

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11)

Publication number:

**0 361 763
A2**

(12)

EUROPEAN PATENT APPLICATION

(21)

Application number: **89309505.9**

(51)

Int. Cl.⁵: **D21H 17/72 , //D21H17:28,
D21H17:37**

(22)

Date of filing: **19.09.89**

(30)

Priority: **26.09.88 GB 8822577**

(43)

Date of publication of application:
04.04.90 Bulletin 90/14

(84)

Designated Contracting States:
AT DE ES FR IT SE

(71)

Applicant: **BLUE CIRCLE INDUSTRIES PLC**
Portland House Stag Place
London SW1E 5BJ(GB)

(72)

Inventor: **Beckett, Christine Anne**
25 The Braes Higham
Rochester Kent ME3 7NA(GB)

(74)

Representative: **Fisher, Adrian John et al**
CARPMAELS & RANSFORD 43 Bloomsbury
Square
London WC1A 2RA(GB)

(54)

Papermaking filler compositions.

(57)

A composition for flocculating paper- or boardmaking filler comprises particles of starch, in aqueous suspension, and a flocculating agent, eg. a polyacrylamide. Preflocculated filler for addition to a paper- or boardmaking stock may be prepared by adding such a composition to an aqueous slurry of filler particles, eg. calcium carbonate. The use of particulate starch that is insoluble in water at temperatures normally encountered in the wet-end of a paper- or boardmaking process, in particular temperatures below 35° C, obviates the need for a preliminary solubilisation step. However, the starch is soluble at temperatures encountered in the drying stage of the paper- or boardmaking process, where a starch solution is formed which is distributed through the paper matrix and imparts thereto additional strength.

EP 0 361 763 A2

PAPERMAKING FILLER COMPOSITIONS

Field of the invention

The present invention relates to compositions for use in manufacture of paper or board, especially a composition for flocculating filler and a composition that contains flocculated filler. The invention also relates to a process for the manufacture of paper or board wherein such a filler-containing composition is incorporated into the paper- or boardmaking furnish.

Background to the invention

10

It is known to add starch in aqueous solution to a papermaking furnish in order to improve the strength, in particular the dry strength, of the resultant paper. All types of starch, such as the cereal starches and the root starches, are effective strength additives and various modified starches are also widely used.

It is also common practice in making various types of paper to add a particulate material, especially a mineral pigment such as clay, titanium dioxide or calcium carbonate, as a filler to the furnish in order to reduce the cost of the paper product and, in many cases, to improve such properties as brightness and opacity. However, as the proportion of filler to papermaking fibre increases, the opacity of the resultant paper increases but the strength properties tend to decrease and, moreover, the filler particles tend to be lost into the water drained from the wet paper web. In order to reduce the loss of filler, it is customary to add retention aids, which are in general polyelectrolytes which encourage coflocculation, usually by neutralising the negative charges on the filler particles and papermaking fibres and fines so that van der Waals forces can hold them together (charge-biasing retention aids), or by forming molecular bridges between particles to which they are adsorbed (bridging polymers).

The use of starch, fillers and retention aids in papermaking is described, for example, in the articles entitled "Paper" and "Papermaking Additives" in the Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 16, pages 768-825.

In order to achieve a high filler content whilst maintaining satisfactory strength, optical and other paper properties, it has been proposed to employ a preflocculated filler composition, that is to say a suspension of filler to which a flocculating agent is added before the filler is incorporated into the papermaking stock (see U.K. patent specification No. 1,552,243 and M.C. Riddell et al., Paper Technology, 17(2), 76 (1976)).

It has also been proposed to include a cold-water-soluble starch in the flocculant composition used in the preparation of a preflocculated filler (see U.K. patent specification No. 2,016,498A). However, the incorporation of starch in an aqueous system containing an organic polyelectrolyte gives rise to a transient but significant increase in the viscosity of the system. To overcome this phenomenon - sometimes referred to as "polymer shock" - it is proposed in British patent specification No. 2,016,498A to moderate the viscosity of the solution containing starch and polyelectrolyte by incorporating therein an inorganic electrolyte, preferably an acid donor such as aluminium sulfate (papermaker's alum). The starch, flocculating agent and viscosity-moderating agent have normally been supplied as a dry composition to the papermaker, who has then had to solubilise the composition, either directly in a filler slurry or first in water before adding it to a filler slurry, to form the preflocculated filler suspension for addition to the papermaking stock. The solubilisation of even cold-water-soluble starches has to be carefully controlled in order to avoid, on the one hand, molecular scission due to excessive shear and, on the other hand, inadequate absorption of water by the initial starch particles, leading to the formation of intractable globules known in the art as "fish-eyes". Although apparatus for the smooth solubilisation of starch and other polymers is known (see U.K. patent specification No. 2,001,088A), the solubilisation step represents an additional cost to the papermaker, due to both capital expenditure on plant and additional consumption of energy.

The teaching in each of the articles and patent specifications identified above is incorporated herein by reference.

There is clearly a need in the art for a system whereby filler, retention aid and starch may be introduced into a papermaking (or boardmaking) furnish in an effective yet economical manner.

Summary of the invention

The present invention now provides a composition for flocculating filler intended for use in a paper- or

boardmaking furnish, which composition comprises (a) particles of starch in aqueous suspension, said starch being insoluble in water at temperatures below 35 °C, and (b) a flocculating agent.

The present invention also provides a preflocculated-filler composition for addition to a paper-or boardmaking furnish, which composition comprises (a) particles of starch in aqueous suspension, said starch being insoluble in water at temperatures below 35 °C, (b) a flocculating agent and (c) particles of a filler. Such a preflocculated-filler composition may be prepared by mixing, in any order, the components (a), (b) and (c) in the presence of water; however, such a composition is conveniently prepared by mixing an aqueous slurry (which term herein includes a suspension) of the filler particles with a composition according to this invention for flocculating filler.

The present invention also provides a process for the manufacture of paper or board by dewatering an aqueous paper- or boardmaking stock, wherein a preflocculated-filler composition according to this invention is added to the stock before dewatering commences.

15 Description of preferred embodiments

The invention is described below with reference to papermaking; however, it can be readily applied also to the manufacture of board.

The starch may be obtained from any source, for example cereals, such as maize or wheat, or root vegetables, such as potato. Although modified starches, eg. carboxylated, phosphorylated or other anionic starches or tertiary amino, quaternary ammonium or other cationic starches, come into consideration, it is at present preferred to use a chemically unmodified starch.

If the size of the starch particles is very small, the rheology of the resultant suspension may be adversely affected, in particular the viscosity may be too high for convenient handling; conversely, if the particle size is too coarse, the starch will tend to settle out of suspension and, moreover, may result in poor formation of the paper product. In general, the median size of the starch particles will be in the range from 5 to 50 µm and will preferably be in the range from 10 to 30 µm.

The starch should remain in particulate form at the temperatures normally encountered in the wet end of the papermaking machine; accordingly, the starch used in this invention should be insoluble in water at temperatures below 35 °C. Preferably, the starch is insoluble in water at temperatures below 50 °C, and, indeed, starches having a higher gel temperature (the first stage of solubilisation), e.g. up to 60 or 65 °C, have proved suitable. However, in order to ensure that the starch is properly distributed in the paper product, it should be soluble in water at temperatures encountered in the drying section of the papermaking process and it is preferred, therefore, that the starch should be soluble in water at temperatures below 100 °C, and, more preferably, below 85 °C. The temperature at which a starch is soluble may be taken as the temperature required before the starch grains swell and burst in water.

It is preferred to use starch which has not been dried during its preparation. In the practice of the present invention, such starch may give paper strength up to 20% better than the strengths obtainable with suspensions prepared from dried starch.

In the compositions for flocculating filler, the concentration of the starch particles will, in general, be between 5% and 75% by weight. It is preferred to use as high a concentration as possible, consistent with ease of handling and it is preferred, therefore, to employ a starch particle concentration of from 25% to 45%, especially 35 to 45%, by weight.

The aqueous suspension of starch particles may contain one or more suspending agents, in order to diminish or prevent settling of the starch particles, and one or more biocides, in order to prevent fermentation or other biological degradation of the starch, especially where the suspension is likely to be subjected to a long period of transportation and/or storage before use.

The compositions according to the present invention for flocculating filler particles also contain a flocculating agent (flocculant) and this may, in principle, be selected from any of the water-soluble synthetic polymers that could be used conventionally in papermaking as flocculants or retention aids.

For any given system, the choice of flocculating agent to give good filler and starch retention in the paper will be influenced by a number of factors. Particularly important are the rheological properties of the final composition. Addition of any type of high molecular weight flocculant, whether anionic, cationic or nonionic, will change the rheological behaviour of the starch suspension from pseudoplastic to visco-elastic, eventually leading in the worst case to an intractable starch/flocculant mass. The nature of the flocculant and its level of addition should therefore be chosen so that the composition maintains as much as possible of its pseudoplastic behaviour. Preferably, the apparent viscosity at 600 s⁻¹ should not exceed 500 cP and a typical viscosity will be 150-250 cP at 600 s⁻¹.

Although the so-called charge-biasing retention aids, typically having molecular weights of the order of 10^3 to 10^5 , come into consideration, it is preferred to use the so-called "bridging" polymers (see Kirk-Othmer, op. cit., page 804). Such polymers have, in general, a high molecular weight (typically of the order of 10^6 to 10^7), amongst which the ionic polymers, especially the ionic copolymers, of acrylamide are preferred. Polymers of low molecular weight (less than 10^6), such as the polyamine epichlorohydrin copolymers and the dimethyldiallylammonium chloride polymers may, however, also prove useful, for they have a dispersing effect on the starch suspension, thereby reducing its viscosity.

Flocculating agents which may be used in the present invention include the anionic polyelectrolytes available under the trade names Percol 155, 90L, 110L or 1206 or Zetag 51 (from Messrs. Allied Colloids), Millfloc F25, F70, A30, EA200 and EA700 (from Messrs. Crosmill Flocculants) and Nalfloc 625, A622 and A626 (from Messrs. Nalfloc); the cationic polyelectrolytes available under the trade names DSR 1256 or 341 or Magnafloc 1597 or 1440 (Messrs. Allied Colloids), Millfloc C50C (Messrs. Crosmill Flocculants) or Nalfloc 605 (Messrs. Nalfloc); or the non-ionic polyelectrolytes available under the trade names Percol 80L (Messrs. Allied Colloids), Millfloc N10 or F10 (Messrs. Crosmill Flocculants) or Nalfloc 8861-SC (Messrs. Nalfloc).

It will be understood by those skilled in the art that the effectiveness of any flocculating agent may be affected by various factors, for example the nature of any additive present in the starch-containing suspension in which it is included (for instance, papermaker's alum has been found to be incompatible with anionic polymers due to coflocculation, giving strings and large sticky flocs), the pH of the suspension and, more particularly, the nature of the sizing system used in the papermaking process, whether it be an acidic, eg. rosin-alum, system or an alkaline or neutral, eg. synthetic cellulose-reactive, sizing system. One or more suitable flocculating agents for any given set of conditions can be readily selected by routine testing.

The flocculating agent may, in turn, influence the choice of any suspending agent that may be included to stabilize the starch suspension. The suspending agent is preferably selected from inorganic swelling clays, e.g. bentonite or hectorite; water-soluble natural gums, e.g. guar gums and xanthan gums; water-soluble synthetic organic substances, e.g. acrylic copolymers and cellulose ethers. Particularly important is the ionic charge of the suspending agent, which agent ideally should be chosen to reduce the net charge in the composition to zero or close to zero. Thus, the presence of a cationic flocculant will usually require an anionic suspending agent, an anionic flocculant will usually require a cationic suspending agent and a nonionic flocculant will usually require a nonionic suspending agent.

The preferred combination of suspending agent/flocculant is that of a nominally nonionic suspending agent/nonionic flocculating agent (e.g. Percol 80L) so that the composition will remain compatible with the presence of other agents, for example dry strength resins of the low molecular weight (less than 10^6), cationic polyacrylamide type.

Since the flocculating agent is, in general, used in aqueous solution, the amount thereof in the composition according to the present invention for flocculating filler will, of course, be limited by the water-solubility of the flocculating agent selected and the amount of water available in the suspension. In general, however, the amount of flocculant in the composition will be from 0.5 to 10% by weight of the total composition (or from 1.25 to 25% by weight relative to the starch solids, in the typical compositions of this invention).

The composition for flocculating filler is intended to be added to the filler before the latter is added to the papermaking stock in the papermaking machine. Thus, the composition containing the particulate starch and the flocculating agent may be supplied, eg. in drums or by road tanker, to the papermaker who can then mix it with an aqueous slurry of filler particles to obtain a preflocculated-filler composition, which is then conveyed to the papermaking machine at any appropriate point. However, and in accordance with another aspect of this invention, it is also possible to prepare a composition containing the particulate starch, the particulate filler and the flocculating agent (a so-called "total slurry") and supply this to the papermaker who may then add it, directly or after appropriate dilution, to the papermaking stock on the machine.

In such a total slurry, the solids content could be typically about 60-70% m/m.

The preflocculated-filler composition, whether it be prepared on-site or supplied as a "total slurry", will preferably be added to the papermaking machine at the fan pump or downstream thereof. It may be possible to add the preflocculated-filler composition as late as the headbox since the closer the addition is to the papermaking wire, the better will be the control over the rate of addition (since the delay in the feedback control loop will be minimised).

Although synthetic polymeric fillers are known, the filler will normally be a particulate mineral. Any of the conventional mineral fillers may be used, including clay, titanium dioxide, talc, aluminium hydroxide, alumina, gypsum, lithopone, barium sulfate, satin white or silica. Calcium carbonate, eg. chalk whiting, is at present preferred.

The filler particle size is entirely conventional and may, for example, be in the range from 0.1 to 20 μm .

The concentration of the starch and of the filler in the preflocculated-filler compositions and the rate at which the composition is added to the papermaking stock will depend upon the desired level of starch and filler in the finished paper product. The level of filler may be, for example, from 3 to 40%, typically from 5 to 30%, and the level of starch on a dry basis may typically be from 0.05 to 1.5%, these percentages being by weight of the finished dry paper. The level of flocculating agents in the preflocculated-filler compositions should be such as to ensure adequate retention of the starch and filler in the paper product.

As a guide, in the preflocculated filler compositions of this invention the filler will be present in an amount usually of 20 to 50% m/m and preferably of 30 to 40%; the starch will be present in an amount usually of 0.5 to 10%, preferably of 1 to 5%, on dry basis relative to the dry filler; and the flocculant will be present in an amount usually of 0.02 to 1.0%, preferably of 0.05 to 0.2%, on dry basis relative to the dry filler.

The preflocculated-filler composition may include any of the conventional papermaking additives, for example drainage aids, defoaming agents, stabilizing agents, slimicides, wet-strength additives and dry-strength additives. Strength additives which are known in the art and which may be included in the preflocculated-filler compositions include the natural gums, in particular the mannogalactans such as locust bean gum, guar gum and tamarind gum, and the cationic or amphoteric derivatives thereof; cellulose ethers, eg. sodium carboxymethyl cellulose; and poly(vinyl alcohol). Synthetic strength additives of the low molecular weight (less than 10^6), cationic polyacrylamide type may also be included. Other possible additives include pH adjusters, for example alkaline agents such as sodium hydroxide, and acidic or acid-reacting agents, for example aluminium sulfate.

Any optional additive that is employed may be incorporated in the composition at any convenient stage. For example, it may be added to the composition after the starch, flocculating agent and filler have been brought together, or it may be incorporated in the initial slurry of filler or in the initial composition containing the starch and flocculating agent.

It will be appreciated that each of the above-discussed components of the compositions of the present invention may be constituted, if appropriate, by a mixture of agents of the appropriate description.

The fibrous component of the papermaking furnish will usually be composed primarily of cellulosic fibres, in particular the fibres obtained from vegetable sources, especially wood. Thus, for example, the furnish may comprise a pulp containing hardwood fibres, softwood fibres or a mixture thereof, and which may be, for instance, a mechanical or chemical pulp, and/or it may comprise recycled fibres. It is also possible to employ cellulose fibres from nonwood vegetable sources, such as cotton, bagasse, esparto or Manila hemp, either alone or as a blend with wood pulp. The so-called synthetic pulps, for example the fibrillated polyolefin materials, also come into consideration; however, for reasons of cost, these will usually be used with a pulp of vegetable origin.

Since the starch used in accordance with the present invention is added in particulate form to the papermaking furnish, the papermaker is spared the need to effect a special solubilisation step. Surprisingly, it is still possible to obtain an improvement in the dry strength of the paper product, even though the swelling and subsequent solubilisation of the starch particles does not take place until the paper reaches the heated, drying section of the papermaking process. It is remarkable that an even distribution of the starch through the paper matrix can be obtained, without adversely affecting the formation of the paper, even though solubilisation does not take place until a late stage of the paper production wherein residual water is being driven out of the web. The distribution of the starch through the paper matrix yields a greater improvement in strength than can be obtained by the application, as by spraying, of a starch to the surface of a formed paper web.

Examples

The present invention is illustrated in and by the following examples.

In these examples, the compositions according to the present invention were prepared from an aqueous suspension of particulate starch obtained from Messrs. P.T. Chemicals Limited under the trade name "Atomyl", which is marketed as a spray-on starch for application to a formed paper web at the size-press in paper production. The starch was found to have a solubilisation temperature of 55°-65° C (depending upon the heating conditions and the amount of shear applied) and a median particle size of 20-25 μm .

For comparison purposes, laboratory handsheets containing non-preflocculated filler were investigated, these handsheets having been made under the same conditions as the laboratory handsheets containing filler preflocculated by means of a composition according to this invention.

In each Example, the compositions according to the present invention were added with stirring to a 40% m/m filler slurry, the filler being a chalk whiting supplied under the trade mark Snowcal 80 by Blue Circle Industries Plc. The compositions were added at a level equivalent to 4% by weight of dry starch on dry filler.

The laboratory handsheets were prepared by using a British Standard sheet former using either an acid or an alkaline sizing regime. The formed handsheets were dried on a conventional rotary photographic-print drier, the temperature rising from ambient to 135° C in order to solubilize the starch grains where such are present in the sheets. The filler loading in the handsheets was determined by ashing at 900° C and the burst and tensile strength of the handsheets were determined on conventional laboratory apparatus.

Example 1

Laboratory handsheets were prepared by using a filler slurry preflocculated by means of a composition comprising Atomyl and the high molecular weight, anionic emulsion polyacrylamide supplied by Messrs. Crosmill Flocculants under the trade name Millfloc EA 200. The polyacrylamide was added in an amount of 0.42%, as received, by weight of dry whiting.

Example 2

Laboratory handsheets were prepared by using a filler slurry preflocculated by means of a composition comprising Atomyl and the high molecular weight, nonionic emulsion polyacrylamide supplied by Messrs. Allied Colloids under the trade name Percol 80L. The polyacrylamide was added in an amount of 0.2% as received, by weight of dry whiting.

Example 3

Laboratory handsheets were prepared using a filler slurry preflocculated by means of a composition comprising Atomyl and the high molecular weight, anionic emulsion polyacrylamide supplied by Messrs. Allied Colloids under the trade name Percol 90L. The polyacrylamide was added in an amount of 0.2%, as received, by weight of dry whiting.

Example 4

Laboratory handsheets were prepared using a filler slurry preflocculated by means of a composition comprising Atomyl and the high molecular weight, nonionic emulsion polyacrylamide Percol 80L (from Messrs. Allied Colloids). The polyacrylamide was added in an amount of 0.13%, as received, by weight of dry whiting.

Results of testing the handsheets are given in Table A for alkaline sized handsheets (the alkaline size being Keydime D1 (supplied by Messrs. Tenneco Malros) and in Table B for acid sized handsheets (the acid size being Bumal 45 supplied by Messrs. Tenneco Malros).

TABLE A

(Alkaline sized systems)			
COMPOSITION	% FILLER IN HANDSHEETS	BURST RATIO	BREAKING LENGTH, m
Snowcal 80	9.70	3.32	5221
	11.85	3.00	4724
	12.66	2.78	4593
Example 1	18.46	3.12	4863
Example 2	7.42	3.60	5957
	9.94	3.44	5355
	13.79	3.12	4900
Example 3	14.32	3.19	5027
	12.44	3.38	5034
	17.25	3.04	4934
Example 4	23.74	2.78	4344
	9.67	3.29	5284
	14.01	3.21	4877

TABLE B

(Acid sized systems)			
COMPOSITION	% FILLER IN HANDSHEETS	BURST RATIO	BREAKING LENGTH, m
Snowcal 80	8.0	3.40	5567
	10.33	3.12	5423
	14.26	2.75	4293
Example 2	8.06	3.58	6040
	11.33	3.30	5485
Example 3	15.54	3.11	5061
	22.81	2.71	4470
Example 4	15.87	3.07	4954

It will, of course be understood that the present invention has been described above purely by way of example, and modifications of detail can be made within the scope of the invention.

Claims

1. A composition for flocculating filler particles intended for use in a paper- or boardmaking furnish, which composition comprises (a) particles of starch in aqueous suspension, said starch being insoluble in water at temperatures below 35° C, and (b) a flocculating agent.
2. A composition according to claim 1, wherein the starch is insoluble in water at temperatures below 50° C.
3. A composition according to claim 1 or 2, wherein the starch is soluble in water at a temperature below 85° C.
4. A composition according to claim 1, 2 or 3, wherein the starch particles have an average particle size of from 5 to 50 μm .
5. A composition according to claim 4, wherein the starch particles have an average particle size of from 10 to 30 μm .
6. A composition according to any of claims 1 to 5, wherein the starch in the particles has not been

dried during its preparation.

7. A composition according to any of claims 1 to 6, wherein the starch is a chemically unmodified starch.

8. A composition according to any of claims 1 to 7, wherein the flocculating agent is a polyacrylamide.

9. A composition according to any of claims 1 to 8, wherein the starch is present in an amount of from 5 to 75% by weight of the total composition on a dry basis.

10. A composition according to claim 9, wherein the starch is present in an amount of from 25 to 45% by weight of the total composition on a dry basis.

11. A composition according to any of claims 1 to 10, wherein the flocculating agent is present in an amount of 0.5 to 10% by weight of the total composition.

12. A preflocculated-filler composition which comprises (a) particles of starch in aqueous suspension, said starch being insoluble in water at temperatures below 35 °C, (b) a flocculating agent and (c) particulate filler.

13. A composition according to claim 12, wherein the particulate starch (a) is as defined in any of claims 2 to 7.

14. A composition according to claim 12 or 13, wherein the flocculating agent is as defined in claim 8.

15. A composition according to claim 12, 13 or 14, wherein the papermaking filler is calcium carbonate.

16. A method of preparing a preflocculated-filler composition, which comprises mixing a composition according to any of claims 1 to 11 with an aqueous slurry of filler particles.

17. A process for the manufacture of paper or board by dewatering an aqueous slurry of fibres, wherein a preflocculated-filler composition is added to the slurry of fibres before the dewatering commences, characterised in that the preflocculated-filler composition comprises (a) particles of starch in aqueous suspension, said starch being insoluble in water at temperatures below 35 °C, (b) a flocculating agent and (c) particulate filler.