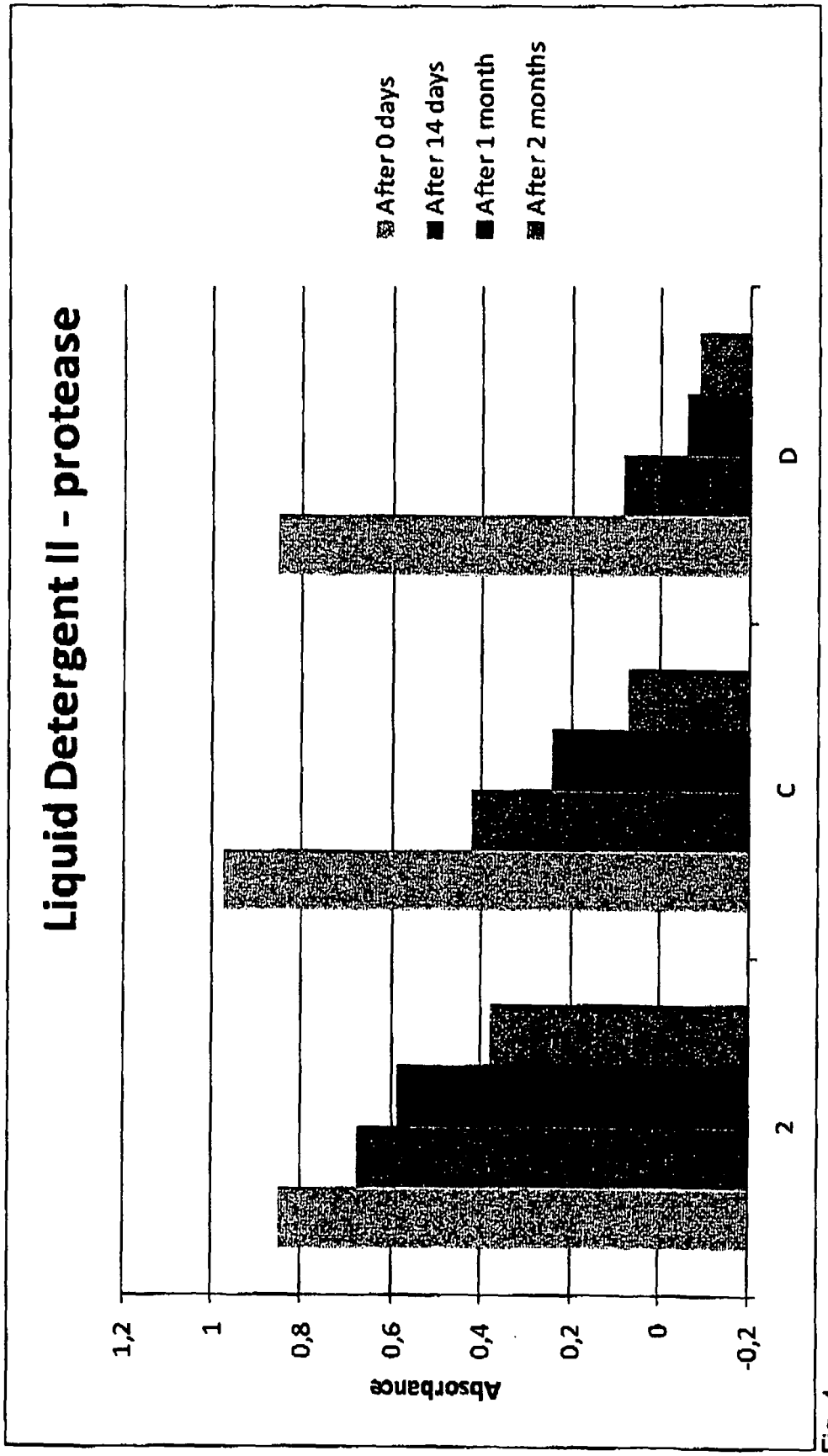

Liquid Detergent II - protease
After 0 days
After 14 days
After 1 month
After 2 months
Absorbance
1,2
1
0,8
0,6
0,4
0,2
0
-0,2
2
C
D

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
EP 12 00 5684

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	21 January 2013	Neys, Patricia

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X : particularly relevant if taken alone
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