**Date de dépôt PCT/PCT Filing Date:** 2000/04/11

**Date publication PCT/PCT Publication Date:** 2000/10/26

**Entrée phase nationale/National Entry:** 2001/10/19

**N° demande PCT/PCT Application No.:** EP 2000/003220

**N° publication PCT/PCT Publication No.:** 2000/063295

**Priorités/Priorities:** 1999/04/20 (199 17 919.0) DE; 1999/07/08 (199 31 720.8) DE

**Cl.Int. 7/Int.Cl. 7:** C08L 101/14, C08J 3/24

**Demandeur/Applicant:** BASF AKTIENGESELLSCHAFT, DE

**Inventeurs/Inventors:**
- RIEGEL, ULRICH, DE;
- HERFERT, NORBERT, DE;
- HAHNLE, HANS-JOACHIM, DE;
- SCHRODER, ULRICH, DE;
- DYLICK-BRENZINGER, RAHNER, DE

**Agent:** BORDEN LADNER GERVEILL LLP

---

**Titre :** MELANGE POLYMERE FORMANT UN HYDROGEL

**Title:** HYDROGEL-FORMING POLYMER MIXTURE

**Abrégé/Abstract:**
The invention relates to a hydrogel-forming polymer mixture containing a) a hydrogel-forming polymer I with acid rests and b) a hydrogel-forming polymer II with amino and/or imino rests. The ratio of acid rests to the sum of amino/imino rests is between 1: 9 and 9: 1. The invention also relates to the use of said mixture in absorbent hygiene articles.
Abstract

A hydrogel-forming polymer mixture including

a) a hydrogel-forming polymer I containing acid radicals and

b) a hydrogel-forming polymer II containing amino and/or imino radicals,

wherein the ratio of said acid radicals to the sum total of said amino/imino radicals is within the range from 1:9 to 9:1, is useful in absorbent hygiene articles.
Hydrogel-forming polymer mixture

The present invention relates to hydrogel-forming polymer mixtures including

a) a hydrogel-forming polymer I containing acid radicals and

b) a hydrogel-forming polymer II containing amino and/or imino radicals,

wherein the ratio of said acid radicals to the sum total of said amino/imino radicals is within the range from 1:9 to 9:1,

and to the use of these mixtures in absorbent hygiene articles.

The development of new hydrogel-forming polymers, often referred to as superabsorbents, having better absorbent properties continues to be of substantial commercial interest, since it is especially in the sector of the disposable hygiene articles such as diapers or incontinence pads where good absorbent properties are associated with high wear comfort. In addition, better superabsorbents permit the use of lower wood pulp quantities, which makes it possible to manufacture thinner hygiene articles and hence is of commercial importance, since it reduces packaging and transportation costs.

Superabsorbents frequently provide satisfactory results with regard to their absorption capacity for deionized water, but they perform less satisfactorily on exchange for body fluids such as urine. This "poisoning" of the superabsorbent is generally attributed to the salt content of body fluids.

To minimize this effect, WO 96/15162, WO 96/15163, WO 96/17681 and WO 98/37149 propose a superabsorbent material comprised of an anionic superabsorbent material and a cationic superabsorbent material, the cationic superabsorbent material having polymer units which are quaternary amine functions and are attributable to bisallylbisalkylammonium ions.

WO 92/20735, WO 96/15180, DE-A-19640329 and WO 98/24832 describe mixtures of anionic and cationic superabsorbent materials, the latter possessing quaternary amine functions, i.e., not being deprotonatable. The polydiallyldimethylammonium hydroxide used therein has to be prepared by polymerization of the corresponding chloride and subsequently has to be first converted into the
hydroxide form (by extensive washing with sodium hydroxide solution) before it can be mixed with the anionic superabsorbent material after drying.

It is further necessary to prevent the gel blocking effect of reduced transmission of fluid into lower superabsorbent layers, so that US 5,599,335, US 5,669,894 and US 5,562,646 describe a test method which relates to this requirement (Saline Flow Conductivity SFC) and the requirements profile resulting therefrom.

EP-A-0210756 teaches an absorbent mixture of a cation exchange material and an anion exchange material where the material is in both cases a modified cellulosic fiber.

It is an object of the present invention to provide a novel hydrogel-forming polymer mixture having good absorption properties, good distribution properties and high mechanical stability.

We have found that this object is achieved by the abovementioned polymer mixtures.

Hydrogel-forming polymers I are water-insoluble polymers having free acid groups. Preference is given to crosslinked polyacids, especially polycarboxylic acids, which may partly be in the form of the salt. Preference is given to polymers I having an acid group density (meq/g) > 4, especially > 8, in particular > 12.

Preference is given to polymers I which are prepared by crosslinking polymerization or copolymerization of monoethylenically unsaturated monomers bearing acid groups. Alternatively, monoethylenically unsaturated monomers bearing acid groups may be (co)polymerized without crosslinker and crosslinked subsequently.

Examples of such monomers bearing acid groups are monoethylenically unsaturated C3- to C25-carboxylic acids or anhydrides such as acrylic acid, methacrylic acid, ethacrylic acid, α-chloroacrylic acid, crotonic acid, maleic acid, maleic anhydride, itaconic acid, citraconic acid, mesaconic acid, glutaric acid, aconitic acid and fumaric acid. It is also possible to use monoethylenically unsaturated sulfonic or phosphonic acids, for example vinylsulfonic acid, allylsulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-acryloyloxypropylsulfonic acid,
2-hydroxy-3-methacyrloyloxypropylsulfonic acid, vinylsulfonic phosphonic acid, allylphosphonic acid, styrenesulfonic acid and 2-acrylamido-2-methylpropanesulfonic acid. The monomers may be used alone or mixed.

Preferred monomers are acrylic acid, methacrylic acid, vinylsulfonic acid, acrylamidopropanesulfonic acid or mixtures thereof, for example mixtures of acrylic and methacrylic acid, mixtures of acrylic acid and acrylamidopropanesulfonic acid or mixtures of acrylic acid and vinylsulfonic acid.

To optimize properties, it can be sensible to use additional monoethylenically unsaturated compounds which do not bear an acid group but are copolymerizable with the monomers bearing acid groups. Such compounds include for example the amides and nitriles of monoethylenically unsaturated carboxylic acids, for example acrylamide, methacrylamide and N-vinylformamide, N-vinylacetamide, N-methyl-N-vinylacetamide, acrylonitrile and methacrylonitrile. Examples of further suitable compounds are vinyl esters of saturated C₁⁻ to C₄⁻carboxylic acids such as vinyl formate, vinyl acetate or vinyl propionate, alkyl vinyl ethers having at least 2 carbon atoms in the alkyl group, for example ethyl vinyl ether or butyl vinyl ether, esters of monoethylenically unsaturated C₃⁻ to C₆⁻carboxylic acids, for example esters of monohydric C₁⁻ to C₁₈⁻alcohols and acrylic acid, methacrylic acid or maleic acid, monoesters of maleic acid, for example methyl hydrogen maleate, N-vinylactams such as N-vinylpyrrolidone or N-vinylcaprolactam, acrylic and methacrylic esters of alkoxylated monoethylic saturated alcohols, for example of alcohols having from 10 to 25 carbon atoms which have been reacted with from 2 to 200 mol of ethylene oxide and/or propylene oxide per mole of alcohol, and also monoacrylic esters and monomethacrylic esters of polyethylene glycol or polypropylene glycol, the molar masses (Mₙ) of the polyalkylene glycols being up to 2000, for example. Further suitable monomers are styrene and alkyl-substituted styrenes such as ethylstyrene or tert-butylstyrene.

These monomers without acid groups may also be used in mixture with other monomers, for example mixtures of vinyl acetate and 2-hydroxyethyl acrylate in any proportion. These monomers without acid groups are added to the reaction mixture in amounts within the range from 0 to 80% by weight, preferably less than 50% by weight.
Possible crosslinkers include compounds containing at least 2 ethylenically unsaturated double bonds. Examples of compounds of this type are N,N′-methylenebisacrylamide, polyethylene glycol diacrylates and polyethylene glycol dimethacrylates each derived from polyethylene glycols having a molecular weight of from 106 to 8500, preferably from 400 to 2000, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, ethylene glycol diacrylate, propylene glycol diacrylate, butanediol diacrylate, hexanediol diacrylate, hexanediol dimethacrylate, allyl methacrylate, diacrylates and dimethacrylates of block copolymers of ethylene oxide and propylene oxide, polyhydric alcohols, such as glycerol or pentaerythritol, doubly or trebly esterified with acrylic acid or methacrylic acid, triallylamine, tetraallylethylene diamine, divinylbenzene, diallyl phthalate, polyethylene glycol divinyl ethers of polyethylene glycols having a molecular weight of from 126 to 4000, trimethylolpropane diallyl ether, butanediol divinyl ether, pentaerythritol triallyl ether and/or divinylethyleneurea. Preference is given to using water-soluble crosslinkers, for example N,N′-methylenebis-acrylamide, polyethylene glycol diacrylates and polyethylene glycol dimethacrylates derived from addition products of from 2 to 400 mol of ethylene oxide with 1 mol of a diol or polyl, vinyl ethers of addition products of from 2 to 400 mol of ethylene oxide with 1 mol of a diol or polyl, ethylene glycol diacrylate, ethylene glycol dimethacrylate or triacrylates and trimethacrylates of addition products of from 6 to 20 mol of ethylene oxide with 1 mol of glycerol, pentaerythritol triallyl ether and/or divinylethyleneurea.

Possible crosslinkers also include compounds containing at least one polymerizable ethylenically unsaturated group and at least one further functional group. The functional group of these crosslinkers has to be capable of reacting with the functional groups, essentially the acid groups, of the monomers. Suitable functional groups include for example hydroxyl, amino, epoxy and aziridino groups. Useful are for example hydroxyalkyl esters of the abovementioned monoethenically unsaturated carboxylic acids, e.g., 2-hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and hydroxybutyl methacrylate, dialkyldiallylammonium halides such as dimethyldiallylammonium chloride, diethyldiallylammonium chloride, allylpiperidinium bromide, N-vinylimidazoles, for example N-vinylimidazole, 1-vinyl-2-methyldimazole and N-vinylimidazolines such as N-vinylimidazoline, 1-vinyl-2-methyldimazoline, 1-vinyl-2-ethylimidazoline or 1-vinyl-2-propylimidazoline, which can be used in the form of the free bases, in quaternized form or as salt in the
polymerization. It is also possible to use dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates such as dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate and diethylaminoethyl methacrylate. The basic esters are preferably used in quaternized form or as salt. It is also possible to use glycidyl (meth)acrylate, for example. Crosslinkers are present in the reaction mixture for example from 0.001 to 20%, preferably from 0.01 to 14%, by weight.

The polymerization is initiated in the generally customary manner, by means of an initiator. Any initiator forming free radicals under the polymerization conditions can be used which is customarily used in the production of superabsorbents. The polymerization may also be initiated by electron beams acting on the polymerizable aqueous mixture. However, the polymerization may also be initiated in the absence of initiators of the abovementioned kind, by the action of high energy radiation in the presence of photoinitiators. Useful polymerization initiators include all compounds which decompose into free radicals under the polymerization conditions, for example peroxides, hydroperoxides, hydrogen peroxide, persulfates, azo compounds and redox catalysts. The use of water-soluble initiators is preferred. In some cases it is advantageous to use mixtures of different polymerization initiators, for example mixtures of hydrogen peroxide and sodium peroxodisulfate or potassium peroxodisulfate. Mixtures of hydrogen peroxide and sodium peroxodisulfate may be used in any proportion. Examples of suitable organic peroxides are acetylaceton peroxide, methyl ethyl ketone peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, tert-amyl perpivalate, tert-butyl perpivalate, tert-butyl perneohexanoate, tert-butyl perisobutyrate, tert-butyl per-2-ethylhexanoate, tert-butyl perisononanoate, tert-butyl permaleate, tert-butyl perbenzoate, di(2-ethylhexyl)

peroxydicarbonate, dicyclohexyl peroxydicarbonate, di(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, diacetyl peroxydicarbonate, allyl peresters, cumyl peroxyneodecanoate, tert-butyl per-3,5,5-trimethylhexanoate, acetyl cyclohexylsulfonyl peroxide, dilauryl peroxide, dibenzoyl peroxide and tert-amyl perneodecanoate. Particularly suitable polymerization initiators are water-soluble azo initiators, e.g., 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethylene)isobutyramidine dihydrochloride, 2-(carbamoylazo)isobutyronitrile, 2,2'-azobis[2-(2'-imidazolin-2-yl)propane] dihydrochloride and 4,4'-azobis(4-cyanovaleric acid). The polymerization initiators
mentioned are used in customary amounts, for example in amounts of from 0.01 to 5%, preferably from 0.1 to 2.0%, by weight, based on the monomers to be polymerized.

5 Useful initiators also include redox catalysts. In redox catalysts, the oxidizing component is at least one of the above-specified per compounds and the reducing component is for example ascorbic acid, glucose, sorbose, ammonium or alkali metal bisulfite, sulfite, thiosulfate, hyposulfite, pyrosulfite or sulfide, or a metal salt, such as iron(II) ions or silver ions or sodium hydroxymethylsulfoxylate. The reducing component in the redox catalyst is preferably ascorbic acid or sodium sulfite. Based on the amount of monomers used in the polymerization, from \(3 \times 10^{-6}\) to 1 mol% may be used for the reducing component of the redox catalyst system and from 0.001 to 5.0 mol% for the oxidizing component of the redox catalyst, for example.

When the polymerization is initiated using high energy radiation, the initiator used is customarily a photoinitiator.

20 Photoinitiators include for example α-splitters, H-abstracting systems or else azides. Examples of such initiators are benzophenone derivatives such as Michler’s ketone, phenanthrene derivatives, fluorene derivatives, anthraquinone derivatives, thioxanethione derivatives, coumarin derivatives, benzoin ethers and derivatives thereof, azo compounds such as the abovementioned free-radical formers, substituted hexaarylbisimidaozoles or acylphosphate oxides. Examples of azides are:

2-(N,N-dimethylamino)ethyl 4-azidocinnamate,
2-(N,N-dimethylamino)ethyl 4-azidonaphthyl ketone,
2-(N,N-dimethylamino)ethyl 4-azidobenzoate, 5-azido-1-naphthyl
2′-(N,N-dimethylamino)ethyl sulfone,
N-(4-sulfonylazidophenyl)maleimide,
N-acetyl-4-sulfonylazidoaniline, 4-sulfonylazidoaniline,
4-azidoaniline, 4-azidophenacyl bromide, p-azidobenzoic acid,
2,6-bis(p-azidobenzylidene)cyclohexanone and
2,6-bis(p-azidobenzylidene)-4-methylcyclohexanone.

35 Photoinitiators, if used, are customarily used in amounts of from 0.01 to 5% of the weight of the monomers to be polymerized.

40 Subsequent crosslinking involves a reaction between polyacids, formed by polymerization of the abovementioned monoethylenically unsaturated acids and optionally monoethylenically unsaturated comonomers and having a molecular weight of above 5000, preferably above 50,000, and compounds which contain at least two groups reactive toward acid groups. This reaction can take place at room temperature or else at elevated temperatures up to 200°C.
Suitable functional groups were already mentioned above, i.e., hydroxyl, amino, epoxy, isocyanate, ester, amido and aziridino groups. Examples of such crosslinkers are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, polyglycerol, propylene glycol, polypropylene glycol, block copolymers of ethylene oxide and propylene oxide, sorbitan fatty acid esters, ethoxylated sorbitan fatty acid esters, trimethylolpropane, pentaerythritol, 1,3-butanediol, 1,4-butanediol, polyvinyl alcohol, sorbitol, polyglycidyl ethers such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol diglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, pentaerythritol polyglycidyl ether, propylene glycol diglycidyl ether and polypropylene glycol diglycidyl ether, polyaziridine compounds such as 2,2-bishydroxymethylbutanol tris[3-(1-aziridinyl)propionate], 1,6-hexamethylenediethyleneurea, diphenylmethanebis-4,4'-N,N'-diethyleneurea, hydroxy epoxy compounds such as glycidol, halo epoxy compounds such as epichlorohydrin and α-methyleneplifluorohydrin, polyisocyanates such as 2,4-tolylene diisocyanate and hexamethylene diisocyanate, alkylene carbonates such as 1,3-dioxolan-2-one and 4-methyl-1,3-dioxolan-2-one, also bisoxazolines and oxazolidones, also polyquaternary amines such as condensation products of dimethylamine with epichlorohydrin, homo- and copolymers of diallyldimethylammonium chloride and also homo- and copolymers of dimethylaminooethyl (meth)acrylate which are optionally quaternized with, for example, methyl chloride.

Further suitable crosslinkers for postcrosslinking are polyvalent metal ions capable of forming ionic crosslinks. Examples of such crosslinkers are magnesium, calcium, barium and aluminum ions. These crosslinkers are added for example as hydroxides, carbonates or bicarbonates to the aqueous polymerizable solution. Further suitable crosslinkers are multifunctional bases likewise capable of forming ionic crosslinks, for example polyamines or their quaternized salts. Examples of polyamines are ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine and polyethylenimines and also polyvinylamines having molar masses of up to 4,000,000 in each case.

Crosslinkers are added to polyacrylic acid or the polyacrylic acid salts in amounts of from 0.5 to 25% by weight, preferably from 1 to 15% by weight, based on the amount of polyacids used. The crosslinked polyacids are preferably used in the polymer
mixture of the invention in non-neutralized form. It may nevertheless be advantageous to partly neutralize the acid functions. The degree of neutralization will be essentially less than 50%, preferably less than 30%. Useful neutralizing agents include:

alkali metal bases or ammonia/amines. Preference is given to the use of sodium hydroxide solution or potassium hydroxide solution. However, neutralization may also be effected using sodium carbonate, sodium bicarbonate, potassium carbonate or potassium bicarbonate or other carbonates or bicarbonates or ammonia. Moreover primary, secondary and tertiary amines may be used.

Industrial processes useful for making these products include all processes which are customarily used to make superabsorbents, as described for example in Chapter 3 of “Modern Superabsorbent Polymer Technology”, F.L. Buchholz and A.T. Graham, Wiley-VCH, 1998.

Polymerization in aqueous solution is preferably conducted as a gel polymerization. It involves 10-70% strength by weight aqueous solutions of the monomers and optionally of a suitable grafting base being polymerized in the presence of a free-radical initiator by utilizing the Trommsdorff-Norrish effect.

The polymerization reaction may be carried out at from 0 to 150°C, preferably at from 10 to 100°C, not only at atmospheric pressure but also at superatmospheric or reduced pressure. As is customary, the polymerization may also be conducted in a protective gas atmosphere, preferably under nitrogen.

By subsequently heating the polymer gels at from 50 to 130°C, preferably at from 70 to 100°C, for several hours, the performance characteristics of the polymers can be further improved.

Useful polymers I further include graft copolymers of one or more hydrophilic monomers on a suitable grafting base, crosslinked cellulose or starch ethers and esters bearing acid groups, crosslinked carboxymethylcellulose, or natural products having acid groups and capable of swelling in aqueous fluids, for example alginates and carrageenans.

Useful grafting bases may be of natural or synthetic origin. Examples are starch, cellulose or cellulose derivatives and also other polysaccharides and oligosaccharides, polyvinyl alcohol, polyalkylene oxides, especially polyethylene oxides and polypropylene oxides, polyamines, polyamides and also hydrophilic
polyesters. Suitable polyalkylene oxides conform for example to the formula

\[
\begin{align*}
X \\
R^1 - O - (CH_2 - CH - O)_n - R^2
\end{align*}
\]

where

10 R\(^1\) and R\(^2\) are independently hydrogen, alkyl, alkenyl or aryl, X is hydrogen or methyl, and n is an integer from 1 to 10,000.

R\(^1\) and R\(^2\) are each preferably hydrogen, (C\(_1\)-C\(_4\))-alkyl, (C\(_2\)-C\(_6\))-alkenyl or phenyl.

With regard to polymer II, the term amino is used herein in accordance with the IUPAC rules as meaning primary amino groups and not amido groups, which are formed when the NH\(_2\) radical combines with a carbonyl radical. Correspondingly, imino is used herein in accordance with the IUPAC rules as meaning secondary amino groups (-NH-) and not imido groups, in which the NHR radical has been combined with a carbonyl radical.

Useful hydrogel-forming polymers II include the following amino- and/or imino-bearing polymers which have been rendered water-insoluble through crosslinking. Preferred polymers are polymers and copolymers, including graft copolymers, of "vinylamine" or ethyleneimine with or without polymer-analogous modification.

a) So-called polyvinylamines, i.e., polymers containing -CH\(_2\)-CH(NH\(_2\))-group as characteristic building block, are obtainable via polymer-analogous reactions. Examples of such polymer-analogous reactions known to one skilled in the art include the hydrolysis of poly-N-vinylamides such as poly-N-vinylformamide, poly-N-vinylacetamide and of poly-N-vinylimides such as poly-N-vinylsuccinimide and poly-N-vinylphthalimide and the Hofmann degradation of polyacrylamide under the action of basic hypochlorite.

Polyvinylamines are preferably prepared by polymerization of N-vinylformamide and subsequent polymer-analogous reaction as described in DE-A-3 128 478. The molar mass of the uncrosslinked polyvinylamine corresponds to a K value (determined by the method
of H. Fikentscher on a 5% by weight aqueous NaCl solution at 25°C containing 1% by weight of polymer) of 30-250.

The N-vinylformamide units of the polymers can be hydrolyzed to the corresponding polymers comprising vinylamine units by acidic, basic or enzymatic hydrolysis. Completely hydrolyzing for example a homopolymer of N-vinylformamide results in polyvinylamine. Basic hydrolysis is particularly preferred. It provides degrees of hydrolysis of for example from 5 to 95%. Particular preference is given to products having a degree of hydrolysis of from 70 to 100 and most preference is given to fully hydrolyzed products, i.e., maximally 100%, customarily 95%. The degree of hydrolysis is determined for example by enzymatic determination of the formate or by polyelectrolyte titration of the available amine functions with potassium polyvinyl sulfate solution.

Crosslinked polyvinylamines used as polymers II are preferably desalted beforehand. Desalted means in this context that the salt content in terms of low molecular weight salts (molecular weight < 500) is ≤ 8% by weight based on the polymer. Desalting is effected for example by means of dialysis or ultrafiltration processes using a membrane having an exclusion limit of 3000 D. The degree of desalting may be verified using gel permeation chromatography (GPC). Desalting is advantageously carried out after the polymer-analogous reaction and before the crosslinking reaction.

Desalted polymer solutions II are customarily crosslinked in aqueous solution. The polymer content of an aqueous solution is generally within the range from 2 to 50% by weight. More concentrated polymer solutions may be crosslinked by adding polar aprotic solvents such as dimethyl sulfoxide or N-methylpyrrolidone.

As mentioned above, preference is given to polymers II obtained by crosslinking polyvinylamine having a K value of 30-250, preferably 50-230, especially 70-200. Since high molecular weight polyvinylamines are slow to crosslink and may not crosslink completely, particular preference is given to crosslinking polyvinylamines which have a K value of 70-180 in the uncrosslinked state.

Useful hydrogel-forming polymers II further include copolymers of "vinylamine", i.e., copolymers formed, for example, from vinylformamide and comonomers and converted into formal
copolymers of vinylamine by the above-described polymer-analogous reactions.

Useful copolymers include in principle all monomers copolymerizable with vinylformamide. The following monounsaturated monomers may be mentioned by way of example:

acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl propionate, styrene, ethylene, propylene,

N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, monomers containing sulfone or phosphonate groups, vinylglycol, acrylamido(methacrylamido)alkylenetrialkylammonium salt, diallyldialkylammonium salts, (C₁-C₄)-alkyl vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, isopropyl vinyl ether,

N-propyl vinyl ether, t-butyl vinyl ether, N-substituted alkyl(meth)acrylamides substituted by (C₁-C₄)-alkyl group such as N-methylacrylamide, N-isopropylacrylamide and N,N-dimethylacrylamide and also (C₁-C₂₀)-alkyl (meth)acrylates such as methyl acrylate, ethyl methacrylate, propyl acrylate,

butyl acrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, 2-methylbutyl acrylate, 3-methylbutyl acrylate, 3-pentyl acrylate, neopentyl acrylate, 2-methylpentyl acrylate, hexyl acrylate, cyclohexyl acrylate,

2-ethylhexyl acrylate, phenyl acrylate, heptyl acrylate, benzyl acrylate, tolyl acrylate, octyl acrylate, 2-octyl acrylate, nonyl acrylate and octyl methacrylate.

Specific copolymers are to be mentioned in detail. For instance, DE-A-3 534 273 describes copolymers of N-vinylformamide with vinyl acetate, vinyl propionate, (C₁-C₄)-alkyl vinyl ethers, methacrylic and acrylic esters, acrylonitrile and acrylamide and also homologs thereof and vinylpyrrolidone.

The concentration of N-vinylformamide can be 10-95 mol%, that of the comonomers 5-90 mol%.

Useful polymers further include graft polymers formed from alkylene oxide units and N-vinylformamide as described in DE-A-1 951 5943 and crosslinked after hydrolysis. Such graft polymers are preparable by free-radical polymerization of N-vinylformamide in the presence of, for example, polyethylene glycols and subsequent basic saponification.

Further advantageous grafting bases are polyvinyl acetate and/or polyvinyl alcohol. According to DE-A-19 526 626, N-vinylformamide can be grafted onto these polymers by free-radical polymerization
and the resulting polymer subjected to hydrolysis with or without desalting and subsequent crosslinking to form polymers II.

Useful grafting bases for N-vinylformamide further include copolymers of vinyl acetate, acrylic acid, methacrylic acid, acrylamide and acrylonitrile. Furthermore, according to DE-A-4 127 733, mono-, oligo- and polysaccharides with or without oxidative, enzymatic or hydrolytic degradation are advantageous grafting bases for N-vinylformamide whose weight fraction is from 20 to 95% based on the total amount of monomer + grafting base. These graft polymers are subsequently converted into the free amines by hydrolysis, optionally desalted and finally crosslinked to form polymers II.

Graft polymers are preferably formed using N-vinylformamide as sole monomer. However, it is possible to replace up to 50% by weight of the N-vinylformamide with the abovementioned comonomers of N-vinylformamide.

Moreover, polyvinylamines and their copolymers, including graft copolymers, may be modified by further polymer-analogous reactions. These reactions are various and may be found in any textbook of organic chemistry, for example "Advanced Organic Chemistry" by Jerry March, 3rd edition, John Wiley & Sons 1985.

Of the many possible reactions involving primary amines, some will now be mentioned by way of illustration. Vicinal amino groups of polyvinylamine react in the presence of formic acid or orthoformates to form six-membered cyclic amidines, as described for example in US-A 5 401 808. It may thus well be the case that some of the amino groups will have reacted with vicinal formamide groups to form cyclic amidine structures. Similarly, according to DE-A 4 328 975, copolymers of acrylonitrile, methacrylonitrile or their homologs and acrylic and methacrylic esters with N-vinylformamide may (during or after the hydrolysis of the formamide groups to the corresponding amino groups) react with adjacent nitrile or carboxylic ester groups in intramolecular condensation reactions to form the corresponding 2-amino-1-imidazoline or the corresponding γ-lactam structures.

The fraction of polymer-analogously converted amino groups can be up to 50 mol%.

As well as these intramolecular, polymer-analogous reactions of polyvinylamines, there are a large number of further possible reactions of this type. These include amidation, alkylation, sulfonamide formation, urea formation, thiourea formation, carbamate formation, acylation with acids, lactones, acid
anhydrides and acyl chlorides, thiocarbamation, carboxymethylation, phosphonomethylation and Michael addition, to name but a few. Polyvinylamine derivatives prepared in this way are likewise useful for preparing crosslinked polymers II. The polymer-analogous reactions are preferably carried out prior to the crosslinking of the polyvinylamines and the copolymers (including graft copolymers) of "vinylamine". The fraction of polymer-analogously converted amino groups is up to 50%, preferably from 10 to 30 mol%, of the amino groups in the polymer used. Polymers obtained by subsequent crosslinking are preferred, especially those which were desalted prior to the crosslinking step.

b) It is further possible to use polyethyleneimines, ethyleneimine-grafted polyamidoamines or ethyleneimine-grafted polyamines and also reaction products of these classes of polymer with \( \alpha,\beta \)-unsaturated carboxylic acids or esters or reaction products with the reaction products of formaldehyde with HCN or formaldehyde with alkali metal cyanides (Strecker reaction) and, if appropriate, subsequent hydrolysis to the corresponding carboxylic acids.

A further class of polymers containing amino groups, preferably ethyleneimine units, is known from WO-A-94/12560. They are water-soluble crosslinked partly amidated polyethyleneimines which are obtainable by

- reaction of polyethyleneimines with monobasic carboxylic acids or their esters, anhydrides, acyl chlorides or amides with amide formation and

- reaction of the amidated polyethyleneimines with crosslinkers containing at least two functional groups.

The molar masses of useful polyethyleneimines may range up to 5 million and are preferably within the range from 1000 to 1 million. Polyethyleneimines are partially amidated with monobasic carboxylic acids so that, for example, from 0.1 to 90%, preferably from 1 to 50%, of the amidatable nitrogen atoms in the polyethyleneimines are present as amide group. Useful crosslinkers containing at least two functional groups are mentioned above. Preference is given to using halogen-free crosslinkers.
Amino-containing compounds may be reacted with crosslinkers by using from 0.1 to 50, preferably from 1 to 5, parts by weight of at least one crosslinker per 1 part by weight of amino-containing compound.

Other amino-containing addition products useful after crosslinking as components in superabsorbents are polyethyleneimines and also quaternized polyethyleneimines. Polyethyleneimines and quaternized polyethyleneimines may, if appropriate, be reacted with a crosslinker containing at least two functional groups. Polyethyleneimines may be quaternized, for example, with alkyl halides such as methyl chloride, ethyl chloride, hexyl chloride, benzyl chloride or lauryl chloride and also with, for example, dimethyl sulfate. These reaction products have to be desalted, if necessary. Further useful amino-containing polymers are polyethyleneimines modified by Strecker synthesis, for example the reaction products of polyethyleneimines with formaldehyde and sodium cyanide with hydrolysis of the resulting nitriles to the corresponding carboxylic acids. These products may, if appropriate, be reacted with a crosslinker containing at least two functional groups or may crosslink with themselves by amide formation and elimination of water.

Also useful are alkoxyalted polyethyleneimines obtainable for example by reacting polyethyleneimine with ethylene oxide and/or propylene oxide. Alkoxyalted polyethyleneimines are reacted with a crosslinker containing at least two functional groups to render them water-insoluble. Alkoxyalted polyethyleneimines contain from 0.1 to 100, preferably 1-3, alkylene oxide units per NH group. Polyethyleneimines may have a molar mass of up to two million. Polyethyleneimines used for alkoxylation preferably have molar masses of from 1000 to 50,000. Further useful water-soluble amino-containing polymers are reaction products of polyethyleneimines with diketenes, for example of polyethyleneimines having a molar mass of from 1000 to 50,000 with distearyldiketene, which are subsequently crosslinked.

Crosslinked polyethyleneimines are described for example in EP 0895 521.

Polyethyleneimine is prepared in a conventional manner by cationic polymerization of ethyleneimine in the presence of polymerization catalysts such as acids, Lewis acids, acidic metal salts or alkylating reagents. Polyethyleneimines having a molecular weight of from 1000 to 5,000,000 (determined by static
light scattering, for example) are preferably crosslinked to form polymers II.

Crosslinkers for preparing said hydrogel-forming polymers II are bi- or polyfunctional, i.e., they have two or more active groups capable of reacting with the amino or imino radicals of the polymers. As well as low molecular weight crosslinkers, useful crosslinkers further include polymers and copolymers, which are preferably water-soluble.

Useful bi- or polyfunctional crosslinkers include for example

(1) di- and polyglycidyl compounds
(2) di- and polyhalogen compounds
(3) compounds having two or more isocyanate groups, which may be blocked
(4) polyaziridines
(5) carbonic acid derivatives
(6) compounds having two or more activated double bonds capable of undergoing a Michael addition
(7) di- and polycarboxylic acids and acid derivatives thereof
(8) monoethylenically unsaturated carboxylic acids, esters, amides and anhydrides
(9) di- and polyaldehydes and di- and polyketones.

Preferred crosslinkers (1) are for example the bischlorohydrin ethers of polyalkylene glycols described in US-A-4 144 123. Phosphoric acid diglycidyl ether and ethylene glycol diglycidyl ether are also suitable.

Further crosslinkers are the products of reacting at least trihydric alcohols with epichlorohydrin to form reaction products having at least two chlorohydrin units, polyhydric alcohols used being for example glycerol, ethoxylated or propoxylated glycerols, polyglycerols having 2 to 15 glycerol units in the molecule and also optionally ethoxylated and/or propoxylated polyglycerols. Crosslinkers of this type are known from DE-A-2 916 356 for example.

Useful crosslinkers (2) are α,ω- or vicinal dichloroalkanes, for example 1,2-dichloroethane, 1,2-dichloropropane, 1,3-dichlorobutane and 1,6-dichlorohexane.

Further, EP-A-0 025 515 discloses α,ω-dichloropolyalkylene glycols having preferably 1-100, especially 1-100 ethylene oxide, units for use as crosslinkers.
Useful crosslinkers further include crosslinkers (3) which contain blocked isocyanate groups, for example trimethylhexamethylene diisocyanate blocked with 2,2,6,6-tetramethylpiperidin-4-one. Such crosslinkers are known; cf. for example from DE-A-4 028 285.

Preference is further given to crosslinkers (4) which contain aziridine units and are based on polyethers or substituted hydrocarbons, for example 1,6-bis-N-aziridinomethane, cf. US-A-3 977 923. This class of crosslinkers further includes products formed by reacting dicarboxylic esters with ethyleneimine and containing at least two aziridino groups, and mixtures thereof.

Useful halogen-free crosslinkers of group (4) include reaction products prepared by reacting ethyleneimine with dicarboxylic esters completely esterified with monohydric alcohols of from 1 to 5 carbon atoms. Examples of suitable dicarboxylic esters are dimethyl oxalate, diethyl oxalate, dimethyl succinate, diethyl succinate, dimethyl adipate, diethyl adipate and dimethyl glutarate. For instance, reacting diethyl oxalate with ethyleneimine gives bis[ß-(1-aziridino)ethyl]oxalamide. Dicarboxylic esters are reacted with ethyleneimine in a molar ratio of 1: at least 4. The reactive groups of these crosslinkers are the terminal aziridine groups. These crosslinkers may be characterized for example with the aid of the formula:

where \( n \) is from 0 to 22.

Illustrative of crosslinkers (5) are ethylene carbonate, propylene carbonate, urea, thiourea, guanidine, dicyandiamide or 2-oxazolidinone and its derivatives. Of this group of monomers, preference is given to using propylene carbonate, urea and guanidine.

Crosslinkers (6) are reaction products of polyetherdiamines, alkyleneamines, polyalkylenepolyamines, alkylene glycols, polyalkylene glycols or mixtures thereof with monoethylenically unsaturated carboxylic acids, esters, amides or anhydrides of monoethylenically unsaturated carboxylic acids, which reaction products contain at least two ethylenically unsaturated double
bonds, carboxamide, carboxyl or ester groups as functional groups, and also methylenebisacrylamide and divinyl sulfone.

Crosslinkers (6) are for example reaction products of polyetherdiamines having preferably from 2 to 50 alkylene oxide units, alkylenediamines such as ethylenediamine, propylenediamine, 1,4-diaminobutane and 1,6-diaminohexane, polyalkyleneopolyamines having molecular weight < 5000 for example diethylenetriamine, triethylenetetramine, dipropylenetriamine, tripropylenetetramine, dihexamethylenetriamine and aminopropylethylene diamine, alkylene glycols, polyalkylene glycols or mixtures thereof with

- monoethylenically unsaturated carboxylic acids,
- esters of monoethylenically unsaturated carboxylic acids,
- amides of monoethylenically unsaturated carboxylic acids, and
- anhydrides of monoethylenically unsaturated carboxylic acids.

These reaction products and their preparation are described in EP-A-873 371 and are expressly mentioned for use as crosslinkers.

Particularly preferred crosslinkers are the therein mentioned reaction products of maleic anhydride with α,ω-polyetherdiamines having a molar mass of from 400 to 5000, the reaction products of polyethyleneimines having a molar mass of from 129 to 50,000 with maleic anhydride and also the reaction products of ethylenediamine or triethylenetetramine with maleic anhydride in a molar ratio of 1: at least 2.

Crosslinkers (6) are preferably compounds of the formula

\[
\text{HO-} \overset{\text{O}}{\text{O}} \overset{\text{X}}{\text{X}} \overset{\text{CH}_2}{\text{m}} \overset{\text{Y}}{\text{Y}} \overset{\text{CH}_2}{\text{n}} \overset{\text{Z}}{\text{Z}} \overset{\text{q}}{\text{q}} \overset{\text{CH}_2}{\text{O}} \overset{\text{OH}}{\text{OH}}
\]

where \( X, Y, Z = O, NH \)

and \( Y \) is additionally \( = \text{CH}_2 \)

\[ m, n = 0 - 4 \]
which are obtainable by reacting polyetherdiamines, ethylenediamine or polyalkylenepolyamines with maleic anhydride.

Further halogen-free crosslinkers of group (7) are at least dibasic saturated carboxylic acids such as dicarboxylic acids and also the salts, diesters and diamides derived therefrom. These compounds may be characterized for example by means of the formula

$$X-\text{CO-}(\text{CH}_2)_n-\text{CO-X}$$

where $X = \text{OH}, \text{OR}^1, \text{N(R}^2\text{)}_2$

$$R^1 = \text{C}_1-\text{C}_{22}-\text{alkyl},$$

$$R^2 = \text{H}, \text{C}_1-\text{C}_{22}-\text{alkyl} \text{ and } n = 0-22.$$

As well as dicarboxylic acids of the abovementioned formula it is possible to use, for example, monoethylenically unsaturated dicarboxylic acids such as maleic acid or itaconic acid. The esters of the contemplated dicarboxylic acids are preferably derived from alcohols having from 1 to 4 carbon atoms. Examples of suitable dicarboxylic esters are dimethyl oxalate, diethyl oxalate, disopropyl oxalate, dimethyl succinate, diethyl succinate, disopropyl succinate, di-n-propyl succinate, diisobutyl succinate, dimethyl adipate, diethyl adipate and diisopropyl adipate or Michael addition products which contain at least two ester groups and are formed from polyetherdiamines, polyalkylenepolyamines or ethylenediamine and esters of acrylic acid or methacrylic acid with, in each case, monohydric alcohols of from 1 to 4 carbon atoms. Examples of suitable esters of ethylenically unsaturated dicarboxylic acids are dimethyl maleate, diethyl maleate, disopropyl maleate, dimethyl itaconate and diisopropyl itaconate. It is also possible to use substituted dicarboxylic acids and their esters such as tartaric acid (D,L-form and as racemate) and also tartaric esters such as dimethyl tartrate and diethyl tartrate.

Examples of suitable dicarboxylic anhydrides are maleic anhydride, itaconic anhydride and succinic anhydride. Useful crosslinkers (7) further include for example dimethyl maleate, diethyl maleate and maleic acid. The crosslinking of amino-containing compounds with the aforementioned crosslinkers
takes place with the formation of amide groups or, in the case of amides such as adipamide, by transamidation. Maleic esters, monoethylenically unsaturated dicarboxylic acids and their anhydrides can bring about crosslinking both by formation of carboxamide groups and by addition of NH groups of the component to be crosslinked (polyamidoamines, for example) in the manner of a Michael addition.

The at least dibasic saturated carboxylic acids of crosslinker class (7) include for example tri- and tetracarboxylic acids such as citric acid, propanetricarboxylic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid, butanetetracarboxylic acid and diethylenetriaminepentaacetic acid. Useful crosslinkers of group (7) further include the salts, esters, amides and anhydrides derived from the aforementioned carboxylic acids, e.g., dimethyl tartrate, diethyl tartrate, dimethyl adipate and diethyl adipate.

Useful crosslinkers of group (7) further include polycarboxylic acids obtainable by polymerizing monoethylenically unsaturated carboxylic acids, anhydrides, esters or amides. Examples of suitable monoethylenically unsaturated carboxylic acids are acrylic acid, methacrylic acid, fumaric acid, maleic acid and/or itaconic acid. Examples of useful crosslinkers are accordingly polyacrylic acids, copolymers of acrylic acid and methacrylic acid or copolymers of acrylic acid and maleic acid. Illustrative comonomers are vinyl ether, vinyl formate, vinyl acetate and vinylactam.

Further useful crosslinkers (7) are prepared for example by free-radical polymerization of anhydrides such as maleic anhydride in an inert solvent such as toluene, xylene, ethylbenzene, isopropylbenzene or solvent mixtures. Besides the homopolymers, copolymers of maleic anhydride are suitable, for example copolymers of acrylic acid and maleic anhydride or copolymers of maleic anhydride and a C₂– to C₃₀-olefin.

Examples of preferred crosslinkers (7) are copolymers of maleic anhydride and isobutene or copolymers of maleic anhydride and diisobutene. Copolymers containing anhydride groups may optionally be modified by reaction with C₁– to C₂₀-alcohols of ammonia or amines and be used as crosslinkers in that form.

Examples of preferred polymeric crosslinkers (7) are copolymers of acrylamide and acrylic esters, for example hydroxyethyl acrylate or methyl acrylate, the molar ratio of acrylamide and acrylic ester varying in the range from 90:10 to 10:90. Besides these copolymers, terpolymers can be used, an example of the
useful combinations being acrylamide, methacrylamide and acrylate/methacrylate.

The molar mass $M_w$ of the homo- and copolymers may be up to 10,000, preferably from 500 to 5000. Polymers of the abovementioned type are described for example in EP-A-0 276 464, US-A-3 810 834, GB-A-1 411 063 and US-A-4 818 795. The at least dibasic saturated carboxylic acids and the polycarboxylic acids may also be used as crosslinkers in the form of the alkali metal or ammonium salts. Preference is given to using the sodium salts. The polycarboxylic acids may be partially neutralized, for example to an extent of from 10 to 50 mol%, or else completely neutralized.

Useful halogen-free crosslinkers of group (8) include for example monoethyleneically unsaturated monocarboxylic acids such as acrylic acid, methacrylic acid and crotonic acid and the amides, esters and anhydrides derived therefrom. The esters may be derived from alcohols of 1 to 22, preferably of from 1 to 18, carbon atoms. The amides are preferably unsubstituted, but may 20 bear a C$_{1-22}$-alkyl substituent.

Preferred crosslinkers (8) are acrylic acid, methyl acrylate, ethyl acrylate, acrylamide and methacrylamide.

25 Useful halogen-free crosslinkers of group (9) include for example dialdehydes or their hemiacetals or acetals as precursors, for example glyoxal, methylglyoxal, malonaldehyde, succinaldehyde, malealdehyde, fumaraldehyde, tartaraldehyde, adipaldehyde, 2-hydroxyadipaldehyde, furan-2,5-dipropionaldehyde, 2-formyl-2,3-dihydropyran, glutaraldehyde, pimelaldehyde and also aromatic dialdehydes such as, for example, terephthalaldehyde, o-phthalaldehyde, pyridine-2,6-dialdehyde or phenylglyoxal. But it is also possible to use homo- or copolymers of acrolein or methacrolein having molar masses of from 114 to about 10,000. 30 Useful comonomers include in principle all water-soluble comonomers, for example acrylamide, vinyl acetate and acrylic acid. Aldehyde starches are similarly useful as crosslinkers.

Useful halogen-free crosslinkers of group (9) include for example diketones or the corresponding hemiketals or ketals as precursors, for example β-diketones such as acetylacetone or cycloalkane-1,n-diones such as, for example, cyclopentane-1,3-dione and cyclohexane-1,4-dione. But it is also possible to use homo- or copolymers of methyl vinyl ketone having 40 molar masses of from 140 to about 15,000. Useful comonomers
include in principle all water-soluble monomers, for example acrylamide, vinyl acetate and acrylic acid.

It will be appreciated that mixtures of two or more crosslinkers may also be used.

Superabsorbents according to the invention are preferably prepared using in particular crosslinkers which are free of organic halogen. It is therefore preferable to use halogen-free crosslinkers for preparing crosslinked polymers II which are each insoluble in water.

The above-described crosslinkers can be used either alone or in mixture in the reaction with water-soluble amino-containing polymers or polyalkyleneamines. The crosslinking reaction is in all cases carried on until the resulting products will still swell but no longer dissolve in water. The crosslinking reaction is effected by heating the reaction components at from room temperature to 220°C, preferably 50 to 180°C. If the crosslinking reaction is carried out in an aqueous medium at above 100°C, it is advantageous to remove the resulting condensate (water, lower alcohols, ammonia, amines) by distillation together with the water of dilution present until the reaction mixture has become solid. The polymer film is then comminuted and, if appropriate, ground while cooling with dry ice.

Preference is further given to polymers II which have not had a crosslinker added to them, but which are capable of self-crosslinking by reason of their comonomers. Such copolymers of vinylformamide are thermally crosslinked after their hydrolysis.

Self-crosslinking comonomers are acrylic acid, methacrylic acid, acrylic esters, methacrylic esters and their homologs and also acrylamide and acrylonitrile.

Self-crosslinking copolymers are based in particular on acrylic esters, methacrylic esters or homologs thereof, but also on acrylic acid, methacrylic acid or homologs thereof. The N-vinylformamide fraction is customarily within the range from 50 to 99 mol%, and the comonomer fraction is customarily within the range from 1 to 50 mol%. It is particularly advantageous to have a comonomer fraction of 5 to 15 mol% and an N-vinylformamide fraction of 85 to 95 mol%, the monomer fractions always adding up to 100 mol%. Such copolymers are first virtually completely saponified under basic conditions, optionally desalted and subsequently crosslinked at 80 to 220°C, preferably 120 to 180°C.
If desired, the crosslinking of such copolymers may be speeded up by further addition of polyvinylamines or polyethyleneimines.

Polyvinylamine too is observed to undergo a thermal self-crosslinking. This is believed to be due to formamide groups remaining even after hydrolysis, and also due to condensation by elimination of ammonia to form secondary amines. The ratio of formamide groups to amino groups may be within the range from 30/70 to 0/100, and is preferably within the range from 15/85 to 5/95. The self-crosslinking of polyvinylamine is carried out in aqueous solution at from 100 to 200°C, preferably from 150 to 180°C. In a preferred embodiment, the polyvinylamine to be crosslinked is applied in thin films. Preference is given to self-crosslinking polyvinylamine having a K value of 70-200, particularly preferably of 100-150, since this leads to hydrogel-forming polymers having advantageous properties.

The ratios in which the two hydrogel-forming polymers I and II are mixed with each other depend in particular on the density of the acid or amine groups (eq/g) and the acid or base strengths as well as other factors. Blend ratios may vary from 20:1 to 1:20 (by weight). Preference is given to blend ratios within the range from 10:1 to 1:10, particularly preferably within the range from 7:3 to 3:7.

There are in principle the following possibilities of preparing the mixture:

a) mixing the separately prepared powders,
b) mixing the water-containing gels,
c) mixing a water-containing gel with a powder,
d) adding powders or gels of one component to the reaction mixture for preparing the other component,
e) specifically constructing a shell-type particle where one component is the core and the other the sheath.

a) Separately prepared powders may be mixed using any commercially available assembly for mixing powders. The particles to be mixed are from 10 to 2000 µm, preferably from 100 to 850 µm, in size. The two components to be mixed may have identical or different particle sizes. The use of different particle sizes of the two components may be advantageous in that differences in the absorption rate or
ion exchange rate of the two components may be accommodated thereby. It may also be advantageous to use one component in a relatively coarsely divided form and the other in a very finely divided form, so that the finely divided component agglomerates on the surface of the coarser component. If appropriate, this process may be augmented by addition of agglomeration assistants such as, for example, polyethylene glycols, water and/or polyols. A further possibility is to use both components in the form of very finely divided powders and to agglomerate them with the aid of agglomeration assistants as listed above to form agglomerates from 100 μm to 1500 μm in size. It may also be advantageous to combine this agglomeration with a surface postcrosslinking in such a way that postcrosslinking will also bring about agglomeration. The advantage of agglomeration (by whatever variant) is that this generates particles which contain the two components together, so that the two components cannot separate when this mixture is used in hygiene articles, for example. This effect is particularly marked in the case of mixtures comprising very different particle sizes for the two components. Separation of the two components has the consequence of long diffusion paths in the ion exchange process leading to locally strongly acidic or basic pH values. This behavior is not acceptable for use in hygiene articles. Agglomeration further offers the advantage that high absorption rates can be actualized without the use of very finely divided powders, which are undesirable because of dusting.

Another way to avoid the above-described problem of component separation is to intimately mix the aqueous gels with each other and subsequently to dry, grind and, if appropriate, sieve them. This provides particles which contain the two components firmly bonded to each other, so that separation of the two components is not possible. It is likely that strong ionic interactions develop at the boundary layer between the two gel components and firmly bind the basic and acidic components together (see DE-A-19640329). The formation of a classic polyelectrolyte complex is unlikely, since the two polyelectrolytes are each part of a separate network. Since both the components are produced as aqueous gels, it is advantageous to use a mixture of these gels. But it is also possible to use gels obtained by swelling dried products with water. It may further be advantageous to partially dry the as-produced gels of the components before they are mixed. The mixing itself may be effected using various types of equipment, for example meat grinders, kneaders, extruders,
including planetary roll extruders, or mixers. The apparatus used has to ensure homogeneous, finely divided mixing of the two components without damaging the network structure of the gels by excessive shearing. The water content of the mixed gels is within the range from 5 to 99.8% by weight, preferably from 60 to 99% by weight. The water content of the two mixed gels may be identical or else different. Another advantage with this variant is the fact that it is quicker to dry, easier to grind, requires in addition no separate drying steps and the gel mixtures obtained have higher gel strength and hence easier handleability.

c) A further possibility is to mix the gel of one component with the powder of the other component. The procedure and the equipment used are the same as in case b). It is likely that this case will generate different structures within a particle than if the gels are mixed with each other. In the latter case, the particles will have a structure in which the components are present side by side in comparatively large domains. The size ratio of the domains is decisively determined by the blend ratio and the solids contents of the gels used and by the intensity of the mixing. In the first case, the component added as a powder will have an island structure in a matrix of the component used in gel form. Depending on the property spectrum desired, it may be advantageous to actualize one structure or the other.

d) A further way of obtaining nonseparating products is to add powders or gels of one component to the reaction mixture of the other component. For instance, the addition of polymer I (polyacrylic acid, for example) as powder or gel to the polyvinylamine solution and subsequent crosslinking of the polyvinylamines leads to mixtures having advantageous properties. This crosslinking may be effected by adding a crosslinker or thermally as self-crosslinking. Similarly, the addition of crosslinked polyvinylamine as powder or gel to a polymer I (for example polyacrylic acid) and subsequent crosslinking provides mixtures having advantageous properties. Care must be taken to ensure in this connection that no unwanted reactions take place. For instance, adding crosslinked polyvinylamine to a reaction mixture of acrylic acid, crosslinker and initiator would immediately set off a Michael addition between the primary amino groups of the gel and the acrylic acid. Subject to the proviso that no unwanted reactions can take place, it is possible to add the powder or else a gel to the reaction mixture of the other component at any time of the reaction sequence. This variant is likely to
generate products whose boundary layer between the components has a different structure than in the case of gel or powder mixtures. One of the two components is present here at least in a still partially uncrosslinked state or even as a monomer mixture. As a result, more regular structures having relatively strong interactions through to polyelectrolyte complexes may develop in the boundary layer, and it is likely that the boundary layer will be significantly thicker than in the case of the preceding variants. This effect should enhance gel stability and also predispose the range of properties which is attainable toward surface postcrosslinking.

e) Another possibility is the formation of a core-shell structure. For this, particles of one component are coated, for example sprayed, with a reaction mixture for preparing the 2nd component. After or during the reaction, the core-shell product obtained is dried. To provide certain layer thicknesses, it may be necessary to repeat the coating a number of times. On the other hand, it is also conceivable that such a process may be used to construct multilayered particles comprising alternating layers of the two components. A particularly suitable way for constructing complex layered structures in particular as well as simple ones is a fluidized bed process. The essential advantage of such a process is that it makes it possible to produce defined structures having uniform and specifically adjustable layer thicknesses.

Hydrogel-forming polymers (polymer I, polymer II or mixtures of polymers I and II) may be dried according to various processes known to one skilled in the art. Examples of useful drying processes are thermal convection drying, for example tray, chamber, duct, flat sheet, disk, rotary drum, free fall tower, foraminous belt, flow, fluidized bed, moving bed, paddle and ball bed drying, thermal contact drying such as hotplate, drum, belt, foraminous cylinder, screw, tumble and contact disk drying, radiative drying such as infrared drying, dielectric drying such as microwave drying, and freeze drying. To avoid unwanted decomposition and crosslinking reactions, it may be advantageous to dry under reduced pressure, under a protective gas atmosphere and/or under gentle thermal conditions where the product temperature does not exceed 120°C, preferably 100°C. Particularly suitable drying processes are (vacuum)belt drying and paddle drying.
Dried hydrogel-forming polymers are, if appropriate, precomminuted and then ground according to processes known to one skilled in the art, for example by means of a roll mill or a hammermill. Subsequent sieving is used to adjust the particle size distribution, which in general ranges from 100 to 1000 µm, preferably from 120 to 850 µm. Oversize particles may be reground, undersize particles may be recycled into the production process.

It may also be sensible to admix the described mixtures additionally with already commercially available superabsorbents, i.e., to add acidic or basic crosslinked polymers whose acidic or basic groups are at least 50% neutralized. The fraction of these commercially available superabsorbents should be less than 50%, preferably less than 25%.

In addition, polymers I and II may in a conventional manner be postcrosslinked in aqueous gel phase or surface-postcrosslinked as dried, ground and classified polymer particles.

In a preferred embodiment of the invention, the absorption properties of the resulting mixtures of polymers I and polymers II are further improved by subsequent surface postcrosslinking. This may take the form of exclusive crosslinking of polymers I, exclusive crosslinking of polymers II or crosslinking of a homogeneous mixture of the two polymer varieties. To this end, compounds capable of reacting with the functional groups of the polymers with crosslinking are applied to the surface of the hydrogel particles, preferably in the form of an aqueous solution. The aqueous solution may contain water-miscible organic solvents. Suitable solvents are alcohols such as methanol, ethanol, i-propanol or acetone.

Suitable surface postcrosslinkers include for example:

- di- or polglycidyl compounds such as diglycidyl phosphonates or ethylene glycol diglycidyl ether, bischlorohydrin ethers of polyalkylene glycols,
- glycidol or epichlorohydrin,
- alkoxysilyl compounds,
- polyaziridines, aziridine compounds based on polyethers or substituted hydrocarbons, for example bis-N-aziridinomethane,
polyamines or polyamidoamines and also their reaction products with epichlorohydrin,

polyols such as ethylene glycol, 1,2-propanediol, 1,4-butanediol, glycerol, methyltriglycerol, polyethylene glycols having an average molecular weight Mw of 200-10,000, di- and polyglycerol, pentaerythritol, sorbitol, the ethoxylates of these polyols and their esters with carboxylic acids or carbonic acid such as ethylene carbonate or propylene carbonate,

carbonic acid derivatives such as urea, thiourea, guanidine, dicyandiamide, 2-oxazolidinone and its derivatives, bisoxazoline, polyoxazolines, di- and polyisocyanates,

di- or polyaldehydes such as, for example, glyoxal, succinaldehyde or aldehyde starch,

di- or polyketones

compounds having two or more activated double bonds capable of entering a Michael addition, for example divinyl sulfone, methylenebisacrylamide or ethylene glycol dimethacrylate,

di- and polycarboxylic acids and also their anhydrides, esters, acyl chlorides and nitriles, for example oxalic acid, glutaric acid, adipic acid, maleic anhydride, tartaric acid, malic acid, tartaric acid or citric acid,

di- and poly-N-methylol compounds such as, for example, methylenebis(N-methylolmethacrylamide) or melamine-formaldehyde resins,

di- and polyhalogen compounds such as α,ω-dichloropolyalkylene glycols, α,ω- or vicinal dichloroalkanes e.g. 1,2-dichloroethane, 1,2-dichloropropane, 1,3-dichlorobutane or 1,6-dichlorohexane,

compounds having two or more blocked isocyanate groups, for example trimethylhexamethylene diisocyanate blocked with 2,2,6,6-tetramethylpiperidin-4-one,

monoethylenically unsaturated carboxylic acids, for example (meth)acrylic acid or crotonic acid, and their esters, amides and anhydrides.
If necessary, acidic catalysts may be added, for example p-toluenesulfonic acid, phosphoric acid, boric acid or ammonium dihydrogenphosphate.

Particularly useful postcrosslinkers are di- or polyglycidyl compounds such as ethylene glycol diglycidyl ether, the reaction products of polyamidoamines with epichlorohydrin and 2-oxazolidinone, which are capable of reacting both with amino and with carboxyl groups to effect crosslinking.

The crosslinker solution is preferably applied by spraying with a solution of the crosslinker in reaction mixers or mixing and drying equipment. Suitable conventional mixing assemblies for spraying the crosslinker solution onto the polymer particles include for example Patterson-Kelly mixers, DRAIS turbulence mixers, Lödige mixers, NARA paddle mixers, screw mixers, disk mixers, fluidized bed dryers, Schugi mixers (Flexo-Mix) or PROCESSALL. Small amounts may be postcrosslinked on a laboratory scale using kitchen blenders, for example a WARING blender. The spraying of the crosslinker solution may be followed by a heat treatment step, preferably in a downstream dryer, at from 80 to 230°C, preferably at 80 to 190°C, particularly preferably at from 100 to 160°C, for a period of from 5 minutes to 6 hours, preferably from 10 minutes to 2 hours, particularly preferably from 10 minutes to 1 hour, during which not only cracking products but also solvent fractions can be removed. The drying can also take place in the mixer itself, by heating the jacket or by blowing in a preheated carrier gas.

If particles comprising structures featuring contiguous domains or areas of polymers I and polymers II are present, an additional crosslinking of these domain or area boundaries may also be effected by means of a heat treatment without addition of a crosslinker. The water content of particles prior to this heat treatment is preferably within the range from 0 to 50% by weight, particularly preferably within the range from 1 to 30% by weight, most preferably within the range from 2 to 20% by weight. The temperature in this tempering step is within the range from 80 to 230°C, preferably 80 to 190°C, particularly preferably within the range from 100 to 160°C, for a period of from 5 minutes to 6 hours, preferably from 10 minutes to 2 hours, particularly preferably from 10 minutes to 1 hour. The heat treatment step may take place after drying of the particles in a downstream dryer, in which case the desired water content for the particles may be effected by spraying with water or with a mixture of water and one or more water-miscible organic solvents. Preferably, however, the heat treatment step takes place in the course of the drying
of the hydrogel particles, by first drying the hydrogel to a desired water content and then subjecting it to the heat treatment. The heat treatment can take place in a separate dryer or preferably in the same drying apparatus as used for drying the hydrogel to the desired water content. Without wishing to be bound by any one theory, the inventors believe that this heat treatment causes the acid groups of polymer I to form covalent amide groups with the amino groups of polymer II at the domain or area boundaries, resulting in additional crosslinking.

In a particularly preferred embodiment of the invention, the hydrophilicity of the particle surface of the mixtures of polymers I and polymers II is additionally modified by formation of complexes. The formation of complexes on the outer shell of the hydrogel particles is effected by spraying with solutions of divalent or more highly valent metal salt solutions and/or divalent or more highly valent anions where the metal cations are capable of reacting with the functional groups of the anionic polymer and the polyvalent anions are capable of reacting with the functional groups of the cationic polymer, to form complexes. Examples of divalent or more highly valent metal cations are Mg$^{2+}$, Ca$^{2+}$, Al$^{3+}$, Sc$^{3+}$, Ti$^{4+}$, Mn$^{2+}$, Fe$^{2+/3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{+/2+}$, Zn$^{2+}$, Y$^{3+}$, Zr$^{4+}$, Ag$^+$, La$^{3+}$, Ce$^{4+}$, Hf$^{4+}$, and Au$^{+3/+4}$, preferred metal cations being Mg$^{2+}$, Ca$^{2+}$, Al$^{3+}$, Ti$^{4+}$, Zr$^{4+}$ and La$^{3+}$, particularly preferred metal cations being Al$^{3+}$, Ti$^{4+}$ and Zr$^{4+}$. Examples of divalent or more highly valent anions are sulfate, phosphate, borate and oxalate. Of the metal cations and polyvalent anions mentioned, any salt is suitable which possesses sufficient solubility in the solvent to be used. Useful solvents for the salts are water, alcohols, DMF, DMSO and mixtures thereof. Particular preference is given to water and water/alcohol mixtures, for example water/methanol or water/1,2-propanediol.

The spraying of the salt solution onto the particles of the mixture of hydrogel-forming polymers I and II may take place both before and after the surface postcrosslinking of the particles. In a particularly preferred process, the spraying with the metal salt solution takes place in the same step as the spraying with the crosslinker solution, the two solutions being sprayed separately in succession or simultaneously via two nozzles, or the crosslinker and salt solutions may be sprayed conjointly through a single nozzle.

Optionally, the particles of the mixture of polymers I and polymers II may be further modified by admixture of finely divided inorganic solids, for example silica, bentonites, aluminum oxide, titanium dioxide and iron(III) oxide, to further
augment the effects of the surface aftertreatment. Particular preference is given to the admixture of hydrophilic silica or of aluminum oxide having an average primary particle size of from 4 to 50 nm, and a specific surface area of 50 to 450 m²/g. The admixture of highly divided inorganic solids preferably takes place after the surface modification through crosslinking/complexing, but may also be carried out before or during these surface modifications.

In a number of process steps it may be sensible to use additives. Additives for the purposes of the present invention are finely divided, pulverulent or fibrous, organic or inorganic substances which are inert toward the production conditions of the components and the mixtures. Examples of such additives are:

finely divided silicon dioxide, pyrogenic silicas, precipitated silicas in hydrophilic or hydrophobic modifications, zeolites, titanium dioxide, zirconium dioxide, talcum, bentonites of any kind, cellulose, silicates of any kind, guar bean flour, tara bean flour, carob bean flour, any kind of starch, clay, barium sulfate, calcium sulfate, synthetic and natural fibers.

They may be used both as processing aids and as carrier material.

The gel to be handled in the course of the production of mixtures according to the invention are all more or less tacky. To overcome this disadvantage, it can be sensible, especially in the comminuting, mixing or drying step, to add from 0.1 to 10% by weight of one or more of the abovementioned additives before or during the processing step. This measure serves to coat the surface of the gel with the finely divided additive and so diminishes or at least drastically reduces the tackiness. This additization also has an effect on the properties of the end product. The fact that the dried powder particles are coated with the additive at the surface improves the flowability of the resulting powders. Furthermore, the dried gels tend to take up water, especially on contact with a moist atmosphere, and to clump together as a result. The addition of the abovementioned additives also reduces this clumping effect. It can therefore be sensible to add such additives to the end product only. This is the case when they are not required in the preceding processing steps.

To enlarge the surface area, to shorten the diffusion paths and to make the functional groups of the gels more easily accessible, it can be sensible to generate the abovementioned acidic or basic gels on a carrier. Such a carrier must therefore have a large
specific surface area. The additives mentioned do have this property, especially pyrogenic silicas, bentonites and talcum are preferred. To prepare such acidic or basic components, the carrier material may simply be added to the reaction mixture in the course of the production of the components. Alternatively, the carrier material may be specifically coated with the reaction mixture, for example by spraying in a fluidized bed. The amounts of carrier material used are within the range from 5% to 80%.

Surfactants and blowing agents may also be used as assistants.

The following test methods were used to investigate the polymer mixtures of the invention:

CRC (Centrifuge Retention Capacity):

CRC I is determined by weighing 0.2 g of polymer powder into a teabag 60 x 85 mm in size, which is subsequently heat-sealed. The teabag is then placed in an excess of 0.9% by weight sodium chloride solution (at least 0.83 l of saline/1 g of polymer powder. After a swell time of 30 minutes, the teabag is removed from the saline and centrifuged at 250 g for three minutes. The centrifuged teabag is weighed to determine the amount of fluid retained by the polymer powder.

PUP 0.7 psi (Performance Under Pressure 0.7 psi):

The test method for determining PUP 0.7 psi (pound/square inch, 0.7 psi = 4826.5 Pa) is described in U.S. 5,599,335.

PUP 1.4 psi (Performance Under Pressure 1.4 psi):

PUP 1.4 psi is determined similarly to PUP 0.7 psi, except under a pressure of 1.4 psi (9653 Pa).

PUP 0.014 psi (Performance Under Pressure 0.014 psi):

PUP 0.014 psi is determined similarly to PUP 0.7 psi, except that the pressure is reduced to 0.014 psi (96.5 Pa), i.e., it is carried out without weight, only with the plastic insert for the weight.

SFC (Saline Flow Conductivity):

The SFC test method is described in U.S. 5,599,335.
SFC Index (Saline Flow Conductivity Index):

The SFC index is obtained from three SFC measurements under different pressures according to the following formula:

\[
SFC \text{ Index} = [SFC \ (0.3 \ \text{psi}) \cdot 10^7 \ \text{g/cm}^3\text{s}] \cdot ([SFC \ (0.6 \ \text{psi}) \cdot 10^7 \ \text{g/cm}^3\text{s}] + [SFC \ (0.9 \ \text{psi}) \cdot 10^7 \ \text{g/cm}^3\text{s}])
\]

The SFC (0.3 psi) corresponds to the above-described SFC (0.3 psi = 2068.5 Pa). In the case of SFC (0.6 psi), the swelling of the hydrogel and the flow measurement take place under a pressure of 0.6 psi (4137 Pa), and in the case of SFC (0.9 psi) the swelling and flow measurement take place under a pressure of 0.9 psi (6205.5 Pa).

PAI (NaCl) (Pressure Absorbency Index (NaCl)):

The Pressure Absorbency Index (NaCl) is determined in accordance with the description of the PAI test method in EP-A-0 615 736, except that the measuring time is extended up to 16 hours.

PAI (Jayco) (Pressure Absorbency Index (Jayco)):

The Pressure Absorbency Index (Jayco) is determined similarly to the above-described determination of the Pressure Absorbency Index (NaCl), except that the fluid to be absorbed is a synthetic urine solution of the following composition: 1000 g of distilled water, 2.0 g of KCl, 2.0 g of Na₂SO₄, 0.85 g of (NH₄)H₂PO₄, 0.15 g of (NH₄)₂HPO₄, 0.19 g of CaCl₂, 0.23 g of MgCl₂.

Diffusing Absorbency Under Pressure:

The method for determining the diffusion absorbency under pressure is similar to the description in EP-A-0712 659, except for the following modifications: The weight of polymer used is 0.9 g instead of 1.5 g; the polymer sample is measured in the particle size range 106 - 850 μm; the pressure during the measurement is 0.7 psi (4826.5 Pa) instead of 0.3 psi (2068.5 Pa); the test solution is synthetic urine solution (see PAI) instead of 0.9% by weight saline; the measuring time is 4 h instead of 1 h.

Wicking Performance:

Wicking performance is measured similarly to the wicking parameter, the measurement of which is described in EP-A-0 532 002. In departure from the method for measuring the
wicking parameter, wicking performance is measured with 2 g of polymer (particle size distribution 106 - 850 µm) only at a preswell of 10 g of 0.9% by weight saline/1 g of polymer. The quantity measured is the wicking distance which indicates the length over which the polymer particles have become swollen with the blue test liquid following a test time of 1 h and the wicking capacity which corresponds to the amount of liquid additionally absorbed in this period.

10 Acquisition Time/Rewet under Pressure:

The test is carried out using laboratory pads. To produce these laboratory pads, 11.2 g of cellulose fluff and 23.7 g of hydrogel are homogeneously fluidized in an air box and by application of a slight vacuum laid down on a mold 12 × 26 cm in size. This composition is then wrapped in tissue paper and compressed for 2 times 15 seconds under a pressure of 20 bar. A laboratory pad produced in this way is attached to a horizontal surface. The center of the pad is determined and marked. Synthetic urine solution is applied through a plate of plastic having a ring in the middle (internal diameter of ring 6.0 cm, height 4.0 cm). The plate is loaded with additional weights so that the total load on the pad is 13.6 g/cm². The plate of plastic is placed on the pad in such a way that the center of the pad is also the center of the application ring. 80 ml of synthetic urine solution are applied three times. The synthetic urine solution is prepared by dissolving 1.14 g of magnesium sulfate heptahydrate, 0.64 g of calcium chloride, 8.20 g of sodium chloride, 20 g of urea in 1 kg of deionized water. The synthetic urine solution is measured out in a measuring cylinder and applied in one shot to the pad through the ring in the plate. At the same time, the time is measured until the solution has completely penetrated into the pad. The time measured is recorded as Acquisition Time 1. Thereafter the pad is weighted with a plate for 20 min, the load being further maintained at 13.6 g/cm². Thereafter the plate is removed, 10 g ± 0.5 g of filter paper (Schleicher & Schuell, 1450 CV) are placed on the central spot and loaded with a weight (area 10 × 10 cm, weight 3.5 kg) for 15 s. After this period the weight is removed, and the filter paper is reweighed. The weight difference is noted as Rewet 1. Thereafter the plastic plate with application ring is again placed on the pad and the liquid is applied for the second time. The time is noted as Acquisition Time 2. The procedure is repeated as described, but 45 ± 0.5 g of filter paper are used for the rewet test. Rewet 2 is noted. The same method is employed to determine Acquisition Time 3. 50 g ± 0.5 g of filter paper are used to determine Rewet 3.
RAC-Factor (Re-Absorbing Capacity Factor of sheared Gel)

The RACF is determined (generally double-determined) by admixing 1.2 g of polymer in an aluminum dish (diameter 4 cm, rim height 3 mm) with 12.0 g of 0.9% by weight NaCl solution and leaving the sample to swell for 30 minutes, in the covered state to protect it against drying out. 1.10 g of the preswollen gel are weighed into a Plexiglas cylinder (25 mm in internal diameter and 33 mm in height) whose bottom surface is a 140 μm sieve and covered with a Plexiglas disk. The cylinder with substance and with disk is weighed and the weight noted as W1. The Plexiglas disk is then loaded with a metal weight (Plexiglas disk + weight = 245 g, corresponding to a pressure of 50 g/cm² or 4095 Pa) and the entire measuring unit is placed in a Petri dish 100 mm in diameter and 10 mm in height filled with 13 ml of 0.9% by weight NaCl solution. After a swell time of 60 minutes, the measuring unit is lifted out of the Petri dish, the weight is removed, excess saline adhering to the sieve bottom is stripped off and the measuring cell with swollen gel and Plexiglas disk is backweighed, the weight being noted as W2. The remainder (11 g) of the preswollen gel after deduction of the gel quantity for the above-described double determination is transferred into a polyethylene bag 30 × 150 mm in size and the open side of the bag is vacuum-sealed. The bag is fixed on a film bag tester using an adhesive strip and then subjected to a Roll-Down test by rolling a roller 2 kg in weight over it 50 times (25 times each in opposite directions). The resulting sheared gel is then subjected to the above-described test of Absorbency under Pressure at 50 g/cm² to arrive at the reabsorbing capacity of sheared gel. The weight of the measuring cell with gel and disk prior to the 60 minute absorption period is noted as W3, and the post-absorption weight is noted as W4. The reabsorbing capacity factor then is the ratio of absorption after to absorption prior to shearing of the gel, multiplied by 100:

RAC-Factor = [{(W4 - W3)/weight of gel sheared/10}] · 100/[(W2 - W1)/(weight of gel unsheared/10)]

DATGLAP 0.7 psi/0.9 psi (Demand Absorbency Through Gel Layer Against Pressure 0.7 psi/0.9 psi)

The method for determining DATGLAP involves 2 steps. The first step comprises a measurement of an AUL (Absorption Under Load) at a pressure of 0.7 psi (0.7 psi = 4826.5 Pa), using the same measuring cell and the same equipment and virtually the same method as for the determination of PUP 0.7 psi described in
US 5,599,335. However, DATGLAP/step 1 differs from PUP in 2 points:

1. After the test substance has been sprinkled on the sieve bottom of the measuring cell, the Plexiglas ring placed on top is 0.32 cm in height and covered on its upper surface with the same sieve fabric as the bottom surface of the measuring cell. The covered ring has an outer diameter of 5.98 cm, so that it can move up in the measuring cell without sticking/jamming as the gel swells, an internal diameter of 4.9 cm and a height of 0.32 cm. The covered ring then has the plastic cover plate placed on top of it with the weight, as described in the above-cited US patent.

2. The test fluid used for DATGLAP is not synthetic urine, but 0.9% by weight saline.

After a measuring time of 1 hour, the covered Plexiglas ring remaining in the measuring cell and resting on the gel has, in the second step, the weight and the plastic cover plate removed from it and replaced by a new measuring unit of the same design as described above (but of smaller diameter to fit into the Plexiglas cylinder of the first measuring step) and left in place for 4 hours. The measurement of the absorption of liquid restarts with the time of the 2nd measuring unit being placed on the sieve ring of the 1st measuring unit. The 2nd measuring cell has the following dimensions: outer diameter = 5.98 cm/internal diameter = 5.03 cm. The test substance distributed over the sieve bottom of the 2nd measuring cell is beforehand covered with a Plexiglas disk (5.018 cm diameter) and loaded with a weight (Plexiglas plate + weight = 1331 g → 67.3 g/cm² = 6606 Pa).

\[ \text{DATGLAP} = (\text{DAAP-TGL/DAAP-Regular}) \times (\text{DAAP-Regular} + \text{DAAP-TGL}) \text{ [g/g]} \]

35 \textbf{DAAP-TGL} = Demand Absorbency Against Pressure Through Gel Layer after 4 hours, in [g/g]

\textbf{DAAP-Regular} = Demand Absorbency Against Pressure after 1 hour, in [g/g]

Preference is given to polymer mixtures having an SFC index of at least 10,000, preferably \( \geq 100,000 \), especially \( \geq 200,000 \), particularly preferably \( \geq 300,000 \).
CRC, PUP 0.014 psi, PUP 0.7 psi and PUP 1.4 psi, PAI (NaCl) and PAI (Jayco) are test methods for characterizing the absorption capacity of the polymer mixture for aqueous saline solutions under different confining pressures. SFC, SFC index and Wicking Performance describe the permeability of swollen gel layers. Diffusing Absorbency Under Pressure and DATGLAP are test methods for the combined capture of absorption capacity and fluid transportation. The RAC factor characterizes the mechanical stability of swollen polymer particles. The Acquisition Time/Rewet under pressure test simulates the behavior of the polymer mixture in hygiene articles such as infant or incontinence diapers.

Useful for application in hygiene articles are in particular polymer mixtures having a Pressure Absorbency Index (NaCl) of ≥ 100, preferably ≥ 130, especially ≥ 150, particularly preferably ≥ 180, after a swell time of 16 h, preferably 4 h.

Preference is given in particular to polymer mixtures having a Pressure Absorbency Index (Jayco) of at least 150, preferably ≥ 200, especially ≥ 225, particularly preferably ≥ 250, after a swell time of 16 h, preferably 4 h.

In addition, polymer mixtures having a Diffusing Absorbency Under Pressure of at least 30 g/g, preferably ≥ 40 g/g, especially ≥ 45 g/g, particularly preferably ≥ 50 g/g, are advantageous.

Also of advantage are polymer mixtures which provide in the Wicking Performance Test a Wicking Distance of at least 5 cm, preferably ≥ 8 cm, especially ≥ 10 cm, particularly preferably ≥ 15 cm, and a Wicking Capacity of at least 5 g, preferably ≥ 8 g, especially ≥ 10 g, particularly preferably ≥ 13 g.

Preference is further given to polymer mixtures which in the Acquisition Time/Rewet under pressure test provide an Acquisition Time 3 of not more than 25 s, preferably ≤ 20 s, especially ≤ 15 s, most preferably ≤ 10 s, and a Rewet 3 of not more than 9 g, preferably ≤ 5 g, especially ≤ 3 g, particularly preferably ≤ 2 g.

Preference is further given to polymer mixtures providing an RAC factor of at least 80, preferably ≥ 90, especially ≥ 100 and particularly preferably ≥ 120.
Additionally of advantage are polymer mixtures having a DATGLAP of at least 50 g/g, preferably ≥ 65 g/g, especially ≥ 80 g/g, most preferably ≥ 90 g/g.

Preference is given in particular to polymers combining a plurality of these preferred properties. For instance, polymer mixtures having an SFC index ≥ 10,000 and a Wicking Distance of ≥ 5 cm and a Wicking Capacity of at least 5 g are preferred. Particular preference is given to polymer mixtures having an Acquisition Time 3 of not more than 25 s and a Rewet 3 of not more than 9 g and an SFC ≥ 10,000 and/or a Diffusing Absorbency under Pressure of ≥ 30 g/g. Most preference is given to polymer mixtures having an SFC index of ≥ 1000, a PAI of ≥ 150 after a swell time of 16 h, a Diffusing Absorbency Under Pressure of at least 30 g/g, a Wicking Distance of ≥ 5 cm, a Wicking Capacity of ≥ 5 g, an Acquisition Time 3 of not more than 25 s and a Rewet 3 of not more than 9 g.

Preference is given to polymer mixtures comprising polymers I based on acrylic acid and/or methacrylic acid.

Preference is given to polymer mixtures whose polymer I is a crosslinked polyacrylic acid where from 0 to 50% of the carboxylic acid groups are present as alkali metal and/or ammonium salt.

Preference is likewise given to polymer mixtures comprising crosslinked copolymers of acrylic acid or methacrylic acid with vinylsulfonic acid or acrylamidopropanesulfonic acid as polymers I.

Preference is further given to polymer mixtures where said polymers I have been crosslinked with oligo- or polyethylene glycol diacrylates or methacrylates whose molecular weight was within the range from 200 to 1000.

Preference is given to polymer mixtures in which polymer II is a polyethyleneimine, an ethyleneimine-grafted polyamidoamine and/or ethyleneimine-grafted polyamine which are each crosslinked.

Preference is also given to polymer mixtures whose polymer II is a crosslinked polyvinylamine.
Preference is further given to polymer mixtures whose polymer II was obtained by copolymerization of vinylformamide and one or more monoethenically unsaturated compounds, subsequent hydrolysis with or without desalting and subsequent crosslinking.

Preference is given to polymer mixtures whose polymer II is a graft copolymer of vinylformamide on polymeric compounds which is subsequently subjected to hydrolysis with or without desalting and crosslinking.

Preference is given to polymer mixtures whose polymer II is a copolymer of vinylformamide and monoethenically unsaturated mono- and/or polypolyacrylic acids which was subsequently subjected to hydrolysis with or without desalting and self-crosslinking by heating, i.e., without crosslinker.

Preference is given to polymer mixtures whose polymer II is a copolymer of vinylformamide and monoethenically unsaturated mono- and/or polycarboxylic acids which was subjected to hydrolysis with or without desalting, crosslinking by heating and subsequent further crosslinking with a cationic polymer or copolymer based on polyvinylamine or polyethyleneimine and/or with at least one bifunctional crosslinker.

Preference is further given to polymer mixtures whose polymer II is a polyethyleneimine, an ethyleneimine-grafted polyamidoamine or an ethyleneimine-grafted polyamine which was polymer-analogously modified by reaction with \( \alpha,\beta \)-unsaturated carboxylic acids or esters or by Strecker reaction and subsequently crosslinked thermally with itself or at least one crosslinker.

Preference is further given to polymer mixtures whose polymer II was obtained by crosslinking a polyvinylamine having a K value of from 40 to 220, especially from 70 to 160.

Preference is further given to polymer mixtures whose polymer II was prepared with one or more crosslinkers of groups (1), (5), (6), (7), (8) and (9).

Preference is given to polymer mixtures having a ratio of the acid moieties to the sum total of amino/imino moieties of from 2:1 to 1:8.

Preference is given to polymer mixtures obtained by mixing polymer gel I and polymer gel II.
Particular preference is given to polymer mixtures obtained by mixing polymer gel I and polymer powder II or polymer powder I and polymer gel II.

5 Particular preference is given to polymer mixtures obtained by addition of a blend component I or II as powder to the reaction mixture of the other component.

Preference is further given to polymer mixtures which include polymer powder I, polymer powder II and agglomeration assistants.

Preference is given to polymer mixtures obtained by mixing surface-postcrosslinked polymer I and surface-postcrosslinked polymer II. The resulting intraparticulate mixtures having a domain structure, an island structure and/or a core-shell construction are preferred.

Preference is further given to polymer mixtures comprising an agglomerated surface-postcrosslinked powder mixture.

20 Polymer mixtures according to the invention have good application properties. They possess an advantageous SFC index, good PAI values not only for sodium chloride but also for Jayco. They further exhibit excellent Diffusing Absorbency Under Pressure. In addition they give good results in the Wicking Performance Test. Their good results in the Acquisition Time/Rewet Test under Pressure are likewise particularly outstanding.

Polymer mixtures according to the invention are notable for outstanding absorption capacity for water and aqueous salt solutions, for the high permeability of the swollen gel layers and for the high mechanical stability of the swollen polymer particles and are therefore very useful as absorbents for water and aqueous fluids especially body fluids such as urine or blood, for example in hygiene articles such as infant and adult diapers, sanitary napkins, tampons and the like. But they may also be used as soil improvers in agriculture and horticulture, as moisture binders for cable sheathing and for thickening aqueous wastes.

30 The Examples which follow illustrate the invention.

Example 1

a) Preparation of a crosslinked polyacrylic acid
350 g (4.86 mol) of acrylic acid and 3.84 g of polyethylene glycol diacrylate of a polyethylene glycol of molar mass 400 and 0.88 g of sodium peroxodisulfate are dissolved in 1046.16 g of distilled water. The solution is transferred to a 2 l Dewar flask at room temperature. The Dewar was sealed with a bung equipped with a gas outlet and a gas inlet tube reaching to the bottom. Nitrogen is passed through the gas inlet tube for 30 min to remove dissolved oxygen. 2.92 g of 0.3% by weight ascorbic acid solution are then added as coinitiator and mixed in homogeneously with a vigorous stream of nitrogen. After the polymerization has started, the nitrogen stream is switched off and the gas inlet tube is withdrawn from the Dewar. After reacting to completion overnight, a portion of the resulting gel block was comminuted in a meat grinder and dried overnight at 85°C under reduced pressure in a vacuum drying cabinet. The second portion was used for further experiments without additional treatment. The dried gel was ground and classified to the particle size fraction from 100 μm to 850 μm.

b) Preparation of a polyvinylamine crosslinked with ethylene glycol diglycidyl ether

2241 g of a 12.3% by weight aqueous polyvinylamine solution (K 85) are mixed homogeneously at room temperature with a solution of 13.77 g of ethylene glycol diglycidyl ether in 100 g of distilled water. The mixture is subsequently heated to 75°C in a waterbath for 2 hours. A portion of the resulting gel is directly used for further experiments, the remainder is dried overnight at 85°C under reduced pressure. The product obtained is ground and classified to the particle size fraction from 100 μm to 850 μm.

c) Preparing the powder mixture

In each case 10 g of the classified powder product obtained according to a) and b) were mixed homogeneously.

Example 2

Preparation of a gel-gel mixture

86.40 g of undried polyacrylic acid gel prepared according to Example 1a) and 157.30 g of undried polyvinylamine gel prepared according to Example 1b) are intimately mixed with each other by passing them 3 times together through a commercially available meat grinder. The gel mixture obtained is dried at 85°C overnight
under reduced pressure. After grinding, the particle size fraction from 100 \( \mu m \) to 850 \( \mu m \) is classified out.

**Example 3**

64.8 g of undried polyacrylic acid gel prepared according to Example 1a) and 183.5 g of undried polyvinylamine gel prepared according to Example 1b) are intimately mixed with each other by passing them 3 times together through a commercially available meat grinder. The gel mixture obtained is dried at 85\(^{\circ}\)C overnight under reduced pressure. After grinding, the particle size fraction from 100 \( \mu m \) to 850 \( \mu m \) is classified out.

**Example 4**

100 g of a 12.5% by weight aqueous polyvinylamine solution (K 85) and a solution of 0.63 g of ethylene glycol diglycidyl ether in 4.38 g of distilled water are homogeneously mixed at room temperature. 12.5 g of the pulverulent crosslinked polyacrylic acid prepared according to Example 1a) are then likewise homogeneously mixed in by vigorous stirring. The reaction mixture is heated to 75\(^{\circ}\)C in a waterbath for 2 hours. The gel obtained is comminuted, dried overnight at 85\(^{\circ}\)C under reduced pressure, ground and classified to the particle size fraction from 100 \( \mu m \) to 850 \( \mu m \).

**Example 5**

a) 100 g of a 13.6% by weight aqueous polyvinylamine solution (K 85) and a solution of 0.41 g of N,N'-methylenbisacrylamide in 9.93 g of distilled water are homogeneously mixed at room temperature. The reaction mixture is heated to 75\(^{\circ}\)C in a waterbath for 2 hours. The gel obtained is comminuted, dried overnight at 85\(^{\circ}\)C under reduced pressure, ground and classified to the particle size fraction from 100 \( \mu m \) to 850 \( \mu m \).

b) In each case 10 g of the classified powder product obtained according to 1a) and 5a) were mixed homogeneously.

**Example 6**

a) 100 g of a 37.4% by weight aqueous polyethyleneimine solution (MW about 500,000) are homogeneously mixed with 2.99 g of ethylene glycol diglycidyl ether at room temperature. The mixture is then heated to 75\(^{\circ}\)C in a waterbath for 2 hours. A portion of the gel obtained is directly used for further
experiments, the remainder is dried overnight at 85°C under reduced pressure. The product obtained is ground with dry ice and classified to the particle size fraction from 100 μm to 850 μm.

b) In each case 10 g of the classified powder product obtained according to 1a) and 6a) were mixed homogeneously.

The advantageous application properties of the polymer mixtures of Examples 1 to 6 according to the invention are compiled in Table 0.
<table>
<thead>
<tr>
<th>Example</th>
<th>AUL 0.7 psi [g/g]</th>
<th>PUP (0.0014 psi, 4h) [g/g]</th>
<th>PUP (1.4 psi, 4h) [g/g]</th>
<th>Diffusing Absorbency under pressure (4h) [g/g]</th>
<th>Wicking Performance Capacity (lh) [g/g]</th>
<th>Wicking Performance Distance (lh) [cm]</th>
<th>SFC Index</th>
<th>SFC Index [10^-7 cm^3/(g-sec)]</th>
<th>PAI Index NaCl (4h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>22</td>
<td>56</td>
<td>45</td>
<td>36</td>
<td>-</td>
<td>-</td>
<td>430</td>
<td>295675</td>
<td>165</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>59</td>
<td>47</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>680</td>
<td>284370</td>
<td>174</td>
</tr>
<tr>
<td>3</td>
<td>23</td>
<td>61</td>
<td>52</td>
<td>52</td>
<td>-</td>
<td>-</td>
<td>820</td>
<td>202640</td>
<td>182</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>55</td>
<td>43</td>
<td>32</td>
<td>-</td>
<td>-</td>
<td>930</td>
<td>276895</td>
<td>153</td>
</tr>
<tr>
<td>5b</td>
<td>24</td>
<td>55</td>
<td>43</td>
<td>32</td>
<td>-</td>
<td>-</td>
<td>650</td>
<td>290</td>
<td>-</td>
</tr>
<tr>
<td>6b</td>
<td>17</td>
<td>45</td>
<td>35</td>
<td>28</td>
<td>-</td>
<td>-</td>
<td>220</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 0:
Example 7

a) A 10 l capacity polyethylene vessel, well insulated by foamed polymer material, is charged with 3450 g of deionized water and 1400 g of acrylic acid. To this solution are added 14 g of allyl methacrylate with stirring, and the solution is inertized by passing nitrogen through it. At a temperature of about 10°C, the initiators, consisting of 0.57 g of 2,2'-azobisamidinopropane dihydrochloride, dissolved in 50 g of deionized water, 69 mg of hydrogen peroxide, dissolved in 50 g of deionized water, and also 27 mg of ascorbic acid, dissolved in 50 g of deionized water, are added in succession and stirred in. The reaction solution is then left to stand without stirring, and the temperature of the polymerization rises to about 92°C. A solid gel is obtained.

b) 1000 g of a 6% by weight aqueous polyvinylamine solution (K 137) and a solution of 4.8 g of methylenebisacrylamide in 240 ml of deionized water are homogeneously mixed at room temperature. The reaction mixture is subsequently maintained at 80°C for 6 h without stirring, and a solid gel is obtained.

c) The two gels are each mechanically comminuted, and the comminuted gels are mixed with each other in a ratio of 1:1, based on the solids contents of the gels, by repeated conjoint meat-grinding. The mixed gel is dried at 80 to 100°C in a vacuum drying cabinet, ground and classified to 106 - 850 µm.

The product has the following properties:

| PUP 0.014 psi | = | 55.2 g/g after 240 min |
| PUP 0.7 psi  | = | 51.4 g/g after 240 min |
| PUP 1.4 psi  | = | 41.7 g/g after 240 min |
| CRC          | = | 20.7 g/g |
| SFC          | = | 1055 x 10^7 cm^3 s/g |

<table>
<thead>
<tr>
<th>SFC Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFC (0.3 psi)</td>
</tr>
<tr>
<td>SFC (0.6 psi)</td>
</tr>
<tr>
<td>SFC (0.9 psi)</td>
</tr>
<tr>
<td>SFC Index</td>
</tr>
</tbody>
</table>
**PAI (NaCl)**

- AUL 0.01 psi = 43.8 g/g after 240 min
- AUL 0.29 psi = 41.6 g/g after 240 min
- AUL 0.57 psi = 37.9 g/g after 240 min
- AUL 0.90 psi = 34.9 g/g after 240 min
- PAI = 158.2

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>50.3 g/g after 16 h</td>
</tr>
<tr>
<td>0.29</td>
<td>47.8 g/g after 16 h</td>
</tr>
<tr>
<td>0.57</td>
<td>44.2 g/g after 16 h</td>
</tr>
<tr>
<td>0.90</td>
<td>40.7 g/g after 16 h</td>
</tr>
<tr>
<td>PAI</td>
<td>183.0</td>
</tr>
</tbody>
</table>

**PAI (Jayco)**

- AUL 0.01 psi = 63.6 g/g after 240 min
- AUL 0.29 psi = 58.1 g/g after 240 min
- AUL 0.57 psi = 55.3 g/g after 240 min
- AUL 0.90 psi = 52.9 g/g after 240 min
- PAI = 229.9

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>70.4 g/g after 16 h</td>
</tr>
<tr>
<td>0.29</td>
<td>64.8 g/g after 16 h</td>
</tr>
<tr>
<td>0.57</td>
<td>61.9 g/g after 16 h</td>
</tr>
<tr>
<td>0.90</td>
<td>58.3 g/g after 16 h</td>
</tr>
<tr>
<td>PAI</td>
<td>255.4</td>
</tr>
</tbody>
</table>

**Diffusing Absorbency Under Pressure = 51.6 g/g**

**Wicking Performance:**
- Wicking Distance = 11 cm
- Wicking Capacity = 13.1 g

**Acquisition Time Rewet under Pressure:**

- Acquisition Time 1 = 38 s
- Acquisition Time 2 = 32 s
- Acquisition Time 3 = 13 s
- Rewet 1 < 0.1 g
- Rewet 2 < 0.1 g
- Rewet 3 < 1.4 g
- RAC Factor = 101
- DATGLAP = 86.2 g/g

Preparation of surface-postcrosslinked polymer I
Base polymer gel A
8.0 kg of glacial acrylic acid are diluted with 24 kg of water in a 40 l plastic bucket. 37 g (0.457% by weight, based on acrylic acid) of pentaerythritol triallyl ether are added with stirring, and the sealed bucket is inertized by passing nitrogen through it. The polymerization is then started by adding 4 g of 2,2' azobisamidinopropane dihydrochloride, dissolved in 100 ml of water, 460 mg of hydrogen peroxide and 170 mg of ascorbic acid, each likewise dissolved in 100 ml of water. About 3 hours after the reaction has ended, the gel is mechanically comminuted.

Polymer A0
The base polymer gel A is dried at 50°C in a drying cabinet under reduced pressure, ground in a coffee grinder and finally classified to 100-800 µm.

Polymer A1
Polymer A0 is placed in a Waring lab mixer and sprayed with crosslinker solution of the following composition: 2.5% by weight of 1,2-propanediol, 2.5% by weight of water, 0.2% by weight of ethylene glycol diglycidyl ether, based on polymer used. The moist product is subsequently tempered at 120°C in a through circulation drying cabinet for 120 minutes. The dried product is screened off at 850 µm to remove clumps.

Polymer A2
Base polymer gel A is admixed with sufficient caustic soda to obtain a neutralization of 10 mol%, based on the acrylic acid used. The partially neutralized gel is then dried, ground, sieved and postcrosslinked similarly to A1.

Polymer A3
Base polymer gel A is admixed with sufficient caustic soda to obtain a neutralization of 20 mol%, based on the acrylic acid used. The partially neutralized gel is then dried, ground, sieved and postcrosslinked similarly to polymer A1.

Polymer A4
Base polymer gel A is admixed with sufficient caustic soda to obtain a neutralization of 30 mol%, based on the acrylic acid used. The partially neutralized gel is then dried, ground, sieved and postcrosslinked similarly to polymer A1.

Polymer A5
Base polymer gel A is admixed with sufficient caustic soda to obtain a neutralization of 40 mol%, based on the acrylic acid
used. The partially neutralized gel is then dried, ground, sieved and postcrosslinked similarly to polymer A1.

Polymer A6
5 Base polymer gel A is admixed with sufficient caustic soda to obtain a neutralization of 40 mol%, based on the acrylic acid used. The partially neutralized gel is then dried on a drum dryer, ground in a pin mill and classified to 100-800 μm. Postcrosslinking takes place in a Lödige mixer by spraying a 10 crosslinker solution of the following composition: 4% by weight of methanol, 6% by weight of water, 0.2% by weight of 2-oxazolidinone, based on polymer powder used, onto 1 kg of polymer powder through a two-material nozzle. The moist product is subsequently tempered at 180°C in a through circulation drying 15 cabinet for 90 minutes. The dried product is screened off at 850 μm to remove clumps.

Polymer A7
Base polymer gel A is neutralized, dried and ground similarly to polymer A6. The powder is then sprayed with crosslinker solution in a Waring lab mixer. The solution has such a composition that the following dosing is obtained based on base polymer used: 0.30% by weight of 2-oxotetrahydro-1,3-oxazine, 3% by weight of 1,2-propanediol, 7% by weight of water and 0.2% by weight of 25 boric acid. The moist polymer is then dried at 175°C for 60 min.

Polymer A8
1040 g of glacial acrylic acid are diluted with 2827 g of completely ion-free water in a 5 l polymerization flask. 5.2 g of 30 allyl methacrylate are added to this solution with stirring, and the sealed flask is inertized by passing nitrogen through it. The polymerization is then started by adding 0.52 g of 2,2'-azobisamidinoproppane dihydrochloride, dissolved in 25 ml of completely ion-free water, 165 mg of 35% by weight hydrogen peroxide, dissolved in 12 g of completely ion-free water, and 20.8 mg of ascorbic acid, dissolved in 15 ml of completely ion-free water. About 3 hours after the reaction has finished, the gel is mechanically comminuted, dried at 50°C in a drying cabinet under reduced pressure, ground in a coffee grinder and 40 finally classified to 150-800 μm.

The polymer thus obtained is placed in a Waring lab mixer and sprayed with crosslinker solution of the following composition: 2.5% by weight of 1,2-propanediol, 2.5% by weight of water, 0.2% by weight of ethylene glycol diglycidyl ether, based on polymer used. The moist product is then tempered at 120°C in a through
circulation drying cabinet for 120 minutes. The dried product is screened off at 850 µm to remove clumps.

Preparation of surface-postcrosslinked polymer II

Polymer B1
4.1 g of ethylene glycol diglycidyl ether were stirred at room temperature into 2123 g of 5.5% by weight salt-free polyvinylamine solution (K 137) until homogeneous, and the solution was tempered overnight at 60°C. The resulting gel was mechanically comminuted, dried at 80°C under reduced pressure, ground and classified to 150-800 µm. This polymer is placed in a Waring lab mixer and sprayed with crosslinker solution having such a composition that the following dosing is obtained based on base polymer used: 0.20% by weight of ethylene glycol diglycidyl ether, 2.5% by weight of 1,2-propanediol and 2.5% by weight of water. The moist polymer is then dried at 120°C for 60 min.

Base polymer B
621 g of a commercially available polyethylene imine (POLYMIN® P, Brookfield viscosity at 20°C, about 22,000 mPas) is stirred with 279 g of distilled water to form a homogeneous solution. 6.0 g of ethylene glycol diglycidyl ether, dissolved in 100 g of distilled water, are stirred in at room temperature and homogenized. The mixture is subsequently tempered in covered form at 80°C for 6 hours. The resulting gel is subsequently mechanically comminuted, dried at 80°C under reduced pressure, ground and classified to 150-850 µm.

Polymer B2
Base polymer B is placed in a Waring lab mixer and sprayed with crosslinker solution of the following composition: 2.5% by weight of 1,2-propanediol, 2.5% by weight of water, 0.2% by weight of ethylene glycol diglycidyl ether, based on polymer used. The moist product is subsequently tempered at 120°C in a vacuum drying cabinet for 120 minutes. The dried product is screened off at 850 µm to remove clumps.

Polymer B3
Base polymer B is placed in a Waring lab mixer and sprayed with crosslinker solution. The solution has such a composition that the following dosing is obtained based on base polymer used: 0.20% by weight of glutaraldehyde, 3.0% by weight of 1,2-propanediol and 2.0% by weight of water. The moist polymer is then dried at 120°C for 60 min and screened off at 850 µm.
Polymer B4
Base polymer B is placed in a Waring lab mixer and sprayed with crosslinker solution. The solution has such a composition that the following dosing is obtained based on base polymer used: 0.5% by weight of polyamidoamine resin (Resamin® VHW 3608 from Hoechst AG), 2% by weight of 1,2-propanediol and 3% by weight of water. The moist polymer is then dried at 120°C for 60 min and screened off at 850 μm.

Polymer B5
Base polymer B is placed in a Waring lab mixer and sprayed with crosslinker solution. The solution has such a composition that the following dosing is obtained based on base polymer used: 0.2% by weight of 2-oxazolidinone, 3.0% by weight of 1,2-propanediol and 2.0% by weight of water. The moist polymer is then dried at 180°C for 60 min and screened off at 850 μm.

The polymers prepared according to the above Examples were individually tested, and the results are summarized below in Table 1:

<table>
<thead>
<tr>
<th>Example</th>
<th>CRC</th>
<th>AUL 0.70 psi</th>
<th>PUP 0.70 psi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 min</td>
<td>SAM-AUL-04-G</td>
<td>1 h</td>
</tr>
<tr>
<td>Polymer A1</td>
<td>g/g</td>
<td>g/g</td>
<td>g/g</td>
</tr>
<tr>
<td>Polymer A2</td>
<td>6.0</td>
<td>6.3</td>
<td>6.9</td>
</tr>
<tr>
<td>Polymer A3</td>
<td>9.3</td>
<td>9.1</td>
<td>7.1</td>
</tr>
<tr>
<td>Polymer A4</td>
<td>16.6</td>
<td>15.6</td>
<td>12.3</td>
</tr>
<tr>
<td>Polymer A5</td>
<td>23.9</td>
<td>19.6</td>
<td>19.8</td>
</tr>
<tr>
<td>Polymer A6</td>
<td>27.0</td>
<td>23.6</td>
<td>23.4</td>
</tr>
<tr>
<td>Polymer A7</td>
<td>25.4</td>
<td>24.8</td>
<td>25.6</td>
</tr>
<tr>
<td>Polymer A8</td>
<td>27.1</td>
<td>23.1</td>
<td>23.3</td>
</tr>
<tr>
<td>Polymer B1</td>
<td>5.1</td>
<td>6.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Polymer B2</td>
<td>9.3</td>
<td>14.2</td>
<td>13.7</td>
</tr>
<tr>
<td>Polymer B3</td>
<td>4.5</td>
<td>6.3</td>
<td>7.9</td>
</tr>
<tr>
<td>Polymer B4</td>
<td>2.2</td>
<td>6.9</td>
<td>7.7</td>
</tr>
<tr>
<td>Polymer B5</td>
<td>2.4</td>
<td>7.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Polymer B6</td>
<td>1.6</td>
<td>6.4</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Examples 8.1 to 8.16
Surface-postcrosslinked polymers A and B were used to create homogeneous mixtures. The polymers used in each case, their blend
ratios and the application measurements of the mixtures are shown in Table 2.

Surface-postcrosslinking of mixtures of base polymer powders of polymers I and II:

Examples 9.1 - 9.3
Polymer powders prepared according to Examples A0 to A8 but without surface postcrosslinking were homogeneously mixed with polymer powders prepared according to Examples B and B1 (without the surface postcrosslinking described therein) and sprayed with crosslinker solution (2.5% by weight of 1,2-propanediol, 0.2% by weight of ethylene glycol diglycidyl ether and 2.5% by weight of water) in a Waring lab mixer and then dried at 120°C for 60 minutes. Polymer types used, blend ratios and test results are summarized below in Table 3.
<table>
<thead>
<tr>
<th>Example</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>15</td>
<td>4.3</td>
<td>160</td>
<td>15420</td>
<td>110</td>
<td>165</td>
<td>41</td>
<td>41</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>15</td>
<td>4.9</td>
<td>150</td>
<td>13970</td>
<td>123</td>
<td>172</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>17.8</td>
<td>112</td>
<td>1230</td>
<td>128</td>
<td>195</td>
<td>49</td>
<td>49</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>20.5</td>
<td>132</td>
<td>1250</td>
<td>139</td>
<td>215</td>
<td>47</td>
<td>47</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>22.6</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>24.7</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>27.1</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>29.3</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>31.5</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>33.7</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>35.9</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>38.1</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>40.3</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>42.5</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>44.7</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>50</td>
<td>B1</td>
<td>50</td>
<td>46.9</td>
<td>128</td>
<td>11780</td>
<td>155</td>
<td>248</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Performance data of powder mixtures of each previously postcrosslinked polymers I and II.
<table>
<thead>
<tr>
<th>Ex-</th>
<th>Diffusing Absor-</th>
<th>RAC</th>
<th>DAT-GLAP</th>
<th>Pad Test Acquisition Time 1 sec</th>
<th>Pad Test Acquisition Time 2 sec</th>
<th>Pad Test Acquisition Time 3 sec</th>
<th>Pad Test Rewet 1 g</th>
<th>Pad Test Rewet 2 g</th>
<th>Pad Test Rewet 3 g</th>
<th>Wicking Performance 1 h Distance/Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>32</td>
<td>91</td>
<td>66</td>
<td>32</td>
<td>26</td>
<td>14</td>
<td>&lt; 0.1</td>
<td>0.2</td>
<td>2.2</td>
<td>6.5 6.9</td>
</tr>
<tr>
<td>8.2</td>
<td>38</td>
<td>87</td>
<td>72</td>
<td>36</td>
<td>21</td>
<td>13</td>
<td>&lt; 0.1</td>
<td>0.4</td>
<td>2.8</td>
<td>7.2 8.5</td>
</tr>
<tr>
<td>8.3</td>
<td>40</td>
<td>102</td>
<td>84</td>
<td>29</td>
<td>19</td>
<td>14</td>
<td>&lt; 0.1</td>
<td>0.3</td>
<td>3.2</td>
<td>8.3 11.7</td>
</tr>
<tr>
<td>8.4</td>
<td>36</td>
<td>93</td>
<td>78</td>
<td>27</td>
<td>18</td>
<td>11</td>
<td>&lt; 0.1</td>
<td>0.8</td>
<td>1.8</td>
<td>9.4 10.7</td>
</tr>
<tr>
<td>8.5</td>
<td>45</td>
<td>123</td>
<td>102</td>
<td>38</td>
<td>22</td>
<td>18</td>
<td>&lt; 0.1</td>
<td>1.2</td>
<td>4.0</td>
<td>8.4 11.2</td>
</tr>
<tr>
<td>8.6</td>
<td>42</td>
<td>107</td>
<td>96</td>
<td>23</td>
<td>17</td>
<td>14</td>
<td>&lt; 0.1</td>
<td>0.4</td>
<td>2.4</td>
<td>11.6 14.8</td>
</tr>
<tr>
<td>8.7</td>
<td>41</td>
<td>107</td>
<td>99</td>
<td>30</td>
<td>24</td>
<td>20</td>
<td>&lt; 0.1</td>
<td>0.2</td>
<td>3.1</td>
<td>13.0 18.0</td>
</tr>
<tr>
<td>8.8</td>
<td>37</td>
<td>106</td>
<td>97</td>
<td>26</td>
<td>13</td>
<td>8</td>
<td>&lt; 0.1</td>
<td>1.6</td>
<td>7.9</td>
<td>9.7 15.5</td>
</tr>
<tr>
<td>8.9</td>
<td>38</td>
<td>97</td>
<td>92</td>
<td>29</td>
<td>15</td>
<td>9</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>0.8</td>
<td>7.6 10.0</td>
</tr>
<tr>
<td>8.10</td>
<td>36</td>
<td>161</td>
<td>102</td>
<td>27</td>
<td>16</td>
<td>10</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>1.5</td>
<td>14.5 15.3</td>
</tr>
<tr>
<td>8.11</td>
<td>38</td>
<td>92</td>
<td>81</td>
<td>28</td>
<td>19</td>
<td>12</td>
<td>&lt; 0.1</td>
<td>0.4</td>
<td>1.8</td>
<td>16.2 14.2</td>
</tr>
<tr>
<td>8.12</td>
<td>33</td>
<td>80</td>
<td>51</td>
<td>30</td>
<td>20</td>
<td>15</td>
<td>&lt; 0.1</td>
<td>0.7</td>
<td>5.2</td>
<td>10.5 13.0</td>
</tr>
<tr>
<td>8.13</td>
<td>45</td>
<td>112</td>
<td>94</td>
<td>25</td>
<td>13</td>
<td>8</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>1.8</td>
<td>15.0 16.2</td>
</tr>
<tr>
<td>8.14</td>
<td>53</td>
<td>97</td>
<td>72</td>
<td>32</td>
<td>24</td>
<td>10</td>
<td>&lt; 0.1</td>
<td>0.2</td>
<td>1.9</td>
<td>16.4 15.4</td>
</tr>
<tr>
<td>8.15</td>
<td>49</td>
<td>114</td>
<td>93</td>
<td>34</td>
<td>22</td>
<td>14</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>1.4</td>
<td>17.2 14.3</td>
</tr>
<tr>
<td>8.16</td>
<td>51</td>
<td>121</td>
<td>87</td>
<td>38</td>
<td>23</td>
<td>13</td>
<td>&lt; 0.1</td>
<td>0.3</td>
<td>1.2</td>
<td>14.9 15.2</td>
</tr>
</tbody>
</table>
Table 3:
Surface postcrosslinking of mixtures of base polymer powders of polymers I and II

<table>
<thead>
<tr>
<th>Example</th>
<th>A % by weight</th>
<th>B % by weight</th>
<th>CRC g/g</th>
<th>SFC *10^{-7} cm^3.s/g</th>
<th>SFC Index</th>
<th>PAI Index NaCl after 4 h</th>
<th>PAI Index Jayco after 4 h</th>
<th>PUP 0.0014 psi 4 h g/g</th>
<th>PUP 0.7 psi 4 h g/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>A2* 50</td>
<td>B1* 50</td>
<td>23.7</td>
<td>1280</td>
<td>367430</td>
<td>165</td>
<td>245</td>
<td>53</td>
<td>48</td>
</tr>
<tr>
<td>9.2</td>
<td>A8* 50</td>
<td>B1* 50</td>
<td>16.9</td>
<td>1150</td>
<td>325490</td>
<td>143</td>
<td>261</td>
<td>56</td>
<td>47</td>
</tr>
<tr>
<td>9.3</td>
<td>A8* 50</td>
<td>B 50</td>
<td>19.8</td>
<td>980</td>
<td>293670</td>
<td>187</td>
<td>253</td>
<td>61</td>
<td>52</td>
</tr>
</tbody>
</table>

* without surface postcrosslinking

<table>
<thead>
<tr>
<th>Example</th>
<th>PUP 1.4 psi 4 h g/g</th>
<th>Diffusing Absorbency Under Pressure g/g</th>
<th>Pad Test Acquisition Time 1 sec</th>
<th>Pad Test Acquisition Time 2 sec</th>
<th>Pad Test Acquisition Time 3 sec</th>
<th>Pad Test Rewet 1 g</th>
<th>Pad Test Rewet 2 g</th>
<th>Pad Test Rewet 3 g</th>
<th>Wicking Performance 1 h Distance/Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>41</td>
<td>45</td>
<td>24</td>
<td>19</td>
<td>11</td>
<td>&lt; 0.1</td>
<td>0.4</td>
<td>3.0</td>
<td>13.4                      15.0</td>
</tr>
<tr>
<td>9.2</td>
<td>38</td>
<td>46</td>
<td>23</td>
<td>16</td>
<td>9</td>
<td>&lt; 0.1</td>
<td>0.3</td>
<td>2.1</td>
<td>15.6                      14.2</td>
</tr>
<tr>
<td>9.3</td>
<td>39</td>
<td>50</td>
<td>32</td>
<td>20</td>
<td>12</td>
<td>&lt; 0.1</td>
<td>0.5</td>
<td>1.7</td>
<td>14.9                      16.2</td>
</tr>
</tbody>
</table>
Example 10

100 g of a graft copolymer based on polyethylene glycol of
5 average molar mass 9000 (70 g) and N-vinylformamide (30 g) and
having a K value of 42 were diluted with 900 g of demineralized
water and stirred with 20 g of a 40% by weight sodium bisulfite
solution and 67 g of 25% by weight aqueous sodium hydroxide
solution at 80°C. A further 20.1 g of 25% by weight NaOH solution
10 were added over 24 h. The degree of hydrolysis was 81.4% by
theory determined at pH 3.5 by polyelectrolyte titration. This
polymer solution was desalted by ultrafiltration using a membrane
(exclusion limit 3000 D).

15 200 g of a vastly desalted polymer solution (nonvolatiles 5%) were mixed with 0.2 g of acrylic acid and crosslinked at 175°C in
a Teflon-coated trough in a vacuum drying cabinet for 10 minutes.
The polymer thus obtained was dry and readily grindable. A 1:1
powder mixture of this polymer and of a crosslinked polyacrylic
20 acid (base polymer A0) were tested for their application
properties.

Absorption capacity (30 min)[g/g]:32.7

25 Absorption capacity (4 h)[g/g]:46.3

CRC (30 min) [g/g]:19.2

AAP (0.7 psi)[g/g]:17.0

Example 11

50 g of a high molecular weight polyethyleneimine (average molar
35 mass 500,000) having a solids content of 49.5% by weight were
admixed with 100 parts of a copolymer of acrylamide (98 g) and
hydroxyethyl acrylate (2 g) K 72.1 and a solids content of 14.8% by
weight and kneaded for 1 hour in a Jahnke & Kunkel lab
kneader. The gel was dried at 70°C under reduced pressure for 24 h
and subsequently ground.

A 1:1 powder mixture of this polymer and a crosslinked
polyacrylic acid (according to Example 1a) were tested for their
absorbing properties.

45 Absorption capacity (30 min)[g/g]:26.5
CRC (30 min) [g/g]: 10.4
AAP (0.3 psi)[g/g]: 17.6

5 Example 12

600 g of a completely ion-free polyvinylamine homopolymer having a K value of 91, a degree of hydrolysis of 90.1% and a solids content of 4% by weight were admixed with 1 g of acrylic acid in a lab kneader and crosslinked at 100°C. A further 600 g of the polyvinylamine were added during this period and a total of 490 g of water were distilled off. After 5 h the polymer was water-insoluble. The gel was then dried at 75°C under reduced pressure for 24 h and subsequently ground. A 1:1 powder mixture of this polymer and a crosslinked polyacrylic acid (base polymer A0) was tested.

Absorption capacity (30 min)[g/g]: 30.3

20 CRC (30 min) [g/g]: 15.1
CRC (4 h) [g/g]: 23.3
Absorption capacity (4h)[g/g]: 42.0

25 AAP (0.7 psi)[g/g]: 16.2
PUP (0.7 psi Jayco)[g/g]: 15.3

30 PUP (0.7 psi Jayco, 4 h)[g/g]: 22.3

Example 13

500 g of a completely ion-free polyvinylamine homopolymer having a K value of 85, a degree of hydrolysis of 92.1% and a solids content of 6.7% by weight were admixed with 1 g of methyl acrylate in a lab kneader and crosslinked at 100°C. A further 500 g of the polyvinylamine were added during this period and a total of 360 g of water was distilled off. After 5 h the polymer was water-insoluble. The gel was then dried at 75°C under reduced pressure for 24 h and subsequently ground. A 1:1 powder mixture of this polymer and a crosslinked polyacrylic acid (base polymer A0) was tested for use as superabsorbent.

45 Absorption capacity (30 min)[g/g]: 28.7
CRC (30 min) [g/g]: 17.9
AAP (0.3 psi)[g/g]: 15.3

5 Example 14

200 g of a completely ion-free polyvinylamine homopolymer solution (nonvolatiles 5%) were mixed with 0.4 g of urea and crosslinked at 175°C in a Teflon-coated trough in a vacuum drying cabinet for 10 minutes. The polymer obtained was brittle and dry after a further drying step at 185°C and readily grindable.

A 1:1 powder mixture of this polymer and a crosslinked polyacrylic acid of Example 1a) was tested.

15 Absorption capacity (30 min)[g/g]: 24.9
CRC (30 min) [g/g]: 10.1

20 Absorption capacity (4h)[g/g]: 41.9
CRC (4 h) [g/g]: 16.5
AAP (0.7 psi 1h)[g/g]: 15.6

25 Example 15

200 g of a completely ion-free polyvinylamine homopolymer solution (nonvolatiles 5%) were mixed with 0.4 g of propylene carbonate and crosslinked at 175°C in a Teflon-coated trough in a vacuum drying cabinet for 10 minutes. The polymer obtained was brittle and dry after a further drying step at 185°C and readily grindable.

35 A 1:1 powder mixture of this polymer and a crosslinked polyacrylic acid of Example 1a) was tested for use as superabsorbent.

Absorption capacity (30 min)[g/g]: 25.0
40 CRC (30 min) [g/g]: 10.6
Absorption capacity (4h)[g/g]: 40.6
CRC (4 h) [g/g]: 16.8
AAP (0.7 psi 1h)[g/g]: 16.4
Example 16

668.9 g of a desalted polyvinylamine of K 137 (nonvolatiles 2.8%) are self-crosslinked at 185°C in a Teflon-coated pan in a vacuum drying cabinet for 2 hours. The resulting product can be peeled off like a film. This gives about 20 g of solid polymer which was ground in an analytical mill.

A 1:1 powder mixture of this polymer and a crosslinked polyacrylic acid (according to Example 1a) was tested for its absorbing properties.

Absorption capacity (30 min)[g/g]:48.5
Absorption capacity (4 h) [g/g]: 64.3
CRC (30 min) [g/g]:25.4
AAP (0.7 psi 1h)[g/g]:16.8

Example 17

337.3 g of a desalted polyvinylamine of K 137 (nonvolatiles 2.5%) are mixed for 45 minutes in a Jahnke & Kunkel lab kneader with 33.37 g of a 25% by weight polyacrylic acid gel according to Example 1a (solids content ratio 1:1) at room temperature. This is followed by crosslinking at 180°C under nitrogen in a Teflon-coated pan in a vacuum drying cabinet at 400 mbar over 1.5 hours. The product was ground in an analytical mill and subsequently sieved through a 500 μ sieve. The absorbent properties of this solid polymer were:

Absorption capacity (30 min)[g/g]:35.1
Absorption capacity (4 h) [g/g]: 43.9
CRC (30 min) [g/g]:11.8
AAP (0.7 psi 1h)[g/g]:23.8

Example 18

200 g of a desalted polyvinylamine (nonvolatiles 2.5%) are mixed at room temperature in a Duplex kneader with 30 g of 25% polyacrylic acid gel according to Example 1a at room temperature (solids content ratio of polyvinylamine to superabsorbent 4:6) for 1 hour and subsequently crosslinked in a Teflon-coated pan at 400 mbar under nitrogen at 180°C for 1.5 hours.

The product was ground in an analytical mill and subsequently sieved through a 500 μ sieve. The absorbent properties of this solid polymer were:
Absorption capacity (30 min) [g/g]: 30.6
Absorption capacity (4 h) [g/g]: 38.4
CRC (30 min) [g/g]: 11.2
AAP (0.7 psi) [g/g]: 21.6.
We claim:

1. A hydrogel-forming polymer mixture including
   
a) a hydrogel-forming polymer I containing acid radicals and
   
b) a hydrogel-forming polymer II containing amino and/or imino radicals which has been made water-insoluble by crosslinking,
   
wherein the ratio of said acid radicals to the sum total of said amino/imino radicals is within the range from 1:9 to 9:1 and said polymer mixture has an SFC Index of > 10,000 obtained from three SFC measurements under different pressures according to the formula

\[
\text{SFC Index} = \frac{[\text{SFC (0.3 psi)} \cdot 10^7 \text{ g/cm}^3\text{s}] \cdot ([\text{SFC (0.6 psi)} \cdot 10^7 \text{ g/cm}^3\text{s}] + [\text{SFC (0.9 psi)} \cdot 10^7 \text{ g/cm}^3\text{s}]).}
\]

2. A hydrogel-forming polymer mixture as claimed in claim 1, wherein said hydrogel-forming polymer I is crosslinked polyacrylic acid where from 0 to 50% of the carboxyl groups are present as alkali metal and/or ammonium salt.

3. A hydrogel-forming polymer mixture as claimed in claim 1 or 2, wherein said hydrogel-forming polymer II is crosslinked and is a polyethyleneimine, an ethyleneimine-grafted polyamidoamine and/or ethyleneimine-grafted polyamine.

4. A hydrogel-forming polymer mixture as claimed in claim 1 or 2, wherein said hydrogel-forming polymer II is a crosslinked polyvinylamine.

5. A hydrogel-forming polymer mixture as claimed in claim 4, wherein the hydrogel-forming polymer II is obtainable by hydrolysis of polyvinylformamide which has a degree of hydrolysis of 70-100% and subsequent thermal postcrosslinking.

6. A hydrogel-forming polymer mixture as claimed in claim 1 or 2, wherein said hydrogel-forming polymer II was obtained by copolymerization of vinylformamide and one or more monoethylenically unsaturated compounds, subsequent hydrolysis with or without desalting and subsequent crosslinking.
7. A hydrogel-forming polymer mixture as claimed in claim 1 or 2, wherein said hydrogel-forming polymer II is a graft copolymer of vinylformamide on polymeric compounds which was subsequently subjected to hydrolysis with or without desalting and crosslinking.

8. A hydrogel-forming polymer mixture as claimed in any one of claims 1, 2 and 6, wherein said hydrogel-forming polymer II is a copolymer of vinylformamide and monoethylenically unsaturated mono- and/or polycarboxylic acid which was subsequently subjected to hydrolysis with or without desalting and crosslinking by heating.

9. A hydrogel-forming polymer mixture as claimed in any one of claims 1, 2 and 6, wherein said hydrogel-forming polymer II is a copolymer of vinylformamide and monoethylenically unsaturated mono- and/or polycarboxylic acid which was subjected to hydrolysis with or without desalting and crosslinking by heating, and subsequently to further crosslinking with a cationic polymer or copolymer based on polyvinylamine or polyethyleneimine and/or with at least one bifunctional crosslinker.

10. A hydrogel-forming polymer mixture as claimed in any of claims 1 to 3, wherein said polymer II is a polyethyleneimine, an ethyleneimine-grafted polyamidoamine or a polyamine polymer which was modified by reaction with α,β-unsaturated carboxylic acids or esters or by Strecker reaction and subsequently thermally crosslinked.

11. A hydrogel-forming polymer mixture as claimed in claim 1 having a PAI index (NaCl) of \( \geq 100 \) after a swell time of 16 h.

12. A hydrogel-forming polymer mixture as claimed in claim 1 having a PAI index (Jayco) of \( \geq 150 \) after a swell time of 16 h.

13. A hydrogel-forming polymer mixture as claimed in claim 1 having a Diffusing Absorbency Under Pressure of \( \geq 30 \) g/g.

14. A hydrogel-forming polymer mixture as claimed in claim 1 having a Wicking Distance \( \geq 5 \) in the Wicking Performance Test and a Wicking Capacity of at least 5 g.
15. A hydrogel-forming polymer mixture as claimed in claim 1 having an Acquisition Time 3 of \( \leq 25 \) s and a Rewet 3 of not more than 9 g in the Acquisition Time/Rewet Test under pressure.

16. A hydrogel-forming polymer mixture as claimed in claim 1 having an RAC Factor of at least 80.

17. A hydrogel-forming polymer mixture as claimed in claim 1 having a DATGLAP of at least 50 g/g.

18. A hydrogel-forming polymer mixture as claimed in claim 1 obtained by mixing polymer gel I and polymer powder II or by mixing polymer powder I and polymer gel II.

19. A hydrogel-forming polymer mixture as claimed in claim 1 obtained by addition of a blend component I or II as powder to the reaction mixture of the other component.

20. A hydrogel-forming polymer mixture as claimed in claim 1 obtained by self-crosslinking of polyvinylamine obtainable by hydrolysis of polyvinylformamide having a degree of hydrolysis of 70-100% on drying a mixture of said polymers I and II at 80-200°C.

21. The method of using the hydrogel-forming polymer mixture of claim 1 as absorbent for water and aqueous fluids.

22. The method of using the hydrogel-forming polymer mixture of claim 1 in hygiene articles used for absorbing body fluids.