

The present invention relates to powdery absorbents for aqueous liquids, which are based on a water-swellaable polymer and do not set up on contact with water or aqueous solutions, such as body liquids, i.e., do not impede the absorption of further liquid by forming a barrier of swollen gel particles and which largely maintain their swelling capacity under load, as is the case when the polymers are used in diapers or incontinence articles.

The manufacture of water-swellaable polymers is known. U.S.-Patent No. 4,698,404 describes a typical method of producing water-swellaable polymer particles by inverse suspension polymerization of an aqueous solution of acrylic acid and alkali or ammonium acrylate in a hydrocarbon and cross-linkage of the polymer.

European patent application No. A1 0 205 674 describes the solvent polymerization of monomers which mainly contain acid groups in the presence of an agent having a cross-linking action. After the acid groups of the polymer have been neutralized by at least 27% and the polymer gel has been dried, a water-swellaable polymer is obtained which has a high gel strength and small amounts of extractable components.

- European patent application No. A2 0 312 952 describes the polymerization of carboxyl-groups-containing monomers which are neutralized to the extent of at least 20% in the presence of dispersed cross-linking agents.

The continuous copolymerization of an acrylic-acid-containing monomer solution, the acrylic acid being neutralized to the extent of at least 20%, is described in European patent application No. A2 0 280 541.

To improve the technical application properties of water-swella-
ble polymers selected from the group consisting of a cross-linked hy-
drolyzate of an acrylamide copolymer, a hydrolyzate of a cross-
linked acrylonitrile copolymer, a cross-linked, partially neutralized
acrylic acid polymer, or to adapt them to their particular function
the polymers are frequently subjected to a post treatment.

European Patent Nos. 0 009 977 and 0 001 706, for example, de-
scribe the surface coating of particle-shaped, water-swella-
ble polymers with hydrophobic compounds or polyethers to improve the
dispersibility in blood.

US-PS 4,587,308 describes the post cross-linkage of water-swella-
ble polymers, dispersed in slightly swollen form, with diglycidyl
ethers, polyvalent metal salts or halogen epoxy compounds.

DE-OS No. 34 29 379 describes a water-absorbing resin obtain-
able by impregnation of a water-swella-
ble resin with a hydrophilic,
reactive, olefinically unsaturated monomer or polymer thereof and
a cross-linking agent.

US-PS 4,666,975 describes the post-cross-linkage of water-swella-
ble polymers in suspension by reaction with diglycidyl ethers.

GB 21 19 384 A claims the post cross-linkage in the particle sur-
face of water-swella-
ble polymers, the carboxyl groups of which
are neutralized by 50 to 99 mol-%, with multifunctional com-
pounds, such as polyols or polyamines.

The secondary cross-linkage in the polymer surface with solutions
of polyols or of diglycidyl compounds is carried out in DE-OS 35
23 617 and EP-A 83 022. The aftertreatment is carried out with
polymers whose carboxyl groups are neutralized to the extent of

50 to 99 mol-% in the presence of water and a hydrophilic organic solvent.

All these processes strive to improve the liquid transport in a layer of polymer particles or to provide a polymer which, after swelling, does not release the stored liquid on exertion of pressure, e.g., by an infant's body on the swollen polymer in a diaper.

However, the object is not only to improve the liquid transport in a layer of water-swellaable polymer particles or the capability of the polymer to retain liquid under subsequent pressure after the polymer could swell freely, i.e., without load, but also to provide a water-swellaable polymer which absorbs liquid even against a load.

This special absorption property is referred to as absorption under pressure/load in the EP 0 339 461.

It was found that water-swellaable, carboxyl-groups-containing polymers, which are present in neutralized form to the extent of 50 to 99 mol-%, can be obtained with a high swelling capacity under load when water-swellaable polymers with a low swellability under load are treated with N-(hydroxyalkyl) β -(meth)-alanine esters and/or their polycondensation products and heated.

In addition, it was found that the post-treatment of carboxyl-groups-containing polymers - which are neutralized by more than 80 mol-% - with polyols or amino alcohols at elevated temperatures does not, or only under impracticable conditions, result in products with improved properties; but that, in contrast to this, an increase in the swelling capacity under load can be obtained by treating said polymers, which are neutralized by more than 80 mol-%, with N-(hydroxyalkyl) β -(meth)alanine esters and/or their polycondensation products at elevated temperatures.

An additional technical advantage of post treating water-swella-
ble polymers with N-(hydroxyalkyl) β -(meth)alanine esters and/or the
resulting polyamides or polyamide ethers results from the fact that
- in contrast to the use of polyols or alkanolamines according to
the methods of GB 21 19 384 and DE-OS 35 33 617 - lower after-
treatment temperatures with an equimolar feedstock of aftertreat-
ment agent or shorter post treatment periods at the same tempera-
ture are necessary to improve the product properties.

The production of N-(hydroxyalkyl) β -(meth)alanine esters and
their capability of forming polyamides or polyamide ethers already
at room temperature is described in detail in "Journal of Polymer
Science", Part A-1, vol. 6, 1195-1207 (1968) and vol. 7, 889-898
(1969).

The production is effected by Michael-addition-reaction of alkanols
or alkanolamines to (meth)acrylic acid ester.

The quantity of N-(hydroxyalkyl) β -(meth)alanine esters and/or their
polycondensation products used according to the present inven-
tion amounts to 0.001 to 5 p/wt. (parts by weight), relative to
100 parts of water-swella-ble polymer. If more than 5 p/wt. are
used, the swelling capacity (retention) of the polymers decreases
excessively. If less than 0.001 p/wt. are used, the swellability un-
der load is not improved.

The aftertreatment agents according to the present invention are
used in aqueous solution. The water serves to dissolve the alco-
hol-insoluble solid polyamides of the N-(hydroxyalkyl) β (meth)
alanine esters and, at the same time, as vehicle for the aftertreat-
ment agents into the water-swella-ble polymer particles. The quan-
tity of water amounts to 0.1 to 5 p/wt. per 100 p/wt. of water-
swella-ble polymer. Since the water-swella-ble polymers which have
not been post-treated would set up on contact with the aqueous

solutions of the after-treatment agent, water-soluble, organic diluents are additionally used in amounts of 0.2 to 10 p/wt. per 100 p/wt. of water-swellable polymer. The following substances are used as water-soluble, organic diluting agents:

- a) those evaporating from the solution of the post treatment agent and the water-swellable polymer on heating said mixture, e.g., monofunctional alcohols having the C-number 1-4, acetone, glycol ether, glycol ester and/or
- b) those which do not evaporate on heating and remain on or in the polymer particle, e.g., butyrolactone, butyrolactam, lactic acid, diacetin.

The diluents stated under a) require certain technical measures when the secondary treatment of the water-swellable polymers is carried out since they are combustible, form explosive mixtures and must not come into the atmosphere.

The diluents stated under b) remain on the polymer and do not require special protective measures. However, they may affect the swelling capacity of the aftertreated polymers when used in larger amounts during the post treatment.

The amount of added water-soluble, organic diluent depends on the amount of water employed. The quantity should be such that a product results which is easy to handle and does not contain agglutinated particles, after said diluent has been mixed with the water-swellable polymer.

The solution of the post treatment agent is mixed with the powdery, water-swellable, carboxyl-groups-containing polymer and subsequently heated. The powdery polymer may either have a

spherical shape, obtainable by polymerizing emulsified, aqueous monomer solutions, or an irregular shape, obtainable by solvent polymerization, e.g., of a 30% monomer solution comprising 50 to 99 mol-% alkali acrylate, 50 to 1 mol-% acrylic acid, and 0.01 to 0.5 %-wt. of an agent having a cross-linking action. The particle size of the water-swellaable polymer to be treated amounts to 0.05 to 1 mm, preferably 0.1 to 0.8 mm.

The mixture consisting of the solution of the agent and the water-swellaable polymer is manufactured in the laboratory with ordinary mixers, such as those used in the household. In large-scale production, blade mixers or paddle mixers operating continuously or discontinuously are used. The solution of the agent is evenly dosed to the powder preparation or into the powder stream.

The mixture of dissolved, diluted post treatment agent and water-swellaable polymer is subsequently heated to 100 to 250°C, preferably 150 to 210°C. The heating temperature and period depend on the amount of agent, with the treatment period in general amounting to between at least 5 min. and one hour.

The amount of post treatment agent, the mode of feeding, and the treatment temperature are advantageously coordinated in such a way that the duration of treatment permits a continuous performance of the process, i.e., that the required heat-up time does not result in excessive dwell times within the dryer and in the following cooler. Suitable dryers include, e.g., the drying oven or the disk dryer.

A water-swellaable polymer which gives a dry impression after swelling, does not impair the advance of liquid by forming a barrier, and that swells against external load having a high swelling capacity (retention) is obtained. Therefore, the polymer according

to the present invention is particularly suitable for embedding it between paper, non-woven fabrics and in diaper constructions.

The aftertreated polymer obtained is examined as follows:

1.) Liquid absorption

The absorbed amount of liquid per gram of water-swellaable polymer is measured. A weighed polymer quantity is enclosed in a tea bag and dipped into a 0.9% solution of sodium chloride. The amount of absorption is determined after 10 minutes, after the tea bag has been centrifuged at 1400 rpm for 5 minutes in a centrifuge having a diameter of 23 cm; the liquid amount absorbed by the tea bag material is deducted.

$$\text{Amount of absorption } \left(\frac{\text{g}}{\text{g}} \right) = \frac{\text{weight after absorption (g)} - \text{weight of the tea bag (g)}}{\text{weight of the polymer (g)}}$$

(retention)

2.) Liquid absorption under load

The absorption under load (AUL) is determined according to the method described in EP 0 339 461, page 7:

The weighed portion of superabsorber is placed in a cylindrical vessel with sieve bottom, and the powder is stressed with a punch exerting a pressure of 20 g/cm². The cylinder is subsequently placed on a Demand-Absorbency-Tester (DAT) where the superabsorber is allowed to suck 0.9% NaCl-solution for one hour.

3.) Shear Modulus

The shear modulus is measured by means of a Carri-Med-Stress-Rheometer with plate-plate-configuration. In order to

determine the shear modulus, 1 g water-absorbing resin is allowed to swell for one hour in 28 g 0.9% NaCl-solution, and this swollen gel is used to measure the shear modulus in correlation to the frequency (0.1 - 10 Hz). The value at 10 Hz is given as storage modulus G' in N/m².

The present invention will be illustrated in more detail by the following examples:

1.) Manufacture of the agents used according to the present invention for the water-swellaable polymers (N-(hydroxyalkyl) β -(meth)-alanine esters and their polycondensation products:

a) Agent A

10 g ethyl acrylate and 10 g ethanol are weighed into a flask and 6.15 g ethanolamine are added under stirring. The warming solution is allowed to stand for 15 hours to terminate reaction.

b) Agent B

10 g methyl methacrylate and 6.15 g ethanolamine are reacted under stirring at 40°C for 15 hours.

c) Agent C

In a flask, 13 g 2-hydroxypropyl acrylate and 10 g ethanol are stirred-up with 6.2 g ethanolamine at room temperature. The solution is allowed to stand for 18 hours to terminate reaction.

d) Agent D

Preparation A, which is a clear solution, is allowed to stand for 14 days at room temperature. During this period, a fine white precipitate forms which is soluble in alcohol or water. The homogenized suspension is used to treat the polymers.

e) Agent E

100 g ethyl acrylate and 100 g ethanol are mixed in a flask with 61 g ethanolamine under stirring; after 18 hours, the clear solution is liberated from volatile components in a rotary evaporator at a bath temperature of 80°C and a pressure of 20 mbar. A highly viscous oil which is slightly turbid at room temperature and that becomes waxy during standing is obtained.

f) Agent F

100 g ethyl acrylate are added to 61 g monoethanolamine in 200 ml methanol within a flask, and the mixture is stirred for 8 hours. 800 ml methanol and 14 g 25% potassium methylate solution are added into the flask and stirring is continued for 80 hours. The resulting white precipitate is filtered off, stirred up in 500 ml methanol, and filtered off once again. The filter cake is dried at 50°C and 25 mbar.

73.2 g of a white powder melting between 195 and 203°C is obtained.

g) Agent G

1000 ml tetrahydrofuran are placed in a flask; 14 g 25% potassium methylate solution, 62 g monoethanolamine and 100 g ethyl

acrylate are added under stirring. The initially clear solution becomes cloudy and then a soft polycondensate settles down at the bottom of the reactor. The supernatant solution is poured off, and the viscous polycondensate is liberated from adhering volatile components at 25 mbar and 50°C.

Total amine: 2.8 mmol/g.

2) Treatment of the water-swellaable polymers according to the present invention:

Example 1 and 2 and

Comparative Example 1 to 3:

A water-swellaable polymer having the particle size of 0.2 to 0.8 mm, obtained by polymerizing a 29% monomer solution of 90 mol-% sodium acrylate and 10 mol-% acrylic acid in the presence of 0.25%-wt. trimethylolpropane triacrylate (relative to acrylic acid) having an absorbency (retention) for 0.9% NaCl-solution of 40.0 g/g and an absorbency under load (AUL) of 6.9 g/g.

100 g of the water-swellaable polymer are placed in a 500 ml plastic cup and mixed under strong stirring using a single-armed domestic mixer with aftertreatment agent, water, and organic diluting agents (amounts as stated in Table 1) within about 3 min. The mixture is spread in a glass dish at a layer thickness of 5 to 10 mm and heated in a recirculating air dryer. The drying periods and temperatures as well as the test results are listed in Table 1. In Comparative Examples 1 to 3, ethanolamine and glycerol were used as treatment agent.

Table 1

Exam. No.	Water (g)	Diluent (g)	Agent (g)	Time (min)	Temp. (°C)	AUL (g/g)	Retention (g/g)
1	2.0	methanol	E	10	190	24.0	32.6
		2.8	1.3				
2	2.0	methanol	A	20	190	30.9	33.2
		2.4	1.0				
Comparative Example							
1	2.0	methanol	ethanolamine	10	190	6.9	39.6
	"	"	"	20	190	7.5	40.7
2	2.0	methanol	glycerol	20	190	8.2	38.1
	"	"	"	60	190	8.6	39.6
3	2.0	2.8	1.0	30	190	13.8	37.9

Examples 3 to 5

A polymer having the grain size 0.15 to 0.8 mm, obtained by solvent polymerization as in Example 1, with the exception that the monomer mixture consists of 70 mol-% of sodium acrylate and 30 mol-% of acrylic acid. The polymer has a retention of 39.5 g/g and an AUL of 7.6 g/g.

100 g of this powdery polymer are mixed as in Example 1 with solutions of preparation F and heated. The treatment conditions and test results are listed in Table 2.

Table 2

Exam. No.	Water (g)	Diluent (g)	Agent (g)	Time (min)	Temp. (°C)	AUL (g/g)	Retention (g/g)
		methanol					
3	2.0	2.8	0.30	15	180	25.8	37.3
		methanol					
4	2.0	2.8	0.15	15	180	28.6	37.6
		ethanol					
5	2.0	2.8	0.05	20	190	32.6	38.1

Example 6

100 g of the water-swellable polymer used in Example 3 are mixed with a solution of 0.1 g Agent E, 2 g water, and 1.0 g 2-pyrrolidone and heated as in Example 1.

Treatment temp. (°C)	time (min)	AUL (g/g)	Retention (g/g)
190	10	26.2	40.4
190	15	30.4	36.2
190	20	29.2	34.9

Example 7 to 12 and Comparative Example 4

The mixture is prepared with 100 g polymer according to Example 3; the conditions, post treatment agents, treatment temperatures and periods are listed in Table 3.

Table 3

Exam. No.	Water (g)	Solvent (g)	Treatment		Time (min)	AUL (g/g)	Retention (g/g)
			Agent (g)	Temp. (°C)			
7	2.0	-	A 8.58	150	10	27.9	39.0
8	2.0	methanol 2	A 2.11	180	10	30.3	34.1
9	2.0	methanol 2	A 1.05	180	14	31.1	36.0
10	2.0	methanol 2	A 0.52	180	20	28.7	36.1
11	2.0	methanol 2	B 5.27	150	60	31.3	35.4
12	2.0	ethanol 2	C 2.4	150	30	27.3	33.6
Comparative Example							
4	2.0	ethanol 3.85	ethanolamine		30	9.0	
	2.0	3.85	0.5	150	60	10.5	

Example 13

100 g of the water-swellable polymer used in Example 3 ($G' = 1800 \text{ N/m}^2$) are mixed with 5.05 g of a solution of 1.05 g of the homogenized suspension of aftertreatment Agent D, 2.0 g water, and 2.0 g methanol and heated in a recirculating air drying oven.

Treatment time (min)	temp. (°C)	AUL (g/g)	Retention (g/g)	G' (N/m ²)
10	180	26.8	36.7	2350

Example 14 to 16

100 g of a cross-linked polyacrylic acid whose carboxyl groups are present in neutralized form to the extent of 60 mol-% and which has a particle size of 0.2 to 0.85 mm, tradename FAVOR 922, a product by Chemische Fabrik Stockhausen GmbH, Krefeld, FRG, are mixed with a solution of preparation A in 2.0 g water and 2.0 g methanol as in Example 1 and heated in an oven with recirculating air.

Exam.	Agent (g)	Temp. (°C)	Time (min)	AUL (g/g)	Retention (g/g)
FAVOR	-	-	-	9.3	41.9
14	2.1	180	10	25.1	30.2
15	4.2	160	10	26.4	34.5
16	4.2	150	15	28.2	34.1

Example 17

1500 g water-swellaable polymer of the particle size 0.15 to 0.85 mm, manufactured by polymerizing a 29% solution of 70 mol-% sodium acrylate, 30 mol-% acrylic acid and 0.17%-wt. of tri-methylol-propane-triacrylate (relative to acrylic acid) having a

retention of 44.8 g/g and an AUL of 7.2 g/g are filled in a Draismixer. A solution of 1.5 g Agent E, 30 g water, and 15 g 2-pyrrolidone is added dropwise into the moved powder bed. The resulting mixture is heated in a free-falling mixer which has been preheated to 210°C. The heating-up periods and temperatures as well as the test results are listed in Table 4.

Table 4

Time (min)	Temperature (°C)	AUL (g/g)	Retention (g/g)
10	146	heating-up phase	
20	177		
25	183		
30	183	30.2	40.4
40	185	29.6	38.6
50	186	28.7	37.8

Example 18

100 g of the water-swellaable polymer used in Example 3 are mixed with a solution of 0.3 g Agent G in 2.0 g water and 2.8 g methanol; the mixture is spread out in a glass dish and stored in a drying oven at 190°C for 15 min. The product cooled to room temperature does not block during swelling, has an AUL of 33.5 g/g and a retention of 37.7 g/g.

Example 19

100 g of the water-swellaable polymer used in Example 3 are mixed with a solution of 0.1 g Agent E in 2.0 g water and 1.0 g diacetin.

For drying purposes, the powdery product is placed in a drying oven preheated to 190°C.

An AUL of 29.9 g/g is measured after cooling.

Example 20

A cross-linked, water-swellaable polymer having the particle size of 0.15 to 0.80 mm and the composition according to Example 3 is used. The polymer has a retention of 35.5 g/g, an AUL of 9.4 g/g and a storage modulus of 2600 N/m².

A mixture of 1.5 g preparation, manufactured as Agent A without ethanol used as diluent, 30 g water and 30 g diacetin is mixed as described in Example 17 with 1500 g of the powdery polymer and heated. After a treatment period of 20 min at 183 to 185°C, the polymer has the following characteristics:

Retention	= 30.7 g/g
AUL	= 31.1 g/g
G'	= 5300 N/m ²

Example 21

100 g of a cross-linked polyacrylic acid whose carboxyl groups are neutralized by 70 mol-% and which has a retention of 47.5 g/g and an AUL of 8.4 g/g, are treated with 4.1 g of the treatment mixture according to Example 20 and stored at a layer thickness of 3 mm in a drying oven preheated to 240°C for 10 min. The obtained polymer has a retention of 35.5 g/g and an AUL of 24.4 g/g.



C L A I M S for the Contracting States:

AT, BE, CH, DE, DK, FR, GB, IT, LU, LI, MC, NL, PT, SE

1. A powdery absorbent for aqueous liquids based on a water-swallowable powdery polymer, obtainable by manufacturing and heating a mixture consisting of 100 parts by weight of at least one water-swallowable carboxyl-groups-containing polymer comprising at least 0.2 equivalents of carboxyl groups per 100 parts by weight which are neutralized to the extent of 50 to 99 mol-%,

a) 0.001 to 5 parts by weight, preferably 0.05 to 2 parts by weight of N-(hydroxyalkyl) β -(meth)-alanine esters and/or

b) 0.001 to 5 parts by weight, preferably 0.05 to 2 parts by weight of polycondensation products of a) in

c) 0.1 to 5 parts by weight of water and

d¹) 0.2 to 10 parts by weight of a water-miscible organic diluting agent which evaporates on heating the mixture and/or

d²) 0.2 to 10 parts by weight of a water-miscible organic diluting agent which does not evaporate on heating the mixture.

2. The powdery absorbent according to claim 1 obtained by heating the mixture according to claim 1 to 100 to 250°C, preferably to 150 to 210°C.

3. The powdery absorbent according to claim 1 and 2 obtained by using β -(meth)-alanine esters substituted at the nitrogen atom by hydroxy-C₁-C₆-alkyl groups.



4. The powdery absorbent according to any one of claims 1 to 3 obtained by using N-(hydroxyalkyl)-substituted β -(meth)alanine- C_1 - C_8 -alkyl esters or - C_1 - C_8 -hydroxyalkyl esters.
5. The powdery absorbent according to any one of claims 1 to 4 obtained by using water-soluble polyamides of N-(hydroxyalkyl) β -(meth-)alanine esters.
6. The powdery absorbent according to any one of claims 1 to 4 obtained by using water-soluble polyamide ethers of N-(hydroxy-alkyl) β -(meth-)alanine esters.
7. The powdery absorbent according to any one of claims 1 to 6 in which at least 80 mol-% of the polymer are neutralized.