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(71) Applicant:  
**INSTITUUT VOOR AGROTECHNOLOGISCH  
ONDERZOEK (ATO-DLO)  
6700 AA Wageningen (NL)**

(72) Inventors:  
• **VAN DE WATERING, Cornelis Gerardus  
6708 CA WAGENINGEN (NL)**

- **VISSER, Hermanna Anthonia Angenita Helena  
3582 XG UTRECHT (NL)**
- **TIMMERMANS, Johannes Wilhelmus  
6714 GG EDE (NL)**
- **SLAGHEK, Theodoor Maximiliaan  
3041 HT ROTTERDAM (NL)**
- **Langerock, Rik Julia Raoul  
6741 AP Lunteren (NL)**

(74) Representative:  
**de Bruijn, Leendert C. et al  
Nederlandsch Octrooibureau  
P.O. Box 29720  
2502 LS Den Haag (NL)**

(54) **Use of oxidised polysaccharides in detergent compositions**

(57) Polycarboxy polysaccharides, in particular dicarboxymaltodextrins, having a molecular weight between 1,600 and 12,000 and having a degree of oxidation (DO) of 0.12-0.6 carboxyl groups per anhydromonose unit, can be used as a cobuilder, in particular as an anti-redeposition and soil dispersing agent in detergent compositions.

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## Description

The invention relates to the use of polycarboxy polysaccharides in detergent compositions.

Detergent compositions contain a builder to neutralise the effect of water hardness, dissolution of soil and the like.

5 Although phosphate is an effective builder, its use is undesired for environmental reasons. Zeolites have largely replaced phosphates as builder. However, they require the presence of a cobuilder which prevents the redeposition of soil and the precipitation of calcium carbonate, and improves whiteness of the washed laundry. Synthetic polymers, such as polyacrylates have found extensive use as cobuilders, but they are poorly biodegradable. Thus there is need for biodegradable and yet effective cobuilder materials for use in textile washing compositions, dish-washing compositions and the like.

10 EP-A-755944 discloses a method for the production of oxidising maltodextrins having a DE (dextrose equivalent) between 2 and 20, especially a DE of 11-14, using oxygen or hydrogen peroxide under alkaline conditions in the absence of a catalyst followed by bleaching. This oxidation results in conversion of the reducing end groups in arabinonic acid groups. The product can be used as a cobuilder in detergent compositions wherein it improves whiteness and reduces inorganic incrustation, or as a binder or thickening agent.

15 An oxidised starch having a molecular weight from 500 to 60,000 wherein at least 60% of the C6 groups have been oxidised to carboxyl groups and 5-40% of the C2-C3 groups have been oxidised to carboxyl groups by catalytic oxidation with  $\text{HNO}_3$  /  $\text{H}_2\text{SO}_4$  /  $\text{NO}_2$ , is described in EP-A-542496. It is useful as a soil dispersant, builder and cleaning auxiliary.

20 The use of dicarboxylic polysaccharides such as dicarboxy starch and dicarboxy amylopectins as a calcium sequestering agent has been described in various documents, e.g. Kohn and Tihlárík, *Coll. Czech. Chem. Commun.* **49** (1984) 2116, EP-A-427349 and NL-A-8802907.

A simpler process for the production of relatively short-chain oxidised polysaccharides has been found, which results in products having improved cobuilder properties. The products especially have excellent anti-redeposition and soil dispersant properties, combined with full biodegradability. The process of the invention is characterised by the features of the appending claims. An advantage of this process is that inexpensive, commercially available starch can be used as a starting material, which can directly yield oxidation products of the required degree of oxidation and required molecular weight.

25 The polysaccharides to be oxidised according to the invention are primarily starch and starch derivatives such as hydrolysed starch and carboxymethyl starch. Other glucans, such as cellulose derivatives, and 1,3-glucans or 1,6-glucans can also be used. Another class of suitable polysaccharides are fructans (e.g. inulin), which can be used with molecular weights from about 240 upwards, especially 500-12,000, most preferably 1600-5000, and pentosans, such as xylans (hemicellulose), e.g. from waste carbohydrates. The degree of oxidation is preferably from 0.12 to 0.6, preferably from 0.2 to 0.55.

30 The oxidised polysaccharides are preferably obtained by treatment of the polysaccharide (e.g. starch) with a hypochlorite solution at pH 7.5-10, especially at pH 8-9, the hypochlorite being added gradually in order to be able to maintain the pH more or less constant by addition of a base. The reaction temperature can be e.g. between 0 and 40 °C, especially at ambient temperature. The oxidised product can be isolated by known techniques, including ethanol precipitation and freeze-drying. Such precipitation has the advantage of removing products that have excessive degrees of oxidation.

35 Other processes that result in C2-C3 oxidation of glucans (or C3-C4 oxidation in fructans) are also suitable, for example oxidation with periodate (cf. WO 95/12619 or Nieuwenhuizen et al, *Starch/Stärke*, **37** (1985) 192-200), followed by chlorite oxidation. Other oxidations can also be used, e.g. oxidation with hydrogen peroxide in the presence of acetylated polysaccharides, or oxidation with hydrogen peroxide in the presence of copper and magnesium or other oxidation catalysts. Combinations of oxidation processes may also be used. For adjusting the chain length of the oxidised products, a hydrolysis step (acid or enzymatic) may precede or follow the oxidation step.

40 The invention also pertains to detergent compositions containing a polycarboxy polysaccharide as described above as a cobuilder, anti-redeposition agent and/or soil dispersant. Typically, the composition contains 0.5-5 wt.% of the cobuilder prepared according to the invention, and further a detergent (12-25, especially 16-20 wt.%), a zeolite or silicate builder (15-30, especially 20-28 wt.%), a carboxylate such as sodium citrate (3-5 wt.%), a bleaching agent such as sodium perborate (10-20 wt.%), a catalyst such as TAED (3-4 wt.%), and optional further components such as enzymes (about 1-2 %: amylases, proteases), foaming or defoaming agents, odorants and the like.

## Example

55 Starch was oxidised generally according to Floor, "Oxidation of maltodextrins and starch with alkaline sodium hypochlorite", Thesis, Chapter 6, Delft (NL), 198.., as follows: 75 g of starch was suspended in 250 ml water. The pH was adjusted to 8.5. The appropriate amount of sodium hypochlorite solution (4% or 16% active chlorine) was added

at a rate of 10 ml/min for the first half hour and 20 ml/min afterwards for 4 % Cl<sub>2</sub> (2.5 and 5 ml/min, respectively, for 15% Cl<sub>2</sub>) at ambient temperature. The pH was maintained at 8.5 by the addition of 5 M NaOH. After 20 h the pH was adjusted to 9 and 500 ml of ethanol 98% was added. The suspension was stored at -4°C for 16 h and then decanted. The precipitate was dissolved in 150 ml water and 300 ml of ethanol was added. The suspension was again stored at -4°C for 16 h and then decanted. The precipitate was dissolved in 150 ml water and the solution was freeze-dried.

By varying the starting material and the amount of hypochlorite, four different products were obtained after precipitation:

DCS-1: Paselli 6 (molecular weight of native starch reduced by a factor 6), 0.55 l 4% Cl<sub>2</sub>, dicarboxy content 9% (carboxyl content 0.36 per anhydromonose unit), MW about 5400;

DCS-2: Paselli 2, 0.50 l 15% Cl<sub>2</sub>, dicarboxy content 19% (carboxyl content 0.48), MW about 3200;

DCS-3: native potato starch, 0.39 l 15% Cl<sub>2</sub>, dicarboxy content 18% (carboxyl content 0.36), MW about 4700;

DCS-4: native potato starch, 0.50 l 15% Cl<sub>2</sub>, dicarboxy content 21% (carboxyl content 0.48), MW about 3600.

The co-builder performance of these dicarboxy starches was tested using a compact no-phosphate detergent formulation (sodium carbonate zeolite A, sodium silicate, LAS, sodium lauryl sulphate, polymer) under US laundry conditions. The "Terg-o-tometer" test conditions were: 40°C, 100 rpm, 100 ppm hardness, 12 min. wash, 2 min. rinse, 723 ppm detergent (40 ppm polymer) 3 soiled + 2 clean cloths per pot, 3 repeat tests per polymer. The effect on clay soil removal and anti-redeposition were measured and compared to the effect of polyacrylate (Acusol 445N): non-polymer = 0%, Acusol 445 N = 100%. The results (average of two repeats) are given below.

*Clay soil removal (% effect vs. A-445N)*

	1x	5x	10x
DCS-1	71	96	79
DCS-2	92	105	88
DCS-3	71	91	109
DCS-4	90	104	95

*Anti-redeposition (whiteness) (% effect vs. A-445N)*

	1x	5x	10x
DCS-1	69	87	94
DCS-2	88	95	102
DCS-3	90	96	100
DCS-4	92	95	99

**Claims**

- Use of a polycarboxy polysaccharide having a molecular weight between 1,600 and 12,000 and having a degree of oxidation (DO) of 0.12-0.6 carboxyl groups per anhydromonose unit, as a cobuilder, in particular as an anti-redeposition and soil dispersing agent in detergent compositions.
- Use according to claim 1, wherein said polysaccharide is a maltodextrin with an average degree of polymerisation (DP) of 10-75, preferably of 12-60 anhydroglucose units.
- Use according to claim 1, wherein said hydrolysed polysaccharide is a pentosan with an average degree of polymerisation (DP) of 12-90, preferably of 15-60 anhydropentose units.
- Use according to any one of claims 1-3, wherein said polycarboxy polysaccharide has a degree of oxidation of

0.15-0.5 carboxyl groups per monosaccharide unit.

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5. Use according to any one of claims 1-4, wherein said polycarboxy polysaccharide is used at a level of 0.5-5 wt.% of the detergent composition.
  6. Use according to any one of claims 1-5' wherein, said polycarboxy polysaccharide is obtained by oxidation of the native or solubilised polysaccharide using hypochlorite at a pH of between 7.5 and 10.
  7. Use according to any one of claims 1-5, wherein said polycarboxy polysaccharide is obtained by oxidation of the native or solubilised polysaccharide using periodate followed by oxidation with chlorite, if necessary including the step of partially hydrolysing the polysaccharide before or after oxidation.
  8. Use according to any one of claims 1-5, wherein said polycarboxy, polysaccharide is obtained by oxidation of the native or solubilised polysaccharide using hydrogen peroxide, optionally in the presence of an acylated polysaccharide or a metal catalyst.
  9. Use according to any one of claims 6-8, wherein the oxidation is followed by a separation step, such as selective precipitation, to remove products having an excessive degree of oxidation.
  10. Detergent composition containing, on dry substance basis, 0.5-5 wt.% of a polycarboxy polysaccharide as defined in any one of claims 1-7 as a cobuilder, in addition to 12-25 wt.% of a detergent, 15-30% of a zeolite builder, and further conventional components.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 97 20 2196

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	EP 0 755 944 A (CERESTAR HOLDING BV. ) 29 January 1997 * claims *	1,2,8	C11D3/22 //C11D3/12
D,A	EP 0 542 496 A (THE PROCTER & GAMBLE CO. ) 19 May 1993 * claims 1-6 *	1,10	
D,A	EP 0 427 349 A (NEDERLANDSE ORGAN. VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOEK TNO) 15 May 1991 * claims *	1,10	
D,A	NL 8 802 907 A (COOPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING VAN AARDAPPELMEEL AVEBE. ) 18 June 1990 * claims *	1	
D,A	WO 95 12619 A (INSTITUUT VOOR AGROTECHNOLOGISH ONDERZOEK) 11 May 1995 * page 1, line 1 - line 21; claims *	1,7	
A	WO 93 08251 A (HENKEL KGAA.) 29 April 1993 * page 4 - page 7; claims 1-10 *	1,5-8,10	C11D
A	EP 0 472 042 A (FERTEC - FERRUZZI RICERCA E TECNOLOGIA SRI. ) 26 February 1992 * the whole document *	1,2,6,7	
A	EP 0 548 399 A (NOVAMONT SPA) 30 June 1993 * claims 1-7,11; example 10 *	1,4	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		8 December 1997	Serbetsoglou, A
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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