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(54) **METHODE POUR AMELIORER LA PLASTICITE DE COMPOSITIONS CERAMIQUES ET POUR INVERSER CET EFFET**

(54) **PROCESS FOR IMPROVING THE PLASTICITY OF CERAMIC COMPOSITIONS AND FOR REVERSING THIS EFFECT**

(57) La plasticité de compositions et de dispersions céramiques peut être améliorée par addition d'au moins un polymère (I) comportant des unités succinyle répétées. Cet effet peut être inversé par addition d'un accélérateur de prise (II); comme accélérateurs de prise, on privilégie les polymères (II) de type polyalkylènepolyamine.

(57) The plasticity of ceramic compositions and dispersions can be improved by addition of at least one polymer (I) with recurring succinyl units. This effect can be reversed by addition of a setting accelerator (II); preferred setting accelerators are polymers (II) of the polyalkylenepolyamine type.

Process for improving the plasticity of ceramic compositions and for reversing this effect

Abstract

The plasticity of ceramic compositions and dispersions can be improved by addition of at least one polymer (I) with recurring succinyl units. This effect can be reversed by addition of a setting accelerator (II); preferred setting accelerators are polymers (II) of the polyalkylenepolyamine type.

Process for improving the plasticity of ceramic compositions and for reversing this effect

The present invention relates to a new process for improving the plasticity of ceramic compositions by addition of auxiliary substances and for reversing the effect by addition of further auxiliary substances. This is understood as meaning improving the dispersion, stabilization and rheological properties, in particular the plasticity, of ceramic compositions, comprising clay minerals and their carbides, nitrides, oxides and silicates, of ceramic pigments and of hydraulic binders, such as cement or concrete, as the phase to be dispersed and water as the dispersing agent, and reversing this effect in the sense of solidification of such dispersions.

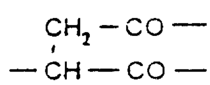
During the preparation of such compositions, e.g. during pulverizing or grinding, during transportation and during storage or processing it is appropriate and necessary to prepare plastic compositions (so-called slurries or slips). Other such compositions are ceramic materials, ceramic pigments inter alia, which do not set themselves and to which hydraulic binders are added. To avoid possible flocculation or sedimentation, to increase the ductility or plasticity at the same or a lower water content and to improve the nature of the ceramic end products, it is known to add stabilizing, dispersing and liquefying agents. Soda- or sodium-water glass solutions, oleic acids and stearic acids, products based on hydroxy- or polyhydroxycarboxylic acids or carboxylic acid esters, alkyl polyglycol ethers, triethanolaminesulfonates and products based on ligninsulfonates are known for this. Known additives are furthermore sucrose, glucose, polyalcohols, adipic, citric, lactic, tartaric, malonic or fumaric acid and inorganic phosphorus compounds, such as ortho-, meta-, pyro- or polyphosphates, as well as hydrophilic melamineformaldehyde resins, ligninsulfonates, sulfite waste lye, protein degradation products and humic acids.

JP 07/172 888 describes the use of polyaspartic acid Na salt with an average molecular weight MW = 31,000 as a flow improver. JP 08/169 741 describes the use of polysuccinimide of MW = 78,000 as a flow improver.

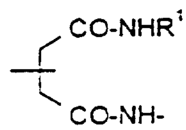
The present invention was based on the object of providing a polymer (I) which improves the rheological properties of ceramic compositions, is distinguished, in particular, by an improved biodegradability, and the effect of which on ceramic compositions is cancelled out and reversed by a setting accelerator (II).

A process has been found for improving the plasticity of ceramic compositions and dispersions having a content of water and for reversing this effect, which is characterized in that, to improve the plasticity, an amount of 0.1 to 5 wt.%, based on the weight of the water content, of at least one polymer (I) with recurring succinyl units and, to reverse this effect, an amount of 0.01 to 1 wt.%, based on the weight of the water content, of at least one setting accelerator (II), which neutralizes the ionic and interface-specific effects of the polymers (I), are added.

The polymers (I) used according to the invention contain recurring succinyl units with at least one of the following structures:



, preferably nitrogen-containing



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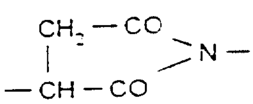
Specifically, these are



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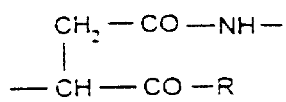
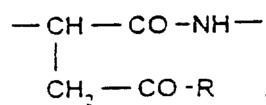


β -Form

or



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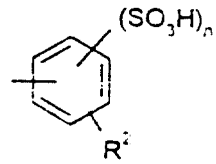
α -Form

in which

R represents OH, OLi, ONa, OK, ONH_4, NH_2, NHR_1 or OR^1, wherein R^1 denotes one of the substituents



or $-Y-SO_3H$, wherein n represents the number 1 or 2, Y represents straight-chain or branched alkylene, alkenylene or alkinylene and R^2 represents hydrogen, alkyl, alkoxy or halogen.

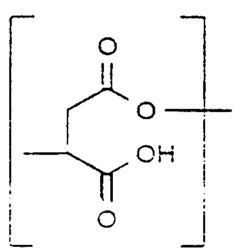
Alkyl has 1-6, preferably 1-2 C atoms and is, for example, methyl, ethyl, propyl, i-propyl, butyl, i-butyl, pentyl or hexyl. Alkylene is derived therefrom by removing an H atom, and is divalent; alkenylene has 2-6, preferably 2 C atoms and a double bond and, analogously to the alkylene, is divalent; alkinylene has a triple bond and is otherwise similar to the alkenylene.

Alkoxy is an alkyl bonded via an ether oxygen atom.

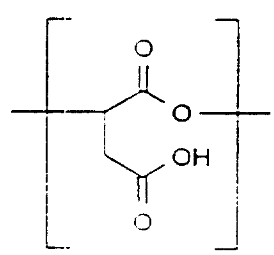
Halogen is fluorine, chlorine or bromine, preferably chlorine.

In addition, further recurring units can be present by a suitable reaction procedure and choice of the educts, e.g.

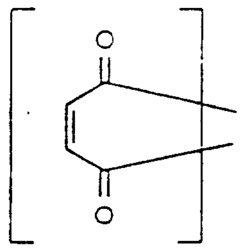
a) malic acid units of the formula



and



b) maleic acid and fumaric acid units of the formula



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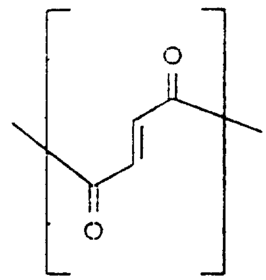


In a particularly preferred embodiment, the polymer (I) to be used according to the invention is a polyaspartic acid.

The preparation and use of polyaspartic acid (PAA) and its derivatives has long been the subject matter of numerous publications and patents. The preparation can be carried out, for example, by thermal polycondensation of aspartic acid in accordance with J. Org. Chem. 26, 1084 (1961). Polysuccinimide (PSI), which is referred to therein as "anhydropolyaspartic acid" first occurs as an intermediate. PSI can be converted into PAA by hydrolysis. US-A 4 839 461 describes the preparation of polyaspartic acid from maleic anhydride, water and ammonia generally, and US-A 5 286 810 specifically at higher temperatures.

In many preparation processes, it is not the pure acids but initially the corresponding anhydrides, for example polysuccinimide (PSI), which are first obtained. Such polymerization products can be converted into a PAA-containing salt by reaction with a base, optionally in the presence of water. This conversion of PSI-containing polymers into PAA-containing polymers then takes place by hydrolysis in a suitable device. A pH of between 5 and 14 is preferably suitable for this. In a particularly preferred form, a pH of 7 to 12 is chosen, in particular by the addition of a base. Suitable bases are alkali metal and alkaline earth metal hydroxides or carbonates, such as, for example, sodium hydroxide solution, potassium hydroxide solution, sodium carbonate or potassium carbonate, ammonia and amines, such as triethylamine, triethanolamine, diethylamine, diethanolamine and further substituted amines. In addition to free PAA acids, their Na, K or Ca salts are particularly preferred as polymers (I). The temperature during the hydrolysis is advantageously in a range up to the boiling point of the PSI suspension, for example at 20 to 150°C. Optionally, the hydrolysis is carried out under pressure. However, it is also possible to obtain the free polyaspartic acid by purely aqueous hydrolysis or treatment of the PAA salt with acids or acid ion exchangers. The term "polyaspartic acid" (PAA) in the present invention also includes the salts, if not expressly stated otherwise. The finished product is obtained by drying, preferably spray drying.

Preferred polymers (I) have a molecular weight, according to analyses by gel permeation chromatography, of Mw = 500 to 10,000, preferably 700 to 5,000, particularly preferably 1,000 to 4,500. In general, the content of the beta form in polyaspartic acids is more than 50%, preferably more than 70%, based on the sum of these units.

In another preferred form, the polymers (I) to be used according to the invention are modified polyaspartic acids which are obtained by reaction of

a) 0.1 - 99.9 mol% PAA or PSI or 0.1 - 99.9 mol% aspartic acid with

b) 99.9 - 0.1 mol% fatty acids, fatty acid amides, polybasic carboxylic acids, their anhydrides and amides, polybasic hydroxycarboxylic acids, their anhydrides and amides, polyhydroxycarboxylic acids, aminocarboxylic acids, sugar-carboxylic acids, alcohols, polyols, amines, polyamines, alkoxylated alcohols and amines, amino-alcohols, amino-sugars, carbohydrates, ethylenically unsaturated mono- and polycarboxylic acids and their anhydrides and amides, protein hydrolysis products, e.g. maize protein hydrolysis products and soya protein hydrolysis products, aminosulfonic acids and aminophosphonic acids.

In a preferred embodiment, the polymer (I) to be used according to the invention is added to the system in a concentration of 0.1 to 5 wt.%, based on the aqueous phase. Particularly preferred amounts are 0.3 to 3 wt.%.

It is also possible to use further additives, such as wetting agents, lubricating auxiliaries, further plasticizing agents and other conventional additives, in addition to the polymers (I) used according to the invention. Concretes, mortars etc. and optionally air pore-forming agents and/or thixotropic agents can also be added to the ceramic compositions prepared using the liquefiers (I) described.

There is often the desire to reverse the liquefaction necessary for transportation and handling. However, this is not the case exclusively, for example, in the processing of ready-mixed concrete. An optimum homogeneity and plasticity is desirable for filling out very fine channels, for transportation by pumping, for pressing out foundation structures, for compacting fine-membered components, for preparing dense bulk concrete or for centrifuging high-grade centrifugal concretes. After the introduction, however, the plasticity should be reversed rapidly in the sense that the consistency increases significantly and the concrete loses its flow properties, sets and solidifies, during which it achieves its final desired properties, such as its strength.

According to the invention, to reverse the plasticizing of ceramic compositions and dispersions which have been plasticized by a polymer (I), a setting accelerator (II) which neutralizes and reverses the ionic and interface-specific effects of the polymer (I) is added.

Setting accelerators, which are added to the ceramic compositions and dispersions shortly before their final processing, are, for example, soluble alkali/alkaline earth metal salts, alkali metal aluminates, alkali metal silicates or a mixture of several of these or, preferably, a polyalkylenepolyamine, called polymer (II) here.

A suitable polymer (II) can be prepared, for examples, by first reacting ammonia with dichloroalkylenes and reacting the products obtainable by this process, e.g. diethylenetriamine, with further dichloroalkylene. Mixtures of polyalkylene-polyamines of various origin can also be employed. The alkylene groups are straight-chain or branched and have 2 to 4 C atoms, for example 1,2-ethylene, 1,2- and 1,3-propylene and 1,2-, 1,3- and 1,4-butylene. 1,2-Ethylene and 1,2-propylene are preferred, and 1,2-ethylene is particularly preferred. Optionally, the polyalkylenepolyamines primarily accessible in this way can be heated under reduced pressure to reduce vinyl chloride contents to below the detection limit in aqueous solution and/or, optionally, they can be degraded by heat under increased pressure to lower the viscosity (DE-OS 2 351 754 and DE-OS 2 833 654). The chloride from the dichloroalkylenes forms the counter-ion to the amino groups formed during the reaction. A specific degree of neutralization can be established by addition of further hydrochloric acid. Chloride can also be replaced by sulfate, phosphate or acetate in a known manner. Particularly suitable poly-alkylenepolyamines have e.g. viscosities in the range from 200 to 800 mPa.s (measured as a 25 wt.% aqueous solution at 25°C). Polyalkylenepolyamines such as are obtained during their preparation, i.e. as a solution in water, can also be employed.

Polyethylenepolyamines which have a molecular weight of 80,000 to 120,000, a viscosity of 250 to 400 mPa.s (measured in 25 wt.% aqueous solution at 25°C) and the lowest possible risk to water are preferably employed.

Setting accelerators (II), in particular the polymers (II), are employed in amounts of 0.01 to 1 wt.%, preferably 0.01 to 0.2 wt.%, based on the weight of the aqueous phase.

Examples

Examples 1 to 4 show the improvement in the plasticity and example 5 shows the reversal of this phenomenon.

Example 1

60 g China clay were stirred at room temperature with 40 ml of an aqueous solution of the stated liquefying agents A to E in graduated concentrations and the mixture was then homogenized for 10 minutes at 750 revolutions per minute with a propeller stirrer such that suspensions (slurries) comprising 60 wt.% solids and 0.1 to 1.0 wt.% liquefying agent were formed. The flow curves of the slurries were then recorded with a rotary viscometer type Haake RV 12. The liquefying agents employed were:

Agent A: Commercially obtainable polyacrylic acid (mol. wt. MW = 3,000)

Agent B: Commercially obtainable acrylic acid/maleic acid copolymer (MW = 4,000)

Agent C: Polyaspartic acid (MW = 1,800)

Agent D: Polyaspartic acid (MW = 2,400)

Agent E: Polyaspartic acid (MW = 8,000)

Table 1 shows the results.

Example 2

The procedure was as above, but 60 ml of an aqueous solution of agents A to E were added to 50 g secondary fine kaolin. Table 2 shows the results.

Example 3

The procedure was as above, but 45 ml of an aqueous solution of agents A to E were added to 55 g fine talc. Table 3 shows the results.

Table 1 (China clay slurries with 60% solids content; 0.1, 0.2, 0.3, 0.4 and 1.0 wt.% agents A to E)

Agent A

Shear rate		0.1%	0.2%	0.3%	0.4%	1.0%
10		111560	38010	875	72.5	121.1
20		66520	24550	525	65.6	98.4
40		43550	13260	284	54.7	78.8
80		25320	7720	164	32.8	62.3
160		18430	4800	115	24.6	61.5
320		10210	3120	115	15.0	60.3

Agent B

Shear rate		0.1%	0.2%	0.3%	0.4%	1.0%
10		118781	2800	70.1	70.1	152.1
20		74440	1530	65.6	65.6	131.3
40		47512	830	54.7	54.7	98.4
80		28320	635	49.2	38.3	82.0
160		20360	545	43.8	38.3	70.5
320		14230	485	49.2	43.8	65.6

Agent C

Shear rate		0.1%	0.2%	0.3%	0.4%	1.0%
10		63350	36426	2450	87.5	69.1
20		58600	19790	1422	65.6	65.6
40		38010	10490	820	54.7	62.3
80		22350	6137	519	32.8	62.3
160		13210	3810	372	24.6	45.1
320		10220	2524	355	15.0	32.4

Agent D

Shear rate		0.1%	0.2%	0.3%	0.4%	1.0%
10		79180	20590	1487	131.3	72.1
20		50680	11870	787	109.4	65.6
40		27110	6530	415	76.7	52.5
80		16629	4250	235	60.2	55.8
160		9403	2670	218	60.2	59.1
320		5920	1730	210	62.9	65.6

Agent E

Shear rate		0.1%	0.2%	0.3%	0.4%	1.0%
10		106110	61760	2012	87.5	181.9
20		69685	39590	1094	87.5	150.9
40		46720	22960	602	65.6	105.5
80		30120	13165	339	54.7	87.1
160		20850	8020	191	52.0	77.1
320		16210	4700	172	57.4	72.2

Table 2 (Secondary fine kaolin as a slurry with 50% solids content; 0.1 to 0.3 wt.% agents A to E)

Agent A

Shear rate		0.10%	0.15%	0.20%	0.30%
10		39260	4216	2523	722
20		22960	3167	1816	547
40		13060	1781	1050	328
80		7720	1039	612	219
160		4550	594	372	126
320		2800	371	137	79

Agent B

Shear rate		0.10%	0.15%	0.20%	0.30%
10		10620	498	112	82.1
20		7920	328	87.5	72.5
40		4750	175	65.6	65.2
80		2770	104	43.8	43.8
160		1680	60	35.5	34.5
320		1340	37	31.4	30.9

Agent C

Shear rate		0.10%	0.15%	0.20%	0.30%
10		43560	14280	982	113.2
20		31670	9800	678	109.4
40		19890	5350	382	98.4
80		12370	3070	202	76.7
160		6680	1730	109	54.7
320		3910	1040	66	41.1

Agent D

Shear rate		0.10%	0.15%	0.20%	0.30%
10		38960	9880	716	148.3
20		27710	7910	612	109.4
40		17820	4350	484	65.6
80		10390	2370	262	43.8
160		5940	1330	150	24.6
320		3360	866	90	19.1

Agent E

Shear rate		0.10%	0.15%	0.20%	0.30%
10		34260	6230	2780	46.2
20		23750	4750	1970	43.8
40		13860	2570	1050	43.8
80		7920	1480	574	32.8
160		4700	792	317	21.9
320		2920	470	177	16.4

Table 3 (Fine talc as a slurry with 55% solids content; 0.1 to 0.4 wt.% agents A to E)

Agent A

Shear rate	0 sample	0.1%	0.2%	0.3%	0.4%
80	71.1	26.2	19.3	12.3	11.5
160	120.3	38.3	30.1	24.6	24.6
320	191.4	76.6	68.4	53.3	52.0
660	382.4	129.9	129.9	109.4	102.5

Agent B

Shear rate	0 sample	0.1%	0.2%	0.3%	0.4%
80	71.1	65.5	38.3	16.4	10.9
160	120.3	93.0	76.6	43.8	38.3
320	191.4	169.5	151.8	95.7	65.6
660	382.4	177.7	143.6	123	109.4

Agent C

Shear rate	0 sample	0.1%	0.2%	0.3%	0.4%
80	71.1	54.7	33.6	8.22	14.0
160	120.3	82.0	49.2	43.8	24.6
320	191.4	157.2	106.6	95.7	60.2
660	382.4	205.1	141.1	123.3	123.1

Agent D

Shear rate	0 sample	0.1%	0.2%	0.3%	0.4%
80	71.1	54.7	43.8	16.4	10.9
160	120.3	101.2	73.8	49.2	54.7
320	191.4	183.2	157.2	109.4	71.1
660	382.4	205.1	170.9	150.4	123.3

Agent E

Shear rate	0 sample	0.1%	0.2%	0.3%	0.4%
80	71.1	27.3	27.3	32.8	32.8
160	120.3	54.7	54.7	57.4	52.0
320	191.4	108	118.9	127.1	110.7
660	382.4	109.9	171.2	164.1	150.4

Example 4

The plasticity of fresh concrete can be improved with the polymers (I) according to the invention. This results not only in the advantage of the effect as a liquefier, but (I), as a dispersing agent, also counteracts demixing during transportation and processing. Testing in this context was carried out in accordance with DIN 1048 T1 (test method for fresh concrete): A slump table with an area of 200 x 200 mm was fixed to a perpendicular guide such that a free fall height of 100 mm was ensured. A cylindrical mould standing centrally on the matt-damp surface of the slump table was filled loosely with the freshly prepared and homogenized mortar. After the mould had been filled, the excess was scraped off flush without a compacting effect, and the mould was raised and placed on one side.

Within 15 s, the plate was now raised to the stop and allowed to fall freely 15 times without jerking. The diameter of the mortar cake was then measured. The experiment was repeated after 1 h, in order to record the setting properties as a function of time in this manner.

Test conditions:

- Portland cement CEMI 32.5 R DIN 1164
- Water/cement ratio: 0.325
- Concentration: 0.25 / 0.5 / 0.75 / 1 wt.% plasticizing agent

Agent C: Polymer (I) MW 1,800
Agent D: Polymer (I) MW 2,400
Agent E: Polymer (I) MW 8,000

Table 4 (Slump of cement slurries)

Active compound C

Test duration [min]	0 sample (duplicate det.)	0.25%	0.50%	0.75%	1.00%
30	152	164	172	176	175
60	147	169	166	179	179
90	138	160	167	178	180
120	135	155	167	174	175
180	130	145	160	166	175
240	solid	139	145	162	172
300		111	113	142	150
360		solid	solid	110	120

Active compound D

Test duration [min]	0 sample (duplicate det.)	0.25%	0.50%	0.75%	1.00%
30	145	165	176	170	178
60	138	165	173	173	178
90	135	165	170	170	173
120	133	160	169	172	172
180	107	157	157	172	174
240	solid	161	161	174	173
300		157	158	169	173
360		150	150	165	173

Active compound E

Test duration [min]	0 sample (duplicate det.)	0.25%	0.50%	0.75%	1.00%
30	143	141	154	155	163
60	143	143	154	155	163
90	140	145	155	155	165
120	138	145	157	156	170
180	125	148	156	156	170
240	solid	158	155	155	168
300		158	158	158	165
360		144	156	156	162

Example 5

The highly liquefying effect of the polymer I shown in examples 1 to 4 could be reversed virtually completely by subsequent addition of a polymer (II). First 0.4%

polymer I and then 0.01 - 0.05% polymer (II) were added to the liquefied kaolin according to example 2.

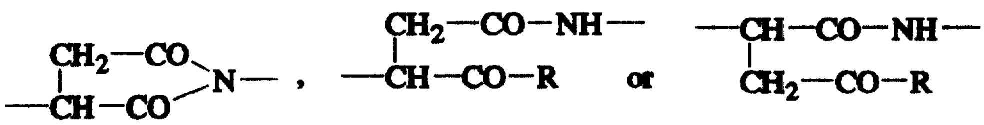
Sample	Viscosity [mPa.s]
Zero sample	6,000
plus 0.4% polymer (I)	23
(I) plus 0.01% polymer (II)	46
(I) plus 0.02% polymer (II)	1,900
(I) plus 0.025% polymer (II)	2,400
(I) plus 0.05% polymer (II)	5,600

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for improving the plasticity of a ceramic composition having a content of water which process comprises adding 0.1 to 5 wt.% based on the weight of the water content, of at least one polymer (I) with recurring succinyl units to the composition.

2. A process for improving the plasticity of a ceramic composition having a content of water and for reversing this effect, which process comprises, to improve the plasticity, adding an amount of 0.1 to 5 wt.%, based on the weight of the water content, of at least one polymer (I) with recurring succinyl units to the composition and, to reverse this effect, adding an amount of 0.01 to 1 wt.%, based on the weight of the water content, of at least one setting accelerator (II), which neutralizes the ionic and interface-specific effects of the polymers (I).

3. A process according to claim 1 or 2, wherein the polymer (I) contains recurring units of at least one of the following structures



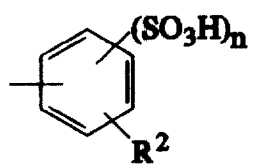
β—Form α—Form

in which

R represents OH, OLi, ONa, OK, ONH_4, NH_2, NHR_1 or OR^1,

wherein

R^1 denotes one of the substituents



or $-Y-SO_3H$,

wherein n represents the number 1 or 2, Y represents straight-chain or branched alkylene, alkenylene or alkinylene and R^2 represents hydrogen, alkyl, alkoxy or halogen.

4. A process according to claim 1, 2 or 3 wherein polymer (I) is a polyaspartic acid or a polysuccinimide or a salt thereof.

5. A process according to any one of claims 1 to 4, wherein polymer (I) has a molecular weight of Mw = 500 to 10,000.

6. A process according to any one of claims 1 to 4, wherein polymer (I) has a molecular weight of Mw = 700 to 5,000.

7. A process according to any one of claims 1 to 4, wherein polymer (I) has a molecular weight of Mw = 1,000 to

4,500.

8. A process according to any one of claims 1 to 7, wherein polymer (I) is a modified polyaspartic acid obtained by the reaction of

a) 0.1 to 99.9 mol% polyaspartic acid or polysuccinimide or 0.1 to 99.9 mol% aspartic acid with

b) 99.9 to 0.1 mol%

of a compound selected from fatty acids, fatty acid amides, polybasic carboxylic acids, their anhydrides and amides, polybasic hydroxycarboxylic acids, their anhydrides and amides, polyhydroxycarboxlic acids, aminocarboxylic acids, sugar-carboxylic acids, alcohols, polyols, amines, polyamines, alkoxylated alcohols and amines, amino-alcohols, amino-sugars, carbohydrates, ethylenically unsaturated mono- and polycarboxylic acids and their anhydrides and amides, protein hydrolysis products, aminosulfonic acids and aminophosphonic acids.

9. A process according to claim 8 wherein component b) is a maize or soya protein hydrolysis product.

10. A process according to any one of claims 1 to 9, wherein polymer (I) is used in an amount of 0.1 to 5 wt.%, based on the aqueous phase.

11. A process according to any one of claims 1 to 10, wherein polymer (II) comprises a polyalkylenepolyamine, with a viscosity in the range from 200 to 800 mPa.s, measured as a 25 wt.% aqueous solution at 25 °C.

12. A process according to any one of claims 1 to 10, wherein polymer (II) comprises a polyethylenepolyamine, with a viscosity in the range from 200 to 800 mPa.s, measured as a 25 wt.% aqueous solution at 25 °C.

13. A process according to any one of claims 1 to 12, wherein polymer (II) is used in an amount of 0.01 to 1 wt.%.

14. A process according to claims 1 to 13 wherein polymer (II) is a polyethylenepolyamine salt which is obtainable by reaction of ammonia with dichloroethylene.

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PATENT AGENTS