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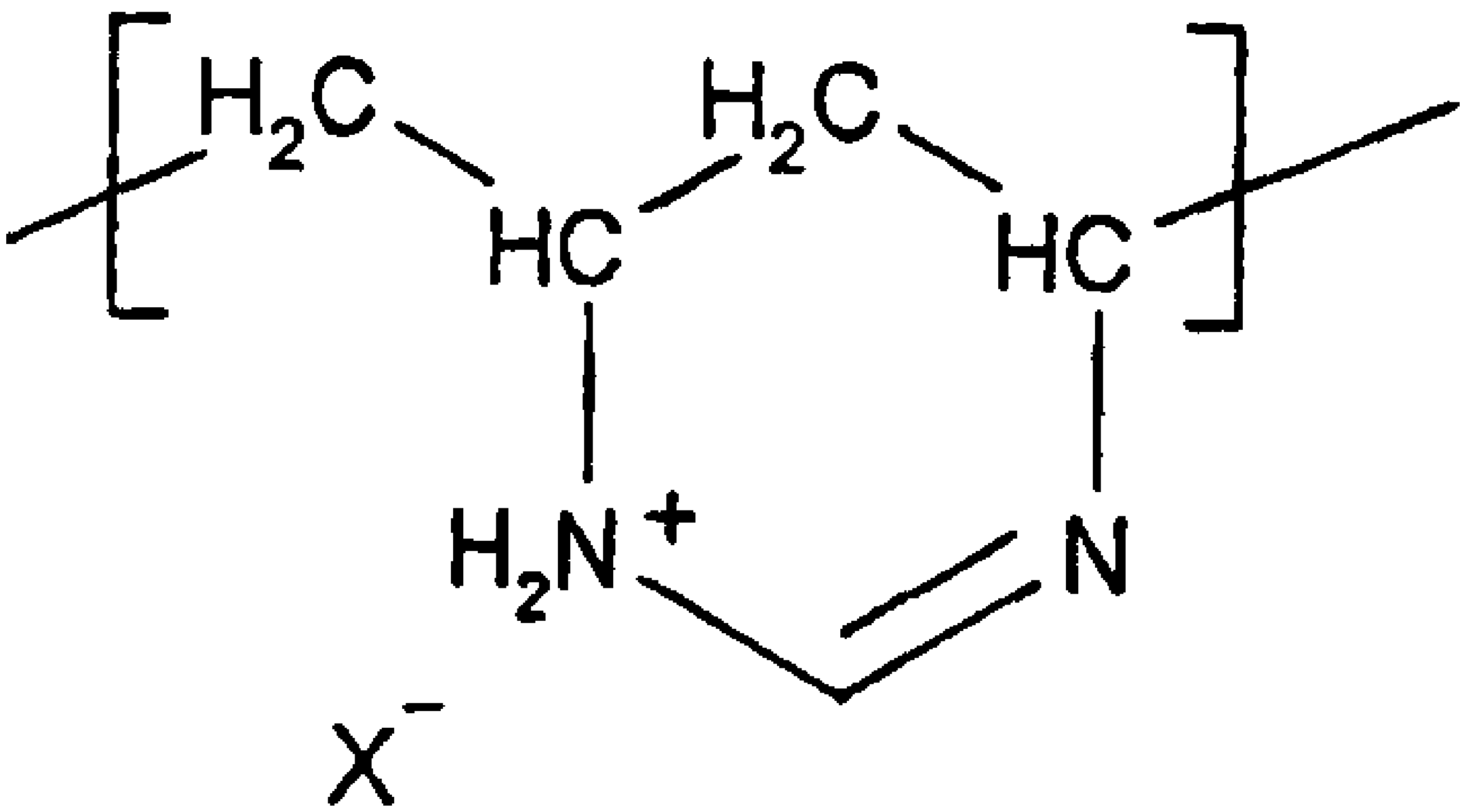
(54) Titre : ELUTRIATIONS AQUEUSES DE MATIERES DE CHARGE A FINES PARTICULES, LEUR PROCEDE DE PRODUCTION ET LEUR UTILISATION POUR LA PRODUCTION DE PAPIERS CONTENANT DES MATIERES DE CHARGE

(54) Title: AQUEOUS ELUTRIATIONS OF FINE-PARTICLED FILLING MATERIALS, METHODS FOR THE PRODUCTION THEREOF AND USE THEREOF IN THE PRODUCTION OF PAPER CONTAINING FILLING MATERIALS



(57) Abrégé/Abstract:
Aqueous elutriations of fine-particled filling materials which are at least partially coated with polymers and which can be obtained by treating aqueous elutriations of fine-particled filling materials with at least one water-soluble amphoteric copolymer which can be obtained by copolymerization of (a) at least one n-vinylcarboxylic acid amide of formula (III), wherein R^1, R^2 = H or C_1- C_6-alkyl, (b)

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(57) Abrégé(suite)/Abstract(continued):
at least one monoethylenically unsaturated carboxylic acid with 3 -8 C atoms per molecule and/or the alkali metal, earth alkali metal or ammonium salts thereof and optionally (c) other monoethylenically unsaturated monomers which are free of nitrile groups, and optionally (d) compounds comprising two ethylenically unsaturated double bonds per molecule, and subsequent partial or full hydrolysis separation of groups CO-R^1 from the monomers III polymerized inside the copolymer. The invention also relates to methods for the production of aqueous elutriations and the use thereof as additives to paper material in the production of paper containing filling materials, cardboard containing filling materials or paperboard containing filling materials by dewatering said paper material.

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(81) Bestimmungsstaaten *(soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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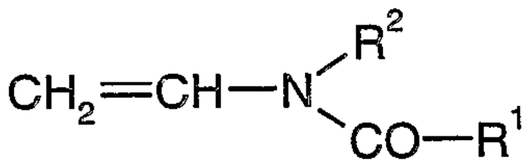
(54) Title: AQUEOUS ELUTRIATIONS OF FINE-PARTICLED FILLING MATERIALS, METHODS FOR THE PRODUCTION THEREOF AND USE THEREOF IN THE PRODUCTION OF PAPER CONTAINING FILLING MATERIALS

(54) Bezeichnung: WÄSSRIGE ANSCHLÄMMUNGEN VON FEINTEILIGEN FÜLLSTOFFEN, VERFAHREN ZU IHRER HERSTELLUNG UND IHRE VERWENDUNG ZUR HERSTELLUNG FÜLLSTOFFHALTIGER PAPIERE



(III)

(57) Abstract: Aqueous elutriations of fine-particled filling materials which are at least partially coated with polymers and which can be obtained by treating aqueous elutriations of fine-particled filling materials with at least one water-soluble amphoteric copolymer which can be obtained by copolymerization of (a) at least one n-vinylcarboxylic acid amide of formula (III), wherein R^1, R^2 = H or C_1- C_6-alkyl, (b) at least one monoethylenically unsaturated carboxylic acid with 3 -8 C atoms per molecule and/or the alkali metal, earth alkali metal or ammonium salts thereof and optionally (c) other monoethylenically unsaturated monomers which are free of nitrile groups, and optionally (d) compounds comprising two ethylenically unsaturated double bonds per molecule, and subsequent partial or full hydrolysis separation of groups CO-R^1 from the monomers III polymerized inside the copolymer. The invention also relates to methods for the production of aqueous elutriations and the use thereof as additives to paper material in the production of paper containing filling materials, cardboard containing filling materials or paperboard containing filling materials by dewatering said paper material.

(57) Zusammenfassung: Wässrige Anschlämmungen von feinteiligen Füllstoffen, die zumindest teilweise mit Polymerisaten überzogen sind, und die erhältlich sind durch Behandeln von wässrigen Anschlämmungen feinteiliger Füllstoffe mit mindestens einem wasserlöslichen amphoteren Copolymerisat, das erhältlich ist durch Copolymerisieren von (a) mindestens einem n-Vinylcarbonsäureamid der Formel (III), in der R^1, R^2 = H oder C_1- bis C_6-Alkyl bedeuten, (b) mindestens einer monoethylenisch ungesättigten Carbonsäure mit 3 bis 8 C-Atomen im Molekül und/oder deren Alkalimetall-, Erdalkalimetall- oder Ammoniumsalzen und gegebenenfalls (c) anderen monoethylenisch ungesättigten Monomeren, die frei von Nitrilgruppen sind, und gegebenenfalls (d) Verbindungen, die mindestens zwei ethylenisch ungesätttigte Doppelbindungen im Molekül aufweisen, und anschliessende teilweise oder vollständige Hydrolyse Abspaltung der Gruppen -CO-R^1 aus den in das Copolymerisat einpolymerisierten Monomeren III, Verfahren zur Herstellung der wässrigen Anschlämmungen und ihre Verwendung als Zusatz zum Papierstoff bei der Herstellung von füllstoffhaltigem Papier, füllstoffhaltigem Karton oder füllstoffhaltiger Pappe durch Entwässern des Papierstoffs.

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GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

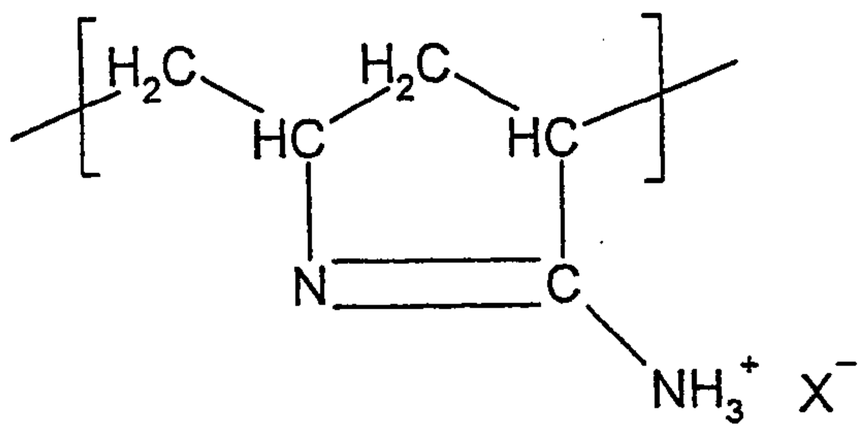
Veröffentlicht:

— *mit internationalem Recherchenbericht*

AQUEOUS ELUTRIATIONS OF FINE-PARTICLED FILLING MATERIALS, METHODS FOR THE PRODUCTION THEREOF AND USE THEREOF IN THE PRODUCTION OF PAPER CONTAINING FILLING MATERIALS

The present invention relates to aqueous slurries of finely divided fillers which are at least partly coated with polymers, processes for their preparation and their use as an additive to the paper stock in the production of filler-containing paper, filler-containing cardboard and filler-containing board.

EP-B-0 251 182 discloses, inter alia, a process for the preparation of polymers, a mixture of N-vinylformamide and acrylonitrile or methacrylonitrile being polymerized in the presence of free radical initiators and the polymers then being modified by treatment with acids. The modified polymers contain vinylamine units in the form of salts, vinylformamide and acrylonitrile or methacrylonitrile units and, if required, acrylamide and acrylic acid units. Reworking of examples from this publication has, however, shown that the polymers hydrolyzed with acids contain considerable amounts of amidine units of the formula



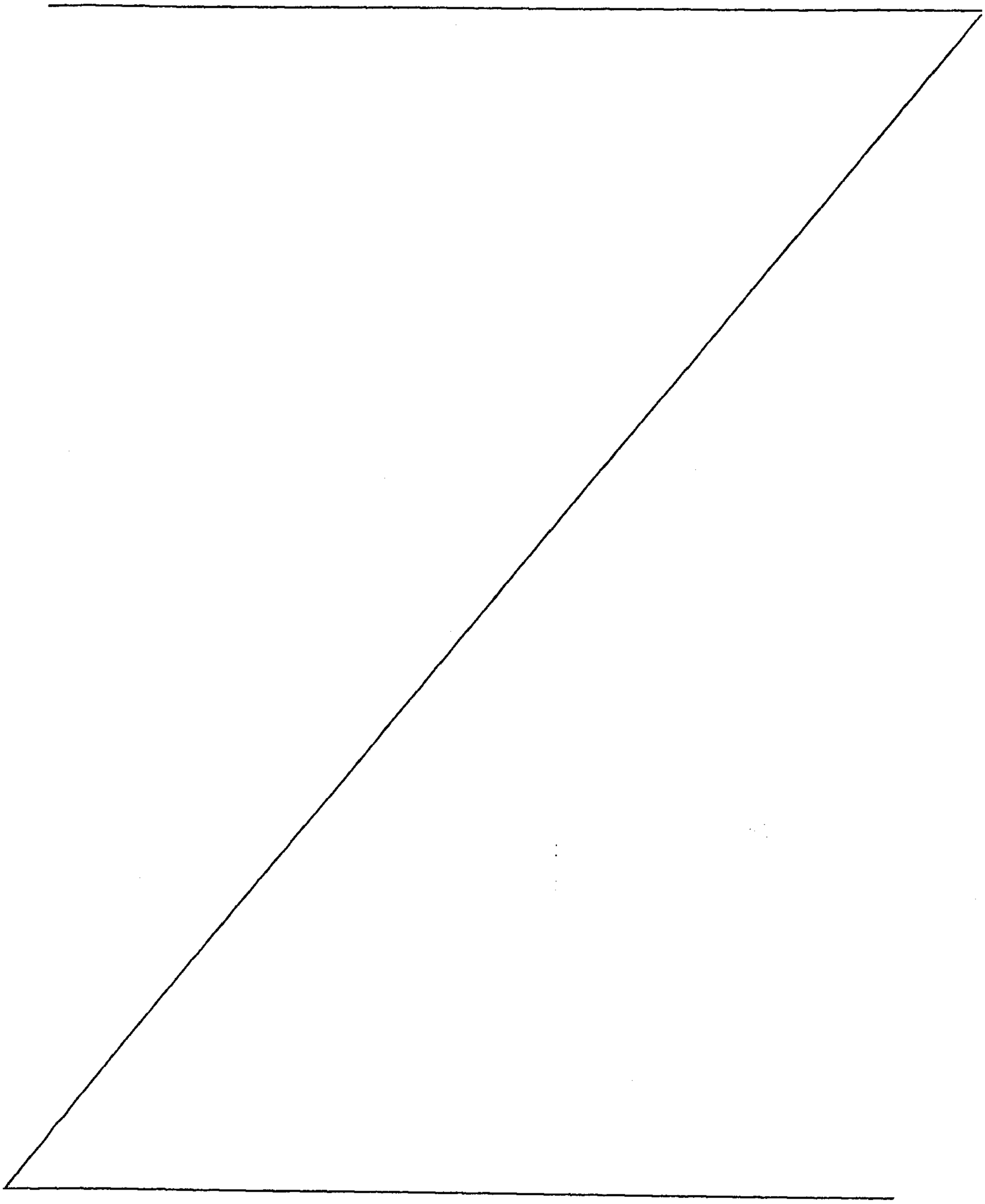
(I)

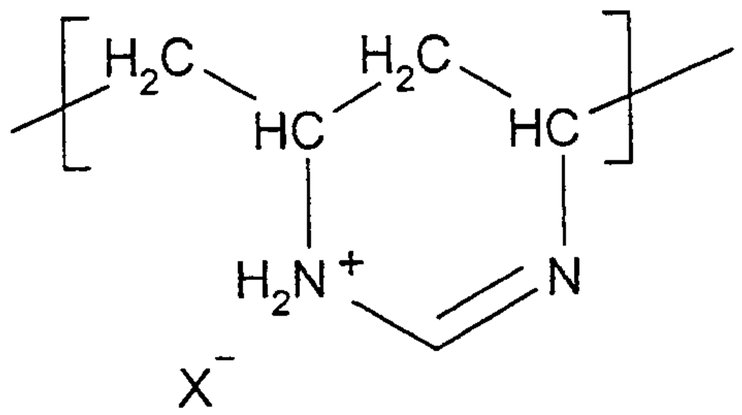
The hydrolyzed polymers are used in papermaking as drainage aids and retention aids and for strengthening paper.

EP-B-0 528 409 discloses cationic copolymers which contain from 20 to 90 mol% of amidine units. They are prepared by copolymerization of N-vinylformamide and acrylonitrile and subsequent hydrolysis of the copolymers with acids. The polymers containing amidine units are used as flocculants for sludges.

EP-B-0 672 212 relates to the use of copolymers which are obtainable by copolymerization of N-vinylcarboxamides, monoethylenically unsaturated carboxylic acids and, if required, vinyl acetate, N-vinylpyrrolidone and/or N-vinylimidazole and, if

required, monomers having at least two double bonds in the molecule and subsequent partial or complete hydrolysis of the vinylcarboxamide units present in the copolymers to give amino or ammonium groups, as an additive to the paper stock in papermaking for increasing the drainage rate and the retention as well as the dry and wet strength of the paper. As analyses have shown, hydrolyzed copolymers of N-vinylformamide and acrylic acid contain considerable amounts of amidine units of the formula

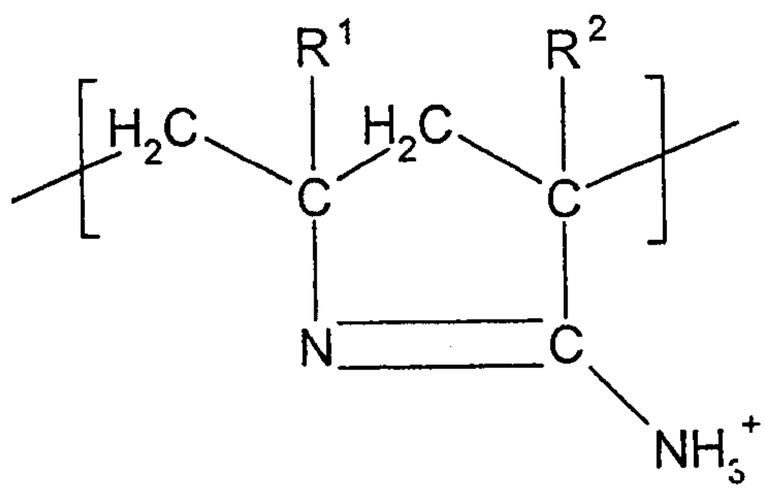




(II),

where X^- is an anion.

JP-A-08059740 discloses that amphoteric water-soluble polymers are added to aqueous suspensions of inorganic particles, at least a part of the polymers being adsorbed on the filler surface. The amphoteric polymers are preferably prepared by hydrolyzing copolymers of N-vinylformamide, acrylonitrile and acrylic acid in the presence of acids. They contain from 20 to 90 mol% of amidine units of the structure



(I)

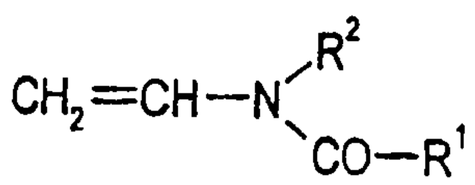
where R^1 and R^2 are each H or methyl and X^- is an anion. The filler slurries treated with such polymers are added to the paper stock in the production of filler-containing papers. The filler treatment leads to an improvement in the drainage of the paper stock and also results in an improvement in various strength properties of the dried paper and an improvement in the filler retention.

US-A-2002/0088579 describes the pretreatment of inorganic fillers with cationic, anionic and amphoteric (zwitterionic) polymers. In each case, the treatment consists of at least two stages. Treatment with a cationic polymer followed by treatment with an anionic polymer is recommended. In further steps, further cationic and anionic polymers can be alternately adsorbed. The aqueous suspensions comprising the pretreated filler particles are added to the paper stock in the production of filler-containing paper. The filler treatment leads to an improvement in various strength properties of the dried paper.

It is an object of the present invention to provide further aqueous slurries of finely divided fillers which can be used in papermaking.

We have found that this object is achieved, according to the invention, by an aqueous slurry of finely divided fillers which are at least partly coated with polymers, wherein said slurry is obtained by treating an aqueous slurry of at least one finely divided filler with at least one water-soluble amphoteric copolymer which is obtained by copolymerization of

(a) at least one N-vinylcarboxamide of the formula



(III),

where R^1 and R^2 are H or C_1- to C_6-alkyl,

(b) at least one monoethylenically unsaturated carboxylic acid having 3 to 8 carbon atoms in the molecule and/or the alkali metal, alkaline earth metal or ammonium salts thereof,

(c) optionally monoethylenically unsaturated monomers which are free of nitrile groups, and

(d) optionally compounds which have at least two ethylenically unsaturated double bonds in the molecule,

to form a copolymerization product, and

subsequent partial or complete elimination of the groups -CO-R^1 from the monomers III incorporated in the form of polymerized units in said copolymerization product.

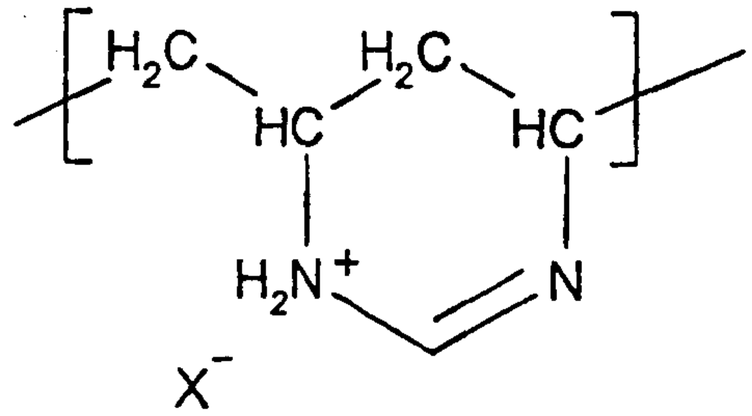
In the invention as claimed, the at least one water-soluble amphoteric copolymer that is used, is however more specifically a copolymer consisting of the following

constituent monomer units:

(I) from 5 to 70 mol% of vinylcarboxamide units,

(II) from 20 to 45 mol% of units of at least one monoethylenically unsaturated carboxylic acid of 3 to 8 carbon atoms and

(III) from 10 to 50 mol% of vinylamine and/or amidine units of the formula



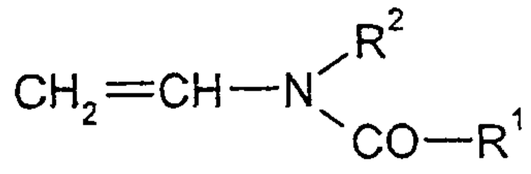
where X^- is an anion, and

(IV) 0 to 30 mol% of units of other monoethylenically unsaturated compounds which are free of nitrile groups.

The aqueous slurries contain, for example, from 1 to 50, preferably from 10 to 40, % by weight of at least one finely divided filler. The amount of amphoteric water-soluble polymer is, for example, from 0.1 to 5, preferably 0.25 – 3, % by weight, based on fillers.

The present invention also relates to a process for the preparation of aqueous slurries, from 0.1 to 5% by weight, based on filler, of at least one copolymer which is obtainable by copolymerization of

(a) at least one N-vinylcarboxamide of the formula



(III),

where R^1 and R^2 are H or C_1- to C_6-alkyl,

(b) at least one monoethylenically unsaturated carboxylic acid having 3 to 8 carbon atoms in the molecule and/or the alkali metal, alkaline earth metal or ammonium salts thereof and, if required,

(c) other monoethylenically unsaturated monomers which are free of nitrile groups and, if required,

(d) compounds which have at least two ethylenically unsaturated double bonds in the molecule

and subsequent partial or complete elimination of the groups -CO-R^1 from the monomers III incorporated in the form of polymerized units in the copolymer being added to an aqueous slurry of at least one finely divided filler, or the aqueous slurry of at least one finely divided filler being introduced into an aqueous solution of said amphoteric copolymer and the components being mixed in each case.

The molar mass of the water-soluble amphoteric polymers is, for example, at least 10 000, preferably at least 100 000, in particular at least 500 000, Dalton.

The present invention furthermore relates to the use of the aqueous slurries described above as an additive to the paper stock in the production of filler-containing paper, filler-containing cardboard or filler-containing board by drainage of the paper stock.

Suitable fillers are all pigments which can be customarily used in the paper industry, e.g. calcium carbonate, which can be employed in the form of ground calcium carbonate (GCC), chalk, marble or precipitated calcium carbonate (PCC), talc, kaolin, bentonite, satin white, calcium sulfate, barium sulfate and titanium dioxide. Mixtures of two or more pigments may also be used. For example, from 40 to 90% of the particles of the finely divided fillers have a diameter of less than 2 µm.

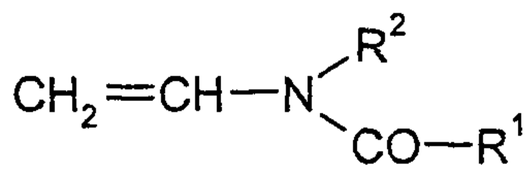
The fillers are processed to an aqueous slurry, for example, by introduction in water. Precipitated calcium carbonate is usually suspended in water in the absence of dispersants. In order to prepare aqueous slurries of the other fillers, an anionic dispersant, e.g. polyacrylic acids having an average molar mass Mw of, for example, from 1 000 to 40 000 Dalton, is generally used. If an anionic dispersant is used, for example, from 0.01 to 0.5, preferably from 0.2 to 0.3, % by weight thereof is employed for the preparation of aqueous filler slurries. The finely divided fillers dispersed in water

in the presence of anionic dispersants are anionic. The aqueous slurries contain, for example, from 10 to 30, in general 15 – 25, % by weight of at least one filler.

In order to prepare the novel aqueous slurries of finely divided fillers, aqueous slurries of finely divided fillers, anionically dispersed if necessary, are treated with at least one water-soluble amphoteric polymer. For example, from 0.1 to 5% by weight, based on fillers, of a water-soluble amphoteric polymer can be added to an aqueous slurry containing from 1 to 50% by weight of at least one finely divided filler, or an aqueous slurry of a finely divided filler can be introduced into an aqueous solution of an amphoteric polymer and the components mixed in each case. The treatment of the aqueous slurry of finely divided filler with the amphoteric polymers can be carried out continuously or batchwise. On combination of aqueous slurries of finely divided fillers and aqueous solutions of amphoteric polymers, the filler particles are at least partly coated or impregnated with the amphoteric polymers. The mixing of the components is effected, for example, in a shear field. In general, it is sufficient if the components are stirred after combination or are treated in a shear field of an Ultraturrax apparatus. The combination and mixing of the components of the aqueous slurries can be effected, for example, at from 0 to 95°C, preferably from 10 to 70°C. In general, the components are mixed at from the respective room temperature to 40°C. The pH of the aqueous filler slurries treated with amphoteric polymers is, for example, from 5 to 11, preferably from 6 to 9, the pH of calcium carbonate-containing slurries preferably being more than 6.5.

The water-soluble amphoteric copolymers are disclosed in EP-B-0 672 212, mentioned as prior art. They are prepared by copolymerization of

(a) at least one N-vinylcarboxamide of the formula



(III),

where R^1 and R^2 are H or C_1- to C_6-alkyl,

(b) at least one monoethylenically unsaturated carboxylic acid having 3 to 8 carbon atoms in the molecule and/or the alkali metal, alkaline earth metal or ammonium salts thereof and, if required,

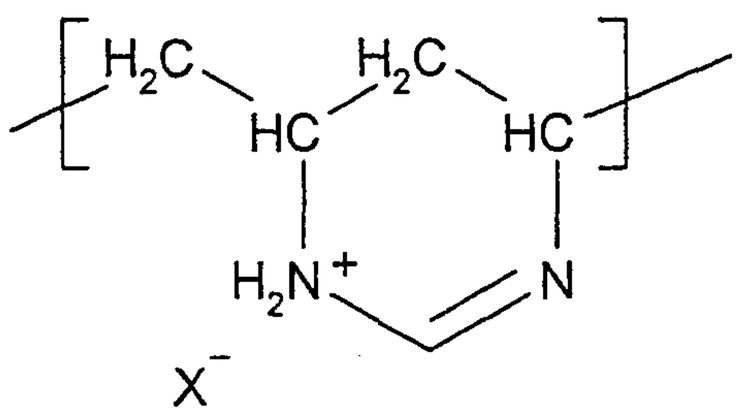
(c) other monoethylenically unsaturated monomers which are free of nitrile groups and, if required,

(d) compounds which have at least two ethylenically unsaturated double bonds in the molecule

and subsequent partial or complete elimination of the groups -CO-R^1 from the monomers III incorporated in the form of polymerized units in the copolymer. Aqueous slurries of finely divided fillers which are treated with amphoteric copolymers which are obtainable by copolymerization of

(a) N-vinylformamide,
(b) acrylic acid, methacrylic acid and/or the alkali metal or ammonium salts thereof and, if required,
(c) other monoethylenically unsaturated monomers which are free of nitrile groups

and subsequent partial or complete hydrolysis of the vinylformamide units contained in the copolymers, in the presence of acids, e.g. hydrochloric acid, or of bases, such as sodium hydroxide solution or potassium hydroxide solution, are preferred. The hydrolysis of the vinylformamide units with acids or bases results in vinylamine and/or amidine units of the formula



(II),

where X^- is an anion. The originally anionic copolymer acquires cationic groups thereby and thus becomes amphoteric. The hydrolysis of the monomer units III incorporated in the form of polymerized units can also be effected enzymatically. The amidine units form by reaction of neighboring vinylamine units with vinylformamide units. For the amphoteric copolymers, the sum of vinylamine units and amidine units which form from the N-vinylcarboxamides incorporated in the form of polymerized units is always stated below.

Examples of monomers of group (a) are N-vinylformamide, N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-N-methylacetamide N-vinyl-N-ethylacetamide, N-vinyl-N-methylpropionamide and N-vinylpropionamide. The monomers of group (a) can be used alone or as a mixture in the copolymerization with the monomers of the other groups.

Suitable monomers of group (b) are monoethylenically unsaturated carboxylic acids of 3 to 8 carbon atoms and the water-soluble salts of these carboxylic acids. This group of monomers includes, for example, acrylic acid, methacrylic acid, dimethacrylic acid, ethacrylic acid, maleic acid, fumaric acid, itaconic acid, mesaconic acid, citraconic acid,

methylenemalonic acid, allylacetic acid, vinylacetic acid and crotonic acid. The monomers of this group can be used alone or as a mixture with one another, in partly or in completely neutralized form, in the copolymerization. For example, alkali metal or alkaline earth metal bases, ammonia, amines and/or alkanolamines are used for the neutralization. Examples of these are sodium hydroxide solution, potassium hydroxide solution, sodium carbonate, potassium carbonate, sodium bicarbonate, magnesium oxide, calcium hydroxide, calcium oxide, triethanolamine, ethanolamine, morpholine, diethylenetriamine or tetraethylenepentamine.

For modification, the copolymers can, if required, contain monomers of group (c) in the form of polymerized units, which monomers are free of nitrile groups, e.g. methyl acrylate, ethyl acrylate, N-butyl acrylate, isobutyl acrylate, isobutyl methacrylate, methyl methacrylate, ethyl methacrylate, vinyl acetate, vinyl propionate, N-vinylpyrrolidone, N-vinylimidazole, acrylamide and/or methacrylamide.

A further modification of the copolymers is possible by using in the copolymerization monomers (d) which contain at least two double bonds in the molecule, e.g. methylenebisacrylamide, glycol diacrylate, glycol dimethacrylate, glyceryl triacrylate, pentaerythrityl triallyl ether, polyalkylene glycols or polyols which are at least diesterified with acrylic acid and/or methacrylic acid, such as pentaerythritol, sorbitol or glucose. If at least one monomer of group (d) is used in the copolymerization, the amounts used are up to 2 mol%, e.g. from 0.001 to 1 mol%.

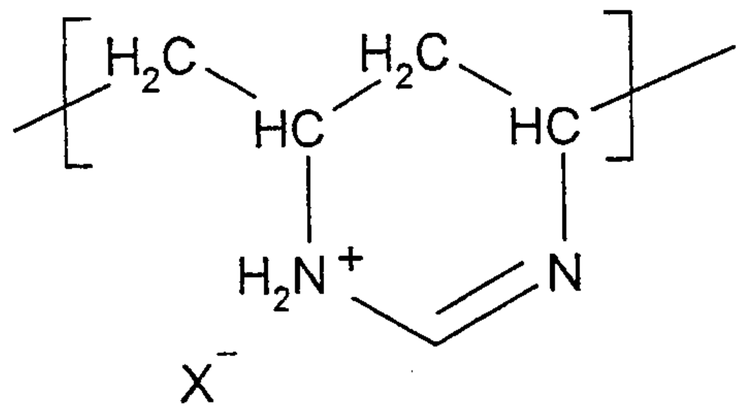
The copolymerization of the monomers is effected in a known manner, cf. EP-B-0 672 212, page 4, lines 13 – 37. The hydrolysis of the copolymers is described on page 4, lines 38 – 58 and on page 5, lines 1 – 25 of said European Patent. Hydrolyzed copolymers for which the hydrolysis was carried out in the presence of acids are preferably used. The degree of hydrolysis of the vinylcarboxamide groups incorporated in the form of polymerized units is, for example, from 1 to 98, in general from 10 to 98, preferably from 20 to 60, mol%.

The hydrolyzed copolymers contain, for example,

(I) from 1 to 98, preferably from 1 to 75, mol% of vinylcarboxamide units,

(II) from 1 to 98, preferably from 1 to 55, mol% of units of at least one monoethylenically unsaturated carboxylic acid of 3 to 8 carbon atoms and

(III) from 1 to 98, preferably from 1 to 55, mol% of vinylamine and/or amidine units of the formula



(II),

where X^- is an anion, and, if required,

(IV) up to 30 mol% of units of other monoethylenically unsaturated compounds which are free of nitrile groups.

Particularly preferred hydrolyzed copolymers are those which contain

(I) from 5 to 70 mol% of vinylformamide units,
(II) from 15 to 45 mol% of acrylic acid and/or methacrylic acid units and
(III) from 10 to 50 mol% of vinylamine units in salt form and amidine units of the formula II.

The amphoteric copolymers may carry an excess anionic or an excess cationic charge or may be electrically neutral if equal numbers of anionic and cationic groups are present in the copolymer. Depending on the charge state of the amphoteric copolymers, the aqueous filler slurries prepared therewith are anionic, cationic or electrically neutral if the amphoteric copolymers comprise equal quantities of cationic and anionic charge.

Preferably used amphoteric copolymers are those which have a charge density of, preferably, not more than 1 meq/g at pH 7, both in the anionic and in the cationic range.

In the examples, percentages are by weight, unless evident otherwise from the context. The electrophoretic mobility or the zeta potential were determined by a laser optical method. For electrophoresis measurements, the samples were diluted with an aqueous KCl solution (e.g. 10 mmol) to a concentration of 1% by volume for the measurement. The measuring instrument used was the Zetasizer 3000 HS from Malvern Instruments Ltd.

The molar masses Mw of the polymers were determined with the aid of static light scattering. The measurements were carried out at pH 7.6 in a 10 millimolar aqueous sodium chloride solution.

The composition of the polymers was determined with the aid of ^{13}C-NMR spectroscopy. For this purpose, the signals of the following carbon atoms were integrated. The solvent used was D_2O.

Group	Signal position [ppm]	Area
-**C**OONa	185	A (acrylate)
H**C**OO$^-$	172	A (formate)
-NH**C**OH	164-174[1)]	A (formamide)
-N=**C**H-N-	152	A (amidines)

[1)] Several signals

The fractions of the individual monomer units in mol% are obtained using the following formulae:

Acrylic acid: 100·A (acrylate) / [A (acrylate) + A (formate) + A (formamide) + A (amidines)]

Vinylamine: 100·A (formate) / [A (acrylate) + A (formate) + A (formamide) + A (amidines)]

Vinylformamide: 100·A (formamide) / [A (acrylate) + A (formate) + A (formamide) + A (amidines)]

Amidines: 100·A (amidines) / [A (acrylate) + A (formate) + A (formamide) + A (amidines)]

Fillers used were precipitated chalk, precipitated calcium carbonate (PCC), ground calcium carbonate (GCC), kaolin and mixtures of said fillers.

Example 1

6 g of a 12% strength aqueous solution of an amphoteric copolymer containing 40 mol% of vinylformamide units, 30 mol% of acrylic acid units and 30 mol% of vinylamine and amidine units and having a molecular weight Mw of about 500 000 were initially taken in a beaker and then diluted with 30 g of water. 150 g of a 20% strength slurry of precipitated calcium carbonate (PCC) in water were then added. During the addition of the PCC slurry and thereafter, the mixture was stirred with the aid of a Heiltof stirrer at 1 000 revolutions per minute (rpm). The pH of the mixture was then brought to 8.5. The mobility of the filler particles at pH 8.5 and at pH 7 was

measured with the aid of microelectrophoresis. The electrophoretic mobility assumed a slightly negative value at both pH settings.

Example 2

6 g of a 12% strength aqueous solution of an amphoteric copolymer containing 5 mol% of vinylformamide units, 45 mol% of acrylic acid units and 50 mol% of vinylamine and amidine units and having a molecular weight Mw of about 400 000 were initially taken in a beaker and then diluted with 30 g of water. 150 g of a 20% strength slurry of precipitated calcium carbonate (PCC) in water were then added. During the addition of the PCC slurry and thereafter, the mixture was stirred with the aid of a Heiltof stirrer at 1 000 rpm. The pH of the mixture was then brought to 8.5. The mobility of the filler particles at pH 8.5 and at pH 7 was measured with the aid of microelectrophoresis. The electrophoretic mobility assumed a slightly negative value at both pH settings.

Example 3

6 g of a 12% strength aqueous solution of an amphoteric copolymer containing 70 mol% of vinylformamide units, 20 mol% of acrylic acid units and 10 mol% of vinylamine and amidine units and having a molecular weight Mw of about 700 000 were initially taken in a beaker and then diluted with 30 g of water. 150 g of a 20% strength slurry of precipitated calcium carbonate (PCC) in water were then added. During the addition of the PCC slurry and thereafter, the mixture was stirred with the aid of a Heiltof stirrer at 1 000 rpm. The pH of the mixture was then brought to 8.5. The mobility of the filler particles at pH 8.5 and at pH 7 was measured with the aid of microelectrophoresis. The electrophoretic mobility assumed a slightly negative value at both pH settings.

Example 4

6 g of a 12% strength aqueous solution of an amphoteric copolymer containing 30 mol% of vinylformamide units, 40 mol% of acrylic acid units and 30 mol% of vinylamine and amidine units and having a molecular weight Mw of about 400 000 were initially taken in a beaker and then diluted with 30 g of water. 150 g of a 20% strength slurry of precipitated calcium carbonate (PCC) in water were then added. During the addition of the PCC slurry and thereafter, the mixture was stirred with the aid of a Heiltof stirrer at 1 000 rpm. The pH of the mixture was then brought to 8.5. The mobility of the filler particles at pH 8.5 and at pH 7 was measured with the aid of microelectrophoresis. The electrophoretic mobility assumed a slightly negative value at both pH settings.

Example 5

6 g of a 12% strength aqueous solution of an amphoteric copolymer containing 30 mol% of vinylformamide units, 30 mol% of acrylic acid units and 40 mol% of vinylamine and amidine units and having a molecular weight Mw of about 400 000 were initially taken in a beaker and then diluted with 30 g of water. 150 g of a 20% strength slurry of precipitated calcium carbonate (PCC) in water were then added. During the addition of the PCC slurry and thereafter, the mixture was stirred with the aid of a Heiltof stirrer at 1 000 rpm. The pH of the mixture was then brought to 8.5. The mobility of the filler particles at pH 8.5 and at pH 7 was measured with the aid of microelectrophoresis. The electrophoretic mobility assumed a slightly negative value at both pH settings.

Example 6

6 g of a 12% strength aqueous solution of an amphoteric copolymer containing 40 mol% of vinylformamide units, 30 mol% of acrylic acid units and 30 mol% of vinylamine and amidine units and having a molecular weight Mw of about 500 000 were initially taken in a beaker and then diluted with 30 g of water. 150 g of a 20% strength slurry of ground calcium carbonate (GCC) in water were then added. During the addition of the PCC slurry and thereafter, the mixture was stirred with the aid of a Heiltof stirrer at 1 000 rpm. The pH of the mixture was then brought to 8.5. The mobility of the filler particles at pH 8.5 and at pH 7 was measured with the aid of microelectrophoresis. The electrophoretic mobility assumed a slightly negative value at both pH settings.

Example 7

6 g of a 12% strength aqueous solution of an amphoteric copolymer containing 40 mol% of vinylformamide units, 30 mol% of acrylic acid units and 30 mol% of vinylamine and amidine units and having a molecular weight Mw of about 500 000 were initially taken in a beaker and then diluted with 30 g of water. 150 g of a 20% strength slurry of kaolin-clay mixture in water were then added. During the addition of this slurry and thereafter, the mixture was stirred with the aid of a Heiltof stirrer at 1 000 rpm. The pH of the mixture was then brought to 8.5. The mobility of the filler particles at pH 8.5 and at pH 7 was measured with the aid of microelectrophoresis. The electrophoretic mobility assumed a slightly negative value at both pH settings.

Comparative example 1 according to example 1 of JP-A-08059740

6 g of a 12% strength aqueous solution of an amphoteric copolymer containing 35 mol% of amidine units of the structure I, 20 mol% of vinylformamide units, 10 mol% of vinylamine units, 5 mol% of acrylic acid units and 30 mol% of nitrile units and having a molar mass Mw of 300 000 Dalton were initially taken in a beaker and then diluted with 30 g of water. The limiting viscosity of the polymers with 2.7 dl/g (measured using an Oswald viscometer in an aqueous NaCl solution at the NaCl content of 0.1 g/dl and 25°C).

150 g of a 20% strength slurry of precipitated calcium carbonate (PCC) in water were then added. During the addition of the slurry and thereafter, the mixture was stirred with the aid of a Heiltof stirrer at 1 000 rpm. The pH of the mixture was then brought to 8.5. With the aid of microelectrophoresis, the mobility of the filler particles was measured at pH 8.5 and at pH 7. The electrophoretic mobility assumed a slightly negative value at both pH settings.

Production of filler-containing paper

Paper type A

Examples 8 - 14

A mixture of TMP (thermomechanical pulp) and groundwood in a ratio of 70/30 and with a solids concentration of 4% was beaten speck-free in a laboratory pulper until a freeness of 60–65 was reached. The pH of the stock was from 7 to 8. The beaten stock was then diluted to a solids concentration of 0.35% by adding water.

In order to determine the behavior of the aqueous filler slurries described above in the production of filler-containing paper, in each case 500 ml of the paper stock suspension were initially taken and in each case the slurries treated according to the examples and the comparative example and a cationic polyacrylamide as a retention aid (Polymin*KE 2020) were metered into these pulps. The amount of retention aid metered was in each case 0.01%, based on solids content of the paper stock

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suspension, of polymer. The amount of slurry was adjusted with the aid of several preliminary experiments so that the ash content of the paper sheets produced using the stock was 32%. Sheets were also produced using the 20% strength aqueous slurries of precipitated calcium carbonate (PCC slurry), ground calcium carbonate (GCC slurry) and kaolin clay, stated in table 1.

The paper sheets were each produced on a Rapid-Köthen sheet former according to ISO 5269/2 with a sheet weight of 80g/m^2, then dried for 7 minutes at 90°C and then calendered at a nip pressure of 200 N/cm.

Testing of the paper sheets of type A

After a storage time in a conditioned chamber at a constant 23°C and 50% relative humidity for 12 hours, the dry breaking length of the sheets, according to DIN 54540, and the porosity of the sheets, according to Bendtsen (ISO 5636-3), were tested. The dry picking resistance was determined using the IGT printability tester (ISO 3783). The results are shown in table 1.

Paper type B
Examples 15 - 20

A mixture of bleached birch sulfate and bleached pine sulfite in a ratio of 70/30 and with a solids concentration of 4% was beaten speck-free in a laboratory pulper until a freeness of 55-60 was reached. An optical brightener (Blankophor® PSG) and a cationic starch (HiCat 5163 A) were then added to the beaten stock. The digestion of the cationic starch was effected in the form of a 10% strength starch slurry in a jet digester at 130°C and with a residence time of 1 minute. The amount of optical brightener metered was 0.5%, based on the solids content of the paper stock suspension, of commercial product. The amount of cationic starch metered was 0.5%, based on the solids content of the paper stock suspension, of starch. The pH of the stock was from 7 to 8. The beaten stock was then diluted to a solids concentration of 0.35% by adding water.

In order to determine the behavior of the aqueous filler slurries described above in the production of filler-containing paper, in each case 500 ml of the paper stock suspension were initially taken and in each case the slurries treated according to the examples and the comparative example and a cationic polyacrylamide as a retention aid (Polymin KE 2020) were metered into these pulps. The amount of retention aid metered was in each case 0.01%, based on solids content of the paper stock suspension, of polymer. The amount of slurry was adjusted with the aid of several preliminary experiments so that the ash content of the paper sheets produced using the stock was 20%. Sheets were also produced using the 20% strength aqueous slurries of precipitated calcium carbonate (PCC slurry) and ground calcium carbonate (GCC slurry), stated in table 2.

The paper sheets were produced in each case on a Rapid-Köthen sheet former according to ISO 5269/2 with a sheet weight of 80g/m^2 and then dried for 7 minutes at 90°C.

Testing of the paper sheets of type B

After a storage time in a conditioned chamber at a constant 23°C and 50% relative humidity for 12 hours, the dry breaking length of the sheets, according to DIN 54540, and the internal strength, according to DIN 54516, were determined. The CIE whiteness was determined using a spectrophotometer of the Elrepho SF 400 type according to DIN 5033. The results are shown in table 2.

Table 1

Example	Slurry acc. to Ex.	Dry breaking length (m)	Porosity (ml/min)	IGT
8	1	2213	1675	very good
9	2	2086	1789	very good
10	3	2016	1811	very good
11	4	1987	1698	good
12	5	2123	1678	very good
13	6	2097	1756	very good
14	7	2145	1541	very good
Comparative examples				
PCC slurry without pretreatment		1356	1734	poor
GCC slurry without pretreatment		1247	1876	poor
Kaolin-clay slurry without pretreatment		1415	1476	poor
Slurry according to comparative example 1		1745	1701	moderate

Table 2

Example	Slurry acc. to Ex.	Dry breaking length (m)	CIE whiteness	Internal strength [N]
15	1	4176	114.6	23.4
16	2	4098	112.5	22.8
17	3	3987	113.5	22.6
18	4	4123	111.4	23.7
19	5	4076	113.6	23.2
20	6	3951	118.8	22.1
Comparative examples				
PCC slurry without pretreatment		3285	110.7	15.6
GCC slurry without pretreatment		3020	119.4	15.2
Slurry according to comparative example 1		3675	111.2	17.8

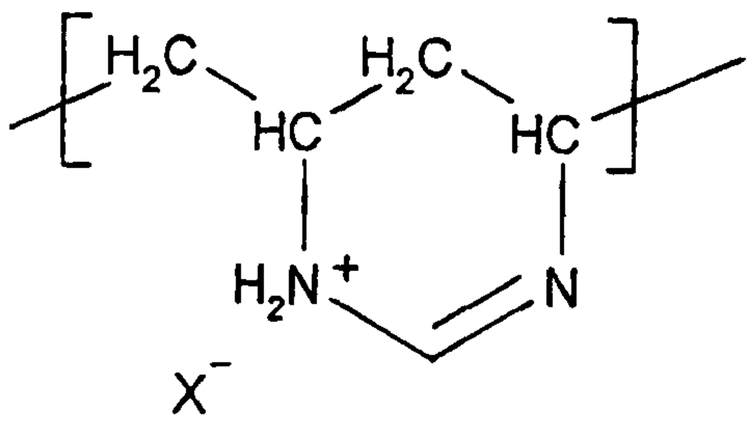
CLAIMS

1. An aqueous slurry of finely divided fillers which are at least partly coated with polymers, wherein said slurry is obtained by treating an aqueous slurry of at least one finely divided filler with at least one water-soluble amphoteric copolymer consisting of the following constituent monomer units:

(I) from 5 to 70 mol% of vinylcarboxamide units,

(II) from 20 to 45 mol% of units of at least one monoethylenically unsaturated carboxylic acid of 3 to 8 carbon atoms and

(III) from 10 to 50 mol% of vinylamine and/or amidine units of the formula



where X^- is an anion, and

(IV) 0 to 30 mol% of units of other monoethylenically unsaturated compounds which are free of nitrile groups.

2. An aqueous slurry as claimed in claim 1, wherein said slurry contains from 1 to 50% by weight of said at least one finely divided filler and wherein the amount of said at least one water-soluble amphoteric copolymer is from 0.05 to 5% by weight, based on said fillers.

3. An aqueous slurry as claimed in claim 1 or 2, which contains from 10 to 40% by weight of said at least one finely divided filler.

4. An aqueous slurry as claimed in any one of claims 1 to 3, wherein said at least one amphoteric copolymer has a molar mass Mw of at least 10 000.

5. An aqueous slurry as claimed in any one of claims 1 to 4, wherein said at least one water-soluble amphoteric copolymer carries an excess anionic charge.

6. An aqueous slurry as claimed in any one of claims 1 to 4, wherein said at least one water-soluble amphoteric copolymer carries an excess cationic charge.

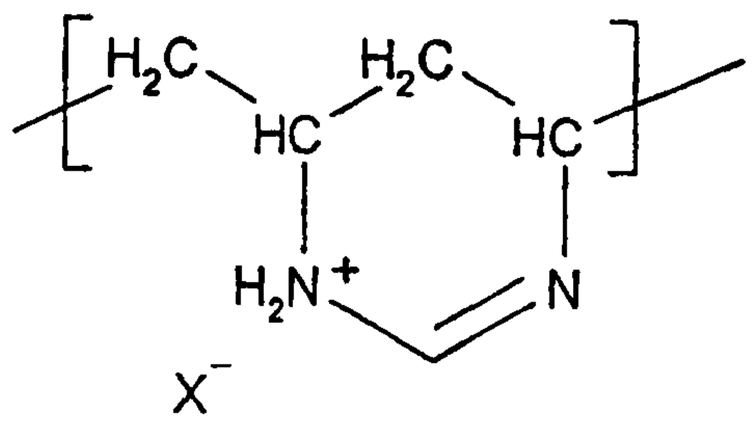
7. An aqueous slurry as claimed in any one of claims 1 to 4, wherein at least one water-soluble amphoteric copolymer have a same amount of cationic and anionic charge.

8. A process for the preparation of an aqueous slurry as claimed in any one of claims 1 to 7, wherein from 0.1 to 5% by weight, based on filler, of at least one water-soluble copolymer consisting of the following constituent monomer units

(I) from 5 to 70 mol% of vinylcarboxamide units,

(II) from 20 to 45 mol% of units of at least one monoethylenically unsaturated carboxylic acid of 3 to 8 carbon atoms and

(III) from 10 to 50 mol% of vinylamine and/or amidine units of the formula



where X^- is an anion, and

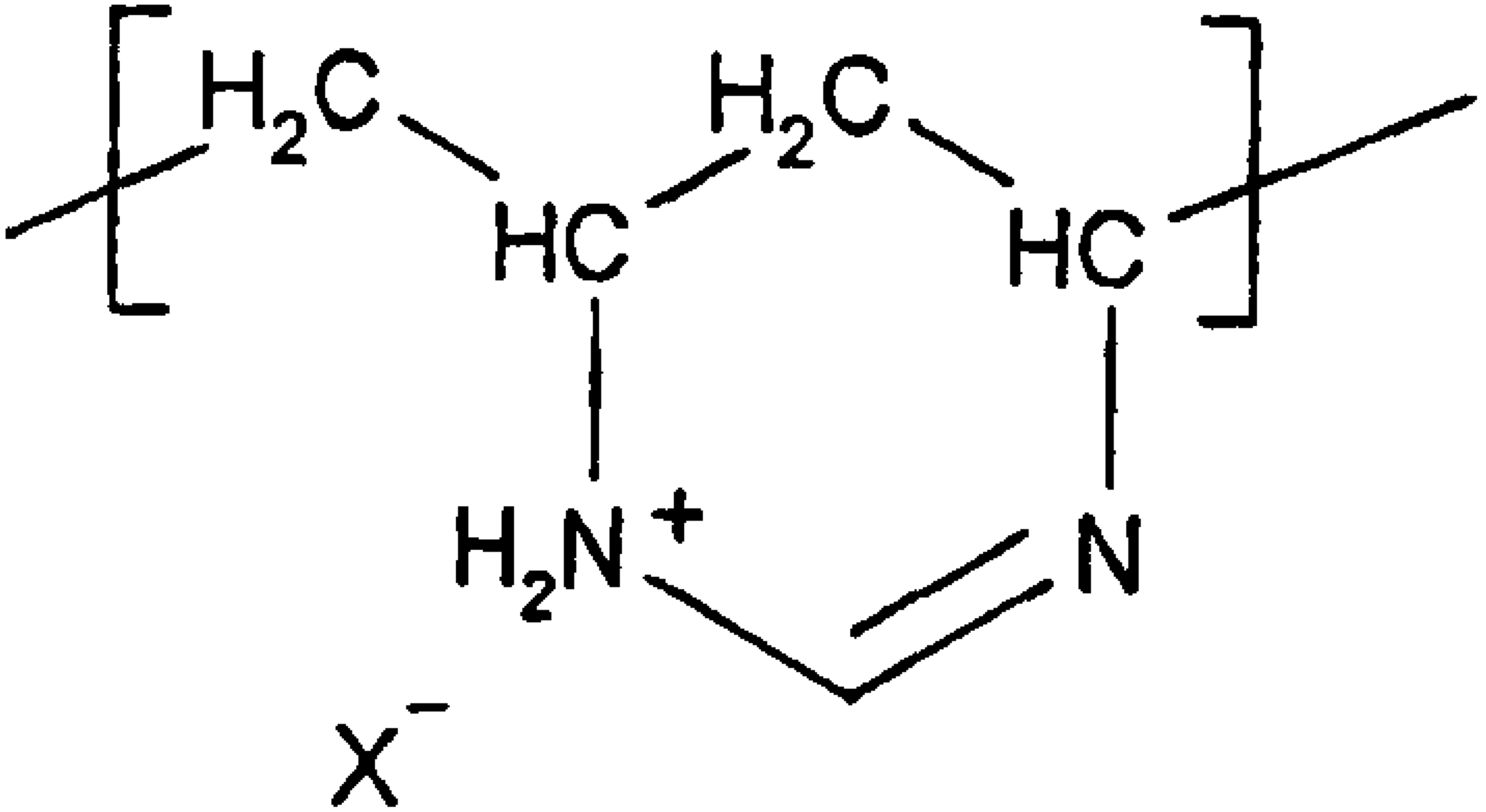
(IV) 0 to 30 mol% of units of other monoethylenically unsaturated compounds which are free of nitrile groups,

are added to the aqueous slurry of said at least one finely divided filler, or the aqueous slurry of said at least one finely divided filler is introduced into the aqueous solution of said at least one water-soluble amphoteric copolymer,

and the components are mixed in each case.

9. A process as claimed in claim 8, wherein the electrophoretic mobility of particles of said at least one finely divided filler of the aqueous slurry is negative or not more than zero at a pH of 7.

10. The use of the aqueous slurry as claimed in any one of claims 1 to 7, as an additive to the paper stock in the production of filler-containing paper, filler-containing cardboard or filler-containing board by draining of the paper stock.


H2C
H2C
HC
HC
H2N+
N
X−