

The present invention relates to the use of amphoteric water-soluble polymers as beater additives and/or dispersing agents for papermaking in the presence of a retention auxiliary aid.

Fillers used in the paper industry as well as in some other areas of industry such as, for example, the paint and dyestuff industries, are available not only in powder form, but also in the form of aqueous dispersions. Various economic reasons, such as the elimination of drying, as well as the potential for a more rational work cycle in the production of paper, favour the use of fillers in the form of dispersions. Furthermore, the use of such dispersions eliminates the problem of dust in the workplace, such as has been experienced heretofore.

The production of filler suspensions is known. Usually, low-molecular water-soluble polymers that contain a high proportion of anionically effective groups, e.g., carboxyl groups are used as dispersing agents. In many instances, commercial products are homopolymers of acrylic acid in the form of its sodium or ammonium salts.

DE-OS 31 23 732 describes a process in which copolymers of acrylic acid and acrylamidomethylpropane sulphonic acid are used as dispersing agents. The process results in highly concentrated aqueous pigment suspensions, the viscosity of which decreases only slightly as temperature increases. Such behaviour is especially favourable for the grinding/beating process.

EP 0 035 640 describes the use of oxalkylated fatty ammonium salts as dispersing agents. Filler suspen-

sions produced with these salts are characterized by extremely high solids concentrations that can be achieved, which can exceed 75%.

DE-OS 32 30 737 describes the use of a combination of an anionic polymer with a cationic polymer for dispersing calcined clay. It is preferred that a cross-linked acrylic emulsion copolymer that contains an acid be used as the anionic polymer and a quaternary polyamine be used as the cationic polymer. The use of such a dispersing agent combination results in a reduced sedimentation of kaolin in the storage tank as well as a reduction of dilatancy that is usually very marked in the case of kaolin.

In EP 0129329 water-soluble copolymers are used for the production of pigment dispersions that contain carboxylic and sulphonic acid groups, wherein the molecular weight is between 1,000 and 5,000 and the polydispersity of the copolymer is less than 1.5. Improved dispersing properties are achieved by the low polydispersity.

Calcium carbonate suspensions with a proportion of at least 87% particle size of less than 2 μm are claimed by EP 0 108 842. Copolymers of acrylic acid and acrylamidomethylpropane sulphonic acid with molecular weights between 1,000 and 2,000 are used as dispersing agents. The dispersions according to the invention are distinguished by an improved flow stability.

CH-A-479 636 describes copolymers of substituted basic acrylamides with ethylenically unsaturated monocarboxylic acids, such as acrylic acid, and further water-insoluble ethylenically unsaturated monomers.

These copolymers are particularly suitable for coating surfaces and may also be used in the form of aqueous emulsions or dispersions in paper and textile finishing, e.g., surface sizing of papers or, in textile finishing, in combination with waterproofing agents, as binders. It is particularly preferred to use said polymers as antithrombogenic coatings with a content of heparin in evenly fine distribution.

DE-A-30 47 688 describes the production of amphoteric copolymers of a basic polymerizable compound, such as a basically reacting substituted (meth)acrylamide or (meth)acrylic ester derivative with a corresponding unsaturated acid, such as methacrylic acid. These amphoteric copolymers are suitable as emulsifiers, in particular for emulsifying pulp and surface sizing agents for paper.

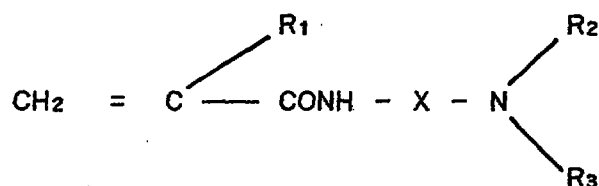
With all their advantages, filler suspensions that are produced conventionally, i.e., by the addition of anionic dispersing agents, display a considerable disadvantage. Ordinarily, in the production of paper, retention agents are used to accelerate the removal of water and to retain the fibre materials and fillers. For the most part, these retention agents are cationically modified polyelectrolytes. The cationic groups of these retention agents react with polymer-bound anionic groups under neutralization, i.e., a quantity of cationic groups that is equivalent to the number of anionic groups is bound and the number of cationic groups required for the retention effect is reduced thereby.

This effect occurs if a filler suspension produced with anionic dispersing agents is used in the paper

pulp. A satisfactory retention effect can then be achieved only by a drastic increase in the quantity of retention agent that is added.

It is the object of the present invention to provide beater additives and/or dispersing agents for the production of filler suspensions applicable in paper-making which do not display this retention-impairing effect.

This object was achieved by the use of amphoteric water-soluble copolymers which contain a) 90 to 30%-wt. acrylic acid and/or methacrylic acid, b) 10 to 60%-wt. of a compound of the formula



wherein R₁ stands for hydrogen or the methyl residue, R₂ and R₃, which are either the same or different, represent the methyl or ethyl residue, and X stands for an optionally branched alkylene residue having 1 to 5 carbon atoms, c) 0 to 50%-wt. acrylamidomethylpropane sulphonic acid, if necessary, and d) 0 to 10%-wt. of another ethylenically unsaturated compound polymerized therein and whose molecular weight, measured at a pH-value of 8.0, is smaller than 100,000, as beater additives and/or dispersing agents in highly concentrated aqueous suspensions of pigments and fillers for papermaking in the presence of a retention aid.

It is preferred that the polymers according to the present invention have a molecular weight of 500 to 50,000, determined by gel permeation chromatography.

N-alkyl substituted acrylamides or methacrylamides that have a tertiary amino group at the alkyl radical may be used as monomer b). Examples of these are dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylamino-2,2-dimethylpropyl acrylamide, dimethylamino-2,2-dimethylpropyl methacrylamide, and dimethylaminopropyl acrylamide. Acrylamide or methacrylamide that is converted after polymerization with formaldehyde and dimethylamine to the corresponding Mannich base can also be used as monomer b).

Acrylamide, methyl acrylate, hydroxypropyl acrylate, and acrylonitrile are examples of the monomer d). The monomers of group d) are used to obtain a modification of the properties of the copolymers.

The dispersing agents can be obtained by polymerization methods known per se.

The polymerization of the monomers is preferably carried out in an aqueous solution or in mixtures of water and water-miscible solvents, such as an alcohol, e.g., isopropanol. Initiation of the polymerization is effected with the help of radical polymerization catalysts. Redox systems and/or thermally disintegrating radical formers of the type of azo compounds as, for example, azoisobutyric acid nitrile can be used. Combinations of hydrogen peroxide, the salts of peroxydisulphuric acid or tertiary butylhydroperoxide with

sodium sulphite or sodium dithionite as reduction component are examples of suitable redox systems.

In order to achieve the molecular weight of less than 100,000 as required according to the present invention, it is expedient to carry out the polymerization in the presence of polymerization regulators. These may be lower alcohols with 1 to 4 carbon atoms, preferably isopropanol. In addition, hydroxyl ammonium salts and mercaptans, e.g., mercaptoethanol or thio-glycollic acid are effective as regulators.

Copolymerization may be carried out such that a part of the monomer mixture is prepared, copolymerization initiated, and the monomer mixture then added continuously. During copolymerization, the temperature may vary within a very wide range. Depending on the type of catalyst used, temperatures between 50°C and 200°C may be optimal. It is also possible to carry out polymerization at the boiling point of the solvent or, under pressure, at temperatures that are above this.

Very frequently, it can be advantageous to carry out the polymerization under adiabatic conditions. In this case, the start of polymerization is effected expediently at low temperatures, e.g., at 20°C. The final temperature that is achieved as a result of the polymerization heat that is liberated will depend on the monomers that are used and on the concentration conditions, and, at a corresponding pressure, may amount, e.g., to up to 180°C.

During copolymerization, the pH-value can also vary over a very wide range. It is advantageous that copo-

lymerization be carried out at low pH-values, although pH-values above the neutral point are also possible.

After polymerization, a pH-value in the range of 5 to 12, preferably 7 to 8, is adjusted by means of an aqueous base, e.g., sodium hydroxide, ammonia, or potassium hydroxide.

The copolymers are used to produce concentrated solid-matter-suspensions. In this connection, the polymer may be added either directly during the grinding process or after that as dispersing agent. Chalk, kaolin, satin white, titanium dioxide, and clay are examples of pigments. The quantities of copolymers that are used, relative to the pigments, amount to 0.02 to 1.0%, preferably 0.05 to 0.2%. The solids contents of the pigment suspensions can amount to up to 80%-wt., depending on the employed pigment, its particle size and particle-size-distribution.

The pigment suspensions produced - according to the present invention - with the copolymers are distinguished by a greatly improved storage life as compared to conventional products based on polyacrylates.

The pigment suspensions are used in the production of paper. Usually, the aqueous pigment dispersions are metered into the paper slush pulp. After dilution to approximately 0.5%, retention agent is added to the paper pulp and passes to the wire section of the paper machine through the headbox. When pigment suspensions that have been produced with the new-type dispersion agent are used, a greatly improved effectiveness of the retention agent can be seen in comparison with

conventional products. This applies to both fibre-material retention and filler retention.

The processes in the headbox and in the adjacent wire section of a papermaking machine can be simulated extremely well with the so-called Britt-Jar tester; whereas, when commercially available dispersing agents are used a reduction of retention by approximately 10% can be established, retention is not degraded when the new type of products are used.

The present invention will be explained in greater detail on the basis of the following examples; parts are parts by weight.

Production of the Copolymers

Copolymer 1

During stirring and cooling, 62 parts dimethylamino-propyl acrylamide were introduced into a mixture of 675 parts water, 38 parts 37%-hydrochloric acid, and 225 parts acrylic acid. This resulted in a pH-value of 1.6. The temperature was 20°C. 42 parts 35%-hydrogen peroxide, 36 parts mercaptoethanol, and 2 parts 1%-iron(II) sulphate solution were then stirred into the monomer solution one after the other, and the stirrer was then stopped. Polymerization which began immediately could be detected by a rise in temperature. After approximately 2 minutes, the final temperature of 95°C was reached. Next, 4.5 parts 35%-hydrogen peroxide and 2 parts 40%-hydroxylamine hydrochloride solution in water were stirred in. This was allowed to react for one hour. The pH-value of 8.0 was set by the addition of 269 parts 45%-sodium hydroxide solution.

The viscosity of the product amounted to 30 mPa.s. Determination of the molecular weight by means of gel permeation chromatography (GPG) resulted in a value of 920.

Copolymer 2

During cooling, 72 parts dimethylaminopropyl acrylamide were introduced into a mixture consisting of 621 parts water, 45 parts 37%-hydrochloric acid, and 263 parts acrylic acid. This resulted in a pH-value of 1.6. The temperature was 20°C. Next, 3 parts 35%-hydrogen peroxide, 1 part mercaptoethanol, and 0.5 parts 1%-iron(II) sulphate solution were stirred into the monomer solution one after the other, and the stirrer was then stopped. Polymerization which began immediately was indicated by a rise in temperature. After approximately 8 minutes, the final temperature of 95°C was reached. Next, 4.5 parts 35%-hydrogen peroxide and 2 parts 40%-hydroxylamine hydrochloride solution in water were stirred in. This was allowed to react for one hour and the pH-value of 8.0 was set by the addition of 309 parts 45%-sodium hydroxide solution. The viscosity of the product amounted to 9,500 mPa.s. Molecular weight determination indicated a value of 44,000.

Copolymer 3

During cooling, 115 parts dimethylaminopropyl methacrylamide were introduced into a mixture consisting of 603 parts water, 72 parts 37%-hydrochloric acid, and 210 parts acrylic acid. This resulted in a pH-value of 1.6. The temperature was 20°C. Next, 19 parts 35%-hydrogen peroxide, 5 parts mercaptoethanol, and

0.5 parts 1%-iron(II) sulphate solution were stirred into the monomer solution one after the other, and the stirrer was then stopped. Polymerization which began immediately was indicated by a rise in temperature. After approximately 4 minutes, the end temperature of 95°C was reached. Next, 4.5 parts 35%-hydrogen peroxide and 2 parts 40%-hydroxylamine hydrochloride solution in water were stirred in. This was allowed to react for one hour and the pH-value of 8.0 was set by the addition of 255 parts 45%-sodium hydroxide solution. The viscosity of the product amounted to 180 mPa.s. Molecular weight determination resulted in a value of 6300.

Copolymer 4

During cooling, 144 parts dimethylamino-2,2-dimethylpropyl acrylamide were introduced into a mixture of 592 parts water, 90 parts 37%-hydrochloric acid, and 175 parts acrylic acid. This resulted in a pH-value of 1.6. The temperature amounted to 20°C. Next, 28 parts 35%-hydrogen peroxide, 24 parts mercaptoethanol, and 1 part 1%-iron(II) sulphate solution were stirred into the monomer solution one after the other and the stirrer then stopped. Polymerization which began immediately was indicated by a temperature increase. After approximately 2 minutes, the final temperature of 95°C was reached. Next, 4.5 parts 35%-hydrogen peroxide and 2 parts 40%-hydroxylamine hydrochloride solution in water were stirred in. This was allowed to react for one hour and the pH-value of 8.0 was set by the addition of 216 parts 45%-sodium hydroxide solution. The viscosity of the product amounted to 39 mPa.s. Molecular weight determination indicated a value of 1800.

Copolymer 5

During cooling, 173 parts dimethylamino-2,2-dimethylpropyl methacrylamide were introduced into a mixture of 580 parts water, 107 parts 37%-hydrochloric acid, and 140 parts acrylic acid. This resulted in a pH-value of 1.6. The temperature amounted to 20°C. Next, 28 parts 35%-hydrogen peroxide, 24 parts mercaptoethanol, and 1 part 1%-iron(II) sulphate solution were stirred into the monomer solution one after the other and the stirrer then stopped. Polymerization which began immediately was indicated by a temperature increase. After approximately 2 minutes, the final temperature of 95°C was reached. Next, 4.5 parts 35%-hydrogen peroxide and 2 parts 40%-hydroxylamine hydrochloride solution in water were stirred in. This was allowed to react for one hour and the pH-value of 8.0 was set by the addition of 174 parts 45%-sodium hydroxide solution. The viscosity of the product amounted to 88 mPa.s. Determination of the molecular weight indicated a value of 4700.

Copolymer 6

During cooling, 72 parts dimethylaminopropyl acrylamide were introduced into a mixture consisting of 621 parts water, 45 parts 37%-hydrochloric acid, 125 parts acrylic acid, 50 parts methacrylic acid, and 200 parts acrylamidomethylpropane sulphonic acid. This resulted in a pH-value of 1.6. The temperature amounted to 20°C. Next, 28 parts 35%-hydrogen peroxide, 24 parts mercaptoethanol, and 1 part 1%-iron(II) sulphate solution were stirred into the monomer solution one after the other, the stirrer was then stopped. Polymeri-

zation which began immediately was indicated by a temperature increase. After approximately 2 minutes, the end temperature of 95°C was reached. Next, 4.5 parts 35%-hydrogen peroxide and 2 parts 40%-hydroxylamine hydrochloride solution in water were stirred in. This was allowed to react for one hour and the pH-value of 8.0 was set by the addition of 309 parts 45%-sodium hydroxide solution. The viscosity of the product amounted to 55 mPa.s. Determination of the molecular weight resulted in a value of 2900.

Copolymer 7

64 parts water, 10 parts acrylic acid, 10 parts 38% aqueous acrylamide solution, and 12 parts 35%-hydrogen peroxide were prepared in a reaction flask and heated to 90°C. A second mixture consisting of 155 parts 38% aqueous acrylamide solution and 177 parts acrylic acid was produced in a second vessel and this second solution was then introduced into the hydrogen-peroxide-containing solution whilst stirring within a period of approximately one hour. 54 parts hydrogen peroxide (35%) and 12 g hydroxylamine hydrochloride (40% in water) were then dosed in through additional inlets, proportionally to the monomer mixture. The temperature was always maintained at 90°C. Once this addition had been ended, 4.5 parts of hydrogen peroxide (35%) and 2 parts hydroxylamine hydrochloride solution (40% in water) were sprayed in. This was allowed to react for one hour and a pH-value of 8.0 was set by the addition of 229 parts 45% sodium hydroxide solution.

After cooling to 20°C, and whilst stirring, 99 parts 40%-dimethylamine hydrochloride and 71.5 parts 37% formalin were added. This was allowed to react for 15 hours. The viscosity of the product amounted to 38

mPa.s. Determination of the molecular weight indicated a value of 1750.

Copolymer 8

According to the manner indicated for copolymer 7, 546 parts water, 329 parts 38%-acrylamide solution, and 125 parts acrylic acid were reacted. The neutralization was effected with 153 parts 45%-sodium hydroxide solution; 198 parts 40%-dimethylamine and 143 parts 37%-formalin were used for the subsequent conversion to the Mannich base. The viscosity of the product amounted to 32 mPa.s. Molecular weight determination resulted in a value of 1360.

Production of the pigment dispersions

General procedure

The quantities of dispersing agent shown in the Table (in each instance 100% polymer) were added to 145 g water in a 400 ml beaker and the pH-value was set to 10.0. Whilst stirring with a high-speed laboratory stirrer equipped with a 30-mm dissolve disk (4000 rpm), 355 g of a finely ground chalk (particle size 90% smaller than 2 μ m) were sprinkled in in portions. Once the total quantity of the pigment had been introduced, it was stirred for an additional 15 minutes at a speed of 5000 rpm. Subsequently, the viscosity of the pigment suspender was determined. The dry substance contents amounted to 71%.

Suspension No.	Dispersing Agent No. Example	Addition in %, relative to pigment	Viscosity mPa.s.	pH-Value
1	1	0.1	90	9.72
2	1	0.05	136	9.77
3	2	0.15	230	9.89
4	3	0.1	245	9.75
5	4	0.15	290	9.39
6	5	0.2	340	9.57
7	6	0.1	86.5	9.63
8	6	0.05	148	9.71
9	7	0.1	80	9.76
10	7	0.05	99	9.87
11	8	0.1	79	9.81
12	8	0.1	260	9.75
13	Comparison	0.1	85	9.82

Retention tests

Retention tests were carried out using the above described dispersing agents and the pigments and filler dispersions produced therefrom; this was done according to the recognized Britt-Jar-Dynamic Drainage/Retention Test that has been described in the literature ("New methods of monitoring retention, K.W. Britt, J.E. Unbehend Tappi, February 1976, Vol. 59, No. 2, pgs. 67-70").

A standard substance composition made up as follows was used for the retention tests:

The fibrous material was composed of 70% of long-fibre-cellulose and 30% of short-fibre-cellulose. 20% filler, in this case chalk of the quality Omya DX 1, was added to the fibrous material; the chalk was pre-treated either

- without dispersing agent,
- with a commercially available anionic dispersing agent (in this instance, Polystabil S 312: homopolymer of sodium acrylate, molecular weight S 312),
- or with one of the novel dispersing agents.

With chalk used as a filler, the pH-value of the paper pulp was approximately 7 to 7.5 (neutral working). The retention on the test substance (fibrous material including filler, 80:20%-wt.) was checked both without the addition of a retention agent as well as (and this was predominantly the case) with the addition of a known cationic polymeric retention aid. Praestol P 411 K: (copolymer of acrylamide and an acrylic ester, cationic portion 25%-wt.): it was used to establish any possible reciprocal action between the products used as dispersing agent and the cationic retention agents that were used.

The conduct of the Britt-Jar test method and the retention established therefrom, is taken to be state of the art. The tests were carried out at a stirrer speed of 600 rpm. The value indicated as "retention" indicates the percentage of mass of the substance used retained on the wire, i.e., how high the amount of material pulp remaining on the wire is for sheet formation (in percentage by weight).

The higher this value, the better the retention, i.e., the more mass of the substance that is used is actually converted to a paper sheet.

It is understandable that in the event of incompatibility between the dispersing agent that is used and the retention aids that are employed the retention ef-

fect of the latter will be diminished: the proportion of the mass of the paper pulp that is retained is smaller, and considerable proportions of the pulp mass escape with the water that drains off and this "impoverishes" the sheet formation.

It was shown during the retention tests that with the generally used anionic dispersant employed at addition concentrations of 0.1 to 0.2% normally used to adjust a stable dispersion state of the suspending agent there is a clearly negative effect on the action of the cationic retention agent, in comparison to the use of the non-dispersed Omya DX1 chalk: According to the examples set out in Table 1, retention, depending on the quantities of cationic retention agent that are added, is between 58.3% and 74.1% when a chalk that has not been dispersed with an anionic dispersing agent is used. When a chalk suspending agent that has been dispersed with the anionic dispersant Polystabil S 312, this results in a retention of only 53.5 or 63.2%-wt., respectively, i.e., the values lie some 10% lower. Here, there is a clear interaction between the anionic dispersing agent and the cationic retention agent, this being in the sense of a clear deterioration of the retention effect compared to the use of a chalk not previously treated with dispersing agent.

Retention tests

Example No.	Pigment suspension from Example No.	Retention %	
		Addition 0.01 %-wt.	Retention Agent 0.02 %-wt.
1 + 2	1	59.2	72.6
3 + 4	2	59.6	74.1
5 + 6	4	60.1	72.6
7 + 8	5	58.8	72.4
9 + 10	6	59.3	72.0
11 + 12	7	59.7	73.1
13 + 14	8	60.1	73.4
15 + 16	9	58.9	72.2
17 + 18	10	58.3	73.0
19 + 20	11	60.3	72.6
21 + 22	12	58.7	73.1
23 + 24	13 (Comparison)	53.5	63.2
25 + 26	Zero sample	60.5	73.4
Zero sample = without dispersing agent			
Comparison = dispersed with Polystabil S 312 (commercial poly-acrylic acid)			

Storage tests

Behaviour during storage of chalk suspensions was assessed after 28 days (storage temperature $20 \pm 5^{\circ}\text{C}$, immobile storage), in particular

- stratification
- the nature ("stirrability") of the bottom settlings or of the suspension if there were no sediments, by grades (see Table).

Table: Grading of Stirrability

Grade Criteria

1	unchanged suspension
2	loose, easily stirrable with a glass rod (length: 20 cm; diameter: 7 mm, rounded end); after insertion and withdrawal of the glass rod the sediment or the suspension, respectively, closed up again
3	stirrable with the glass rod; when the glass rod was inserted and then withdrawn the base or suspension, respectively, did not run together again
4	still stirrable with the glass rod, compact
5	no longer stirrable with the glass rod, compact; still stirrable with a laboratory dissolver (at 5000 rpm min ⁻¹)
6	hard ("stone-like") cannot be stirred either with the glass rod or with the laboratory dissolver.

- the viscosity and the pH-value of the suspension after stirring with the laboratory dissolver.

The chalk suspensions produced with the present dispersing agents displayed only a slight tendency to form layers, a good "stirrability" (grade: 2) and

proved to be pH stable. The viscosity remained unchanged to a very great extent.

Assessment after 28 Days

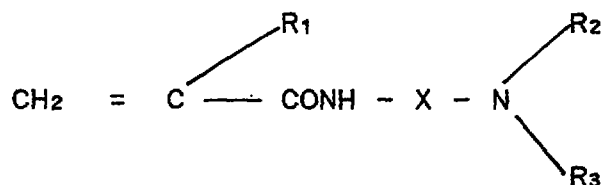
Suspension No.	Stratification in %	Stirrability (Grade)	Viscosity mPa.s.	pH-Value
1	8	2	92	9.75
2	6	2	131	9.75
3	5	2	225	9.93
4	9	2	248	9.82
5	5	2	295	9.47
6	7	2	325	9.48
7	8	2	82	9.68
8	6	2	143	9.79
9	5	2	86	9.83
10	7	2	104	9.87
11	4	2	78	9.77
12	6	2	242	9.63
13	16	5	87	9.87
(Comparison)				



C L A I M S

1. The use of amphoteric water-soluble polymers in which

- a) 90 to 30%-wt. acrylic acid and/or methacrylic acid,
- b) 10 to 60%-wt. of a compound of the formula



wherein R₁ stands for hydrogen or the methyl residue, R₂ and R₃, which are either the same or different, stand for the methyl or ethyl residue, and X stands for an optionally branched alkylene residue having 1 to 5 carbon atoms,

- c) 0 to 50%-wt. acrylamidomethylpropane sulphonic acid, if necessary, and

- d) 0 to 10%-wt. of another ethylenically unsaturated compound

are incorporated by polymerization and whose molecular weight, measured at a pH-value of 8.0, is less than 100,000,

as beater additives and/or dispersing agents in aqueous suspensions consisting of pigments and fillers and having a solids content of up to 80%-wt. for paper-making, in the presence of a retention agent.

2. The use according to claim 1 characterized in that calcium carbonate or kaolin is used as pigment.



3. The use according to claim 1 or 2 characterized in that the aqueous pigment suspension has a pH-value in the alkaline range.