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(54) A process for controlling the deposition of pitch in paper making.

(57) There is disclosed a process for controlling the deposition of pitch in a pulping or paper making process, wherein there is incorporated into the composition comprising paper making fibres up to 1.0% by weight, based on the weight of dry fibres in the composition, of a cationic polyelectrolyte which is a poly(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight greater than 500,000.

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This invention relates to a process for controlling the deposition of pitch in paper making and to a reagent for use in such a process. Specifically, the reagent is suitable for incorporation in cellulose pulp compositions to reduce the adverse effects of the deposition of pitch derived from wood pulp in the manufacture of paper and board. The invention also relates to a process for preparing paper pulp which is reduced in its pitch content and to a process for manufacturing paper or board.

Pitch is the name given by paper manufacturers to the substance derived from wood resins which accumulates on the wire mesh belts, or "wires" of paper making machines and on the rolls and dewatering felts. The pitch deposits are sticky and can block holes in the wire thus reducing drainage through the wire, and can also reduce the absorptive capacity of the felt. They can pick fibres from the formed paper web, often causing holes or weak areas, and occasionally appear in the paper as brown lumps or patches.

Pitch is a mixture of chemical compounds of which the principal components which can be extracted by means of organic solvents are organic acids, for example fatty and resin acids, and neutral organic material such as fats. We have found that it is possible to simulate pitch in the laboratory in order to investigate means for the control of pitch in preparing paper pulp and in paper making by preparing mixtures of oleic acid and triolein in various proportions, according to the relative proportions of organic acids and neutral organic material in the pitch which it is required to model. The oleic acid mimics the behaviour of the organic acids in the pitch, and our new investigations show that the triolein mimics the behaviour of the neutral organic material.

Both hardwoods and softwoods contain fatty acids and neutral organic materials, but only softwoods contain significant amounts of resin acids. This latter material occurs in wood mainly in the ray cells and resin canals or ducts. Softwoods or gymnosperms such as pine, spruce and fir, therefore, in general cause more serious pitch problems than hardwoods such as birch, maple, oak and poplar. Certain species of pine are particularly rich in resin acids.

The process by which the paper pulp is prepared is also important. The wood may be reduced to pulp by mechanical grinding alone, or with the aid of a chemical cooking process. The two most important chemical cooking processes are the sulphite process in which the ground wood is cooked in an acid solution of calcium bisulphite saturated with sulphur dioxide, and the sulphate or Kraft process in which the cooking is performed in an alkaline solution comprising sodium hydroxide, sodium sulphide and sodium hydrosulphide. When pulp is prepared by the sulphate process the pitch problem is less severe than when the pulp is prepared by the mechanical or sulphite processes because, in the sulphate process, the cooking solution is alkaline and most of the pitch-forming material is saponified and removed in solution by washing.

Two methods are commonly used for controlling pitch in preparing paper pulp and in paper making. In the first method an adsorbent material is introduced which will adsorb the pitch in the form of small droplets, generally smaller than about 2μm in diameter. Adsorbent materials commonly used for this purpose include bentonite, talc and diatomaceous silica. In the second method the pitch is chemically stabilised so that it remains in suspension in process water and is removed from the process.

GB-A-1375161 describes the use as a pitch control agent in paper making of a clay pigment which has been coated with an organic material which adheres strongly to the clay pigment and which renders the surface of the particles of the clay pigment oleophilic. The organic material may be an alkyl pyridinium salt, a quaternary ammonium salt or the like, and the dose rate of the organic material on the dry clay is preferably in the range of from 0.5% to 5% by weight. This is an example of the adsorption method of pitch control.

GB-A-2224019 describes a process for controlling the deposition of pitch in a paper making process, wherein there is incorporated into the paper making composition a coated inorganic particulate material which comprises a clay mineral coated with (a) a cationic polyelectrolyte which is a water-soluble substituted polyolefin containing quaternary ammonium groups or with (b) an inorganic gel or with (c) a mixture of (a) and (b). The cationic polyelectrolyte is preferably a poly(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight in the range from about 10,000 to 100,000. This again is an example of the adsorption method of pitch control.

WO 89/06294 describes a method of reducing pitch in pulping and paper making which comprises adding to a pitch-containing furnish a particulate composite substance comprising (a) a water soluble cationic polymer, especially a poly(dialkyldiallylammonium halide) having an average molecular weight of from about 100,000 to about 500,000, adsorbed onto (b) an essentially water insoluble particulate substrate, the polymer being sufficiently electropositive that the composite substance has a zeta potential of at least about +30mV, and preferably in the range from +60mV to +80mV, and adsorbing pitch onto the composite substance to form discrete, finely dispersed pitch-containing aggregates in the furnish. Although the pitch-containing aggregates are said to be "finely dispersed" they are still large enough to cause problems in the paper making process.

CA-A-1194254 describes the use as a pitch control agent in paper making of poly(diallyl dimethyl ammonium chloride), which preferably has a molecular weight in the range of from 50,000 to 100,000, and the amount used is preferably in the range of from 0.1 to 1 kg of the polymer per tonne of pulp based on dry fibre weight. Poly(diallyl dimethyl ammonium chloride) having a molecular weight within the preferred range would cause flocculation of the pitch, and therefore deposition in relatively large aggregates.

According to a first aspect of the present invention, there is provided a process for controlling the deposition of pitch in a pulping or paper making process, wherein there is incorporated into the composition comprising paper making fibres up to 1.0% by weight, based on the weight of dry fibres in the composition, of a cationic polyelectrolyte which is a poly(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight greater than 500,000.

Preferably the cationic polyelectrolyte is incorporated in the composition in an amount of at least 0.005% by weight, based on the weight of dry fibres in the composition.

The process is especially advantageous in cases in which the pitch which is present in the fibre-containing composition has a relatively high weight ratio of neutral organic material, for example fats, to organic acids, for example fatty and resin acids, for instance a ratio of at least 1:1.

The process of the invention is believed to give more effective control over the deposition of pitch in a pulping or paper making process than the prior art processes because the cationic polyelectrolyte, which has a higher molecular weight than the cationic polyelectrolytes which are referred to in the prior art, is believed to cover or envelop substantially completely the surface of small droplets of pitch with the non-polar, or oleophilic, part of the polyelectrolyte molecules being orientated towards the surface of the pitch droplet and the positively charged part positioning itself on the outside of the droplet. The result is that each small droplet is encased, in effect, in a highly positively charged shell, so that the droplets strongly repel each other in suspension in water. A very stable emulsion of the pitch droplets is thus formed, the droplets being found to be of about 0.8 to 3.0μm in diameter, and these droplets are generally captured by the negatively charged fibres which are present in the pulping or paper making process, and are thus removed from the environment of the process, without causing any harmful deposits of pitch on the pulp or on the paper web or on the surfaces of the paper making machinery, and without causing an accumulation of pitch in the recirculated waste water or "white water" which is produced by the paper forming operation. In the absence of the cationic polyelectrolyte the small droplets of pitch have a tendency to coalesce when they collide in suspension in water as a result of Brownian movement, and thus form larger drops which eventually adhere to the pulp or paper or the surfaces of the paper making machine. If a cationic polyelectrolyte of number average molecular weight less than about 500,000 is used, the pitch droplets are only incompletely encased with positively charged polymer, so that the droplets do not repel each other so strongly and can still coalesce and adhere to other surfaces. It has been found that, when the cationic polyelectrolyte has a molecular weight above about 500,000, the polymer-encased pitch droplets have a zeta potential (as measured by means of photon correlation spectroscopy and particle electrophoresis using a Zeta Sizer 4 instrument - for instance as manufactured by Malvern Instruments Limited) of at least +25mV and preferably at least +35mV. The cationic polyelectrolyte preferably has a molecular weight of at least about 750,000 and preferably no greater than about 1,250,000. Where the cationic polyelectrolyte is a poly(diallyl di(lower alkyl) ammonium salt), the lower alkyl groups, which may be the same or different, may, for example, have up to four carbon atoms, preferably methyl. The ammonium salt may be, for example, a chloride, bromide, iodide, HSO_4^-, $CH_3SO_4^-$ or nitrite. Preferably the salt is a chloride. Most preferably the cationic polyelectrolyte is poly(diallyl dimethyl ammonium chloride).

Preferably there is incorporated into the fibre-containing composition, in addition to the cationic polyelectrolyte, from 0.05 to 5.0% by weight, based on the weight of dry fibres in the composition, of a smectite clay. The smectite clay may be incorporated in the composition before, after or simultaneously with the cationic polyelectrolyte. The smectite clay may be bentonite, montmorillonite, saponite, hectorite, beidellite, nontronite or fullers' earth. Bentonite has been found to be particularly suitable, especially when the exchangeable cations are predominantly sodium.

The smectite clay has been found to be especially effective in adsorbing the organic acid component of the pitch; it is theorized that this is a result of the hydrophilic surface and the high specific surface area of the clay. There is evidence that the presence of the smectite clay enhances the control of the neutral organic material component also. There appears to be a synergistic effect so that, in a given fibre-containing composition containing pitch, a mixture of a cationic polyelectrolyte of the type described above and a smectite clay controls, by a combination of stabilisation and adsorption, an amount of pitch which is greater than the sum of the amounts of pitch which are controlled by a cationic polyelectrolyte and a smectite clay when used on their own.

According to a second aspect of the present invention, there is provided the use, as an agent for controlling the deposition of pitch in a pulping or paper making process, of a cationic polyelectrolyte which is a poly(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight greater than 500,000.

According to a third aspect of the present invention, there is provided a composition suitable for use in a pulping or paper making process to control the deposition of pitch comprising a cationic polyelectrolyte which is a poly(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight greater than 500,000 and a smectite clay.

According to a fourth aspect of the present invention there is provided a pulping or paper making process in which there is incorporated into the composition comprising paper making fibres up to 1.0% by weight, based on the weight of dry fibres in the composition, of a cationic polyelectrolyte which is a poly-(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight greater than 500,000.

The invention will now be illustrated by reference to the following Examples.

EXAMPLE 1

Samples to simulate pitch containing a high proportion of neutral organic material were prepared by mixing various different amounts of triolein, measured in micromols, with 10cm^3 of ethanol. Each 10cm^3 sample of solution of triolein in ethanol was mixed with 99g of water, and there was then added thereto, as a pitch control reagent, either:-

(a) 1g of a bentonite having an average particle diameter of about 250nm, an approximate mineralogical analysis of 95% by weight of montmorillonite, 3% by weight of quartz and 1% by weight of feldspar and a cation exchange capacity of 101meq/100g, the exchangeable cations being sodium, calcium and magnesium in approximately equal proportions;

(b) 0.2g of a poly(diallyl dimethyl ammonium chloride) polyelectrolyte of number average molecular weight of approximately 1,000,000; or

(c) A combination of 1g of (a) and 0.2g of (b).

In each case the pitch control reagent was shaken with the diluted suspension of triolein for 15 minutes, after which the solid component of the mixture, if any, was removed by means of a centrifuge and the triolein which remained in suspension unadsorbed by the bentonite or unstabilised by the polyelectrolyte was extracted first with 10cm^3 of hexane and then with three successive 10cm^3 aliquots of chloroform. The hexane and chloroform solutions were combined together in a vessel and the solvents were removed by passing a current of air through the mixed solutions at 60°C to leave a deposit of fat on the walls of the vessel. This fat deposit was then extracted with 20cm^3 of the mobile phase of a high performance liquid chromatography (HPLC) system and the solution shaken for 30 minutes. A small quantity of the solution was then injected into an HPLC column and the quantity of triolein measured by determining the area of the appropriate peak. The difference between the original quantity of triolein introduced and the quantity of triolein present in the hexane and chloroform solvents gave the quantity which had been controlled.

The results are set forth in Table I which appears at the end of this description. The results show that, when the quantity of simulated pitch exceeds about 150μmol per 100g of aqueous suspension, the quantity of pitch removed by a combination of the polyelectrolyte and bentonite is greater than the sum of the quantities of simulated pitch removed by the polyelectrolyte and by the bentonite when used on their own.

The mixtures prepared as described above of various quantities of triolein with the polyelectrolyte alone and with the polyelectrolyte and bentonite were also tested for triolein droplet size and zeta potential by means of particle electrophoresis using a Zeta Sizer 4 instrument manufactured by Malvern Instruments Limited. As a control, the droplet size and zeta potential of the triolein droplets were also measured for the same quantities of triolein dispersed in 10cm^3 of ethanol and then added to 99g of water, but in the absence of any pitch control agent.

The results obtained are set forth in Table II which appears at the end of this description. These results show that the addition of 0.2g of poly(diallyl dimethyl ammonium chloride) to 109cm^3 (99g water + 10cm^3 ethanol) of an aqueous suspension of triolein causes dispersion of the triolein in the form of droplets of size which varies in the range from about 1.5μm to 3.0μm according to the concentration of triolein. The droplets have a zeta potential in the range from about +40mV to about +45mV which is sufficient to enable the droplets to repel each other and resist coalescence almost indefinitely. In the presence of a mixture of 0.2g of the polyelectrolyte and 1g of bentonite to 109cm^3 of triolein suspension the droplet size of the triolein is reduced to 0.7 - 0.9μm and the zeta potential to 29 - 34mV, but this is still sufficient to enable the triolein droplets to resist coalescence for a very long period. Where no pitch control reagent was

present the zeta potential was found to be in the range 11 - 16mV, and this would be insufficient to enable the droplets to repel each other strongly and rapid coalescence of the droplets would occur with consequent damaging deposition of pitch.

Table I

Quantity of triolein added (µmol)	Quantity of triolein (µmol) controlled by polyelectrolyte	bentonite	polyelectrolyte and bentonite
22.0	11.7	3.0	4.5
55.0	26.4	9.7	29.9
87.7	38.0	17.6	45.0
110.0	41.0	29.9	60.2
154.0	63.4	19.2	93.8
220.2	81.1	50.5	154.9
229.6	86.0	54.0	165.0

Table II

Quantity of triolein added (µmol)	Polyelectrolyte Droplet size (µm)	Polyelectrolyte Zeta potential (mV)	Polyelectrolyte and bentonite Droplet size (µm)	Polyelectrolyte and bentonite Zeta potential (mV)	No pitch control agent Droplet size (µm)	No pitch control agent Zeta potential (mV)
22.0	2.7	+43.3	0.7	+31	0.2	+15.9
55.0	3.0	+44.4	0.9	+32.4	0.3	+11.0
110.0	2.8	+39.4	1.0	+34.0	0.3	+14.1
154.0	2.2	+41.9	1.0	+31.3	0.3	14
220.0	1.7	+39	0.9	+29.6	0.4	+14

Claims

1. A process for controlling the deposition of pitch in a pulping or paper making process, wherein there is incorporated into the composition comprising paper making fibres up to 1.0% by weight, based on the weight of dry fibres in the composition, of a cationic polyelectrolyte which is a poly(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight greater than 500,000.3

2. A process according to claim 1, wherein the cationic polyelectrolyte is incorporated in the composition in an amount of at least 0.005% by weight, based on the weight of dry fibres in the composition.

3. A process according to claim 1 or 2, wherein the cationic polyelectrolyte has a number average molecular weight of at least 750,000.

4. A process according to claim 1, 2 or 3, wherein the cationic polyelectrolyte has a number average molecular weight no greater than 1,250,000.

5. A process according to any preceding claim, wherein there is incorporated into the fibre-containing composition, in addition to the cationic polyelectrolyte, up to 5.0% by weight, based on the weight of dry fibres in the composition, of a smectite clay.

6. A process according to claim 5, wherein the smectite clay is incorporated in the composition in an amount of at least 0.05% by weight, based on the weight of dry fibres in the composition.

7. A process according to claim 5 or 6, wherein the smectite clay is a bentonite, preferably one in which the exchangeable cations are predominantly sodium.

8. The use, as an agent for controlling the deposition of pitch in a pulping or paper making process, of a cationic polyelectrolyte which is a poly(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight greater than 500,000.

9. A composition, suitable for use in a pulping or paper making process to control the deposition of pitch, comprising a cationic polyelectrolyte which is a poly(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight greater than 500,000 and a smectite clay.

10. A pulping or paper making process in which there is incorporated into the composition comprising paper making fibres up to 1.0% by weight, based on the weight of dry fibres in the composition, of a cationic polyelectrolyte which is a poly(diallyl di(hydrogen or lower alkyl) ammonium salt) having a number average molecular weight greater than 500,000.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 6134

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 464 993 (NALCO CHEMICAL COMPANY) * claim 1 *	1,8,10	D21H21/02 D21C9/08 D21H17/45
A,D	CA-A-1 194 254 (ALCHEM INC.) * the whole document *	1,8,10	
A	EP-A-0 444 788 (NALCO CHEMICAL COMPANY) * the whole document *		
A,D	WO-A-8 906 294 (CYPRUS INDUSTRIAL MINERALS COMPANY) * the whole document *		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D21H D21C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 FEBRUARY 1993	SONGY Odile

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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