

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 280 445
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 88301208.0

(51) Int. Cl.4: D21H 3/38 , A01N 25/10

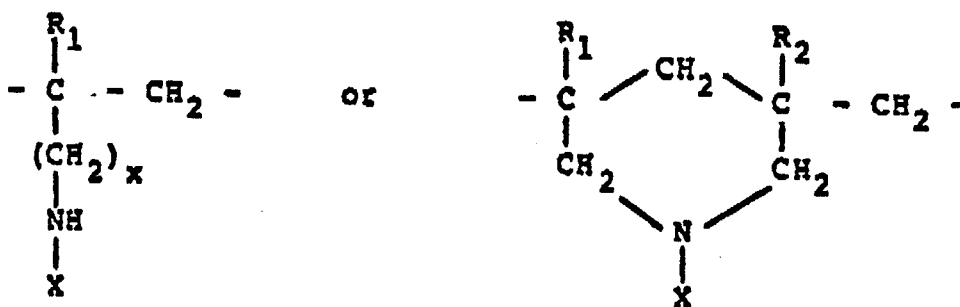
(22) Date of filing: 12.02.88

(30) Priority: 13.02.87 GB 8703304

(43) Date of publication of application:
31.08.88 Bulletin 88/35(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE(71) Applicant: W.R. GRACE & CO.
Grace Plaza 1114 Avenue of the Americas
New York New York 10036(US)(72) Inventor: Greaves, Brian
23 Bunbury Drive
Runcorn Cheshire WA7 4AL(GB)(74) Representative: Ellis-Jones, Patrick George
Armine et al
J.A. KEMP & CO. 14 South Square Gray's Inn
London WC1R 5EU(GB)

(54) Pitch control aid.

(57) A method for the control of pitch in an aqueous system used in pulp or paper making is disclosed which comprises adding to the system, or to the pulp making or paper making machinery, a water soluble polymer or copolymer possessing recurring units of the formula:



where each of R₁ and R₂ independently represents hydrogen or methyl, X represents hydrogen, --(CH₂CH₂NH)_nH or --(CH₂CH₂CH₂NH)_nH, x represents 0 or 1, preferably 1, and n represents 1 to 3, preferably 1, or an acid addition salt or quaternary ammonium salt thereof.

EP 0 280 445 A1

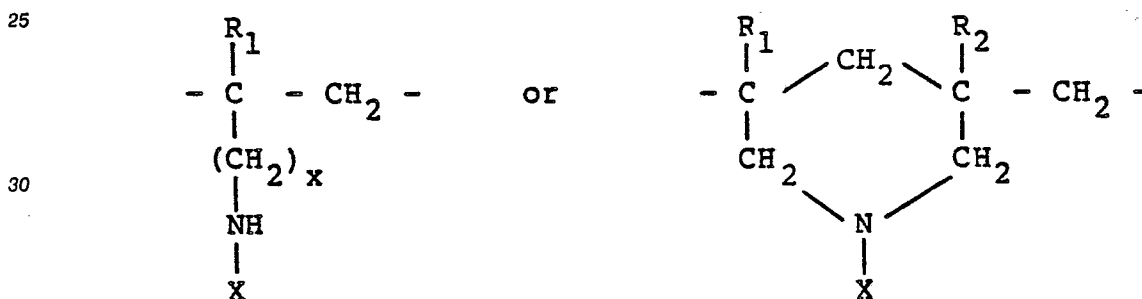
PITCH CONTROL AID

This invention relates to the control of pitch in the manufacture of pulp and paper.

It is well known that "pitch" can accumulate in paper making and also in the manufacture of pulp, causing significant problems. "Pitch" is the term used to describe the sticky materials which appear in paper making; these originate from the wood from which the paper is made. However, nowadays when more recycled paper is used, "pitch" is now used as a general term for all material soluble in organic solvents but not soluble in water, for example the ink or adhesive present in recycled paper. The pitch can accumulate at various points in the system. For example, it can block the felt and thus hinder drainage of the paper web. In addition, it can adhere to the wires or drying cylinders causing it to pick holes in the paper. Deposits may also build up at any earlier stage in the papermaking process. When these deposits break loose they may form a defect in the paper such as a spot or a hole. Such defects may even create a weakness in the paper sufficient to induce a breakage in the paper during the production resulting in unappreciated production down-time.

Many materials have been used in an attempt to eliminate these problems. Such materials include inorganic treatments such as talc and anionic dispersants. However, conventional dispersants can be ineffective in a closed system as there can be a build-up of "pitch". In such systems the pitch particles have to be removed from the water system in a controlled way without being allowed to accumulate on the felt or rolls or, for example, the pipe work used in the paper making machinery. These products have also been found to give a limited effect and there is a need for further improved treatments.

It has now been found, according to the present invention, that certain water soluble allyl amine polymers are particularly effective for this purpose. Accordingly, the present invention provides a method for the control of pitch in an aqueous system used in pulp or paper making which comprises adding to the system or to the pulp making or paper making machinery, a water soluble substantially linear polymer or copolymer possessing recurring units of the formula:

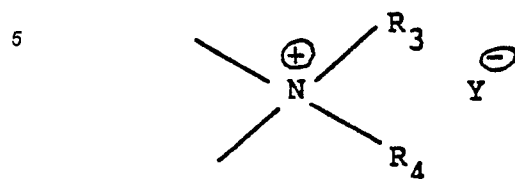


where each of R_1 and R_2 independently represents hydrogen or methyl, X represents hydrogen, $-(\text{CH}_2\text{CH}_2\text{NH})_n\text{H}$ or $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH})_n\text{H}$, x represents 0 or 1, preferably 1, and n represents 1 to 3, preferably 1, or an acid addition salt or quaternary ammonium salt thereof. It will, of course, be appreciated that the presence of the cyclic structure does not mean that the polymer is crosslinked and is therefore substantially linear.

A special feature of the products used in the present invention is that they may combine with dissolved anionic material originating from the wood from which the pulp and paper is produced, providing a method of removing these anionic materials thereby lowering the concentration of such materials in the process water. Water soluble anionic materials are released from the wood during pulp manufacture. These components interfere with paper production negatively in several ways: they decrease the efficiency of many products used in the papermaking process to alter the character of the paper. Examples of such additives include sizes, wet and dry strength agents and dyes. Anionic dissolved materials also reduce the efficiency of retention agents. They limit the extent to which the water system can be closed and they may also lower the quality of the paper such as its strength. Reference is made to TAPPI papermakers Conference 1979 p49-66 which further discusses the significance of anionic dissolved materials.

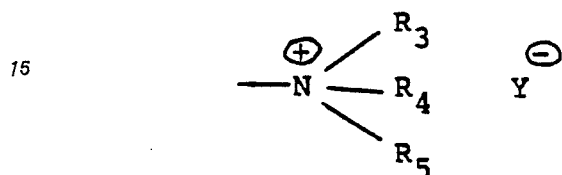
The polymers used in the present invention are polymers and copolymers of (meth)allyl amine, vinylamine and di(meth)allyl amine. Particular copolymers which may be used are those derived from allylamine and diallylamine as well as those in which the co-monomer is sulphur dioxide or acrylamine. The proportion of non-allylic amine monomer in the copolymer desirably does not exceed 50 mole % and preferably not exceed 25 mole %.

One or more of the nitrogen atoms in the polymer can be quaternised or be in the form of an acid addition salt. When X represents hydrogen, the side chain is then terminated by, say,



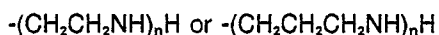
in the case of a diallyl unit,

or



in the case of a monoallyl unit

20 in the case of the monoallylamine units, wherein each of R_3 , R_4 and R_5 independently represents hydrogen, a straight or branched chain alkyl or hydroxylalkyl group containing 1 to 5 carbon atoms, an optionally nuclear substituted benzyl group or a cyclohexyl group, or R_3 and R_4 together with the nitrogen atom form a morpholino or piperidino ring and Y represents an anion, typically a chloride, bromide, iodide, nitrate, bisulphate or dihydrogenphosphate ion. Preferred values for R_3 , R_4 and R_5 include hydrogen, methyl, hydroxyethyl and hydroxypropyl. A particularly preferred quaternary group is trimethylamino. When X represents



the terminal nitrogen atom can be quaternised or be in the form of an acid addition salt in a similar manner with similar substituents and anions.

30 By varying the relative proportion of quaternised and unquaternised amino groups a whole range of different polymers can be prepared to suit individual circumstances.

Preferred polymers which can be used include poly(allyl amine) hydrochloride, copolymers of allylamine hydrochloride and diallylamine hydrochloride, as well as copolymers of diallylamine hydrochloride and sulphur dioxide.

35 In general the molecular weight of the polymers used will be from 5,000 to 100,000 or 500,000, preferably from 25,000 to 100,000 and especially from 50,000 to 100,000. Typical polymers which can be used may have molecular weights of, say, 7,500 to 11,000 or 50,000 to 85,000.

40 The polymers used in the present invention can generally be prepared by polymerising an inorganic acid salt of the appropriate monomer, e.g. allylamine hydrochloride, in the presence of a radical-polymerisation initiator possessing an azo group or a cationic nitrogen atom, generally in a polar solvent such as water, an aqueous solution of an inorganic or organic acid, dimethylformamide or dimethyl sulphoxide. A typical initiator which can be used is 2,2'-diamidiny-2,2'-azopropane hydrochloride. The copolymers can be obtained in a similar manner by radical initiation. Further details regarding the preparation of such polymers can be found in, for example, EP 140309 and 142962. As indicated, the

45 polymers should be substantially linear without crosslinking. The polymers in which X represents an aminoalkyl group can generally be obtained from the corresponding polymer in which X is hydrogen. For example cyanoethylation will produce a polymer where X is CH_2CH_2CN which can be subjected to catalytic hydrogenation with, for example, Raney nickel. Alternatively the starting polymer can be converted to an amine, for example by reaction with acrylamide giving, in this instance X as $CH_2CH_2CONH_2$ which can be subjected to a Hoffmann degradation, for example, with hypochlorite and alkali. These are, of course, all well known reactions.

50 The polymer is generally added to the aqueous system with the furnish containing the paper pulp but it is possible to add it at different points in the system depending on the precise nature of the problem. The pulp will generally be present in an amount from 0.5 to 10%, more usually 0.5 to 5% by weight based on

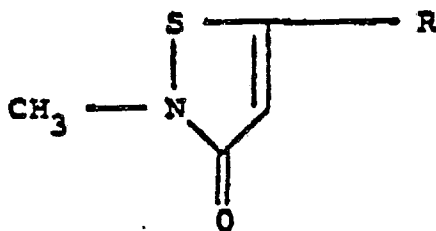
55 the weight of the water. The amount of polymer required will, of course, depend to some extent on the nature of the wood or other material used to prepare the paper pulp. Also, some polymer once added will tend to recirculate in the system thus requiring a lower addition rate. In general, however, from 0.1 to 20 ppm of polymer by

weight based on the aqueous medium is suitable. Preferably, the amount is 1 to 10 ppm. This corresponds in the normal case to an addition of 10 to 2,000 grams, preferably 100 to 1,000 grams, polymer per tonne fibre. However, in cases where the polymer is required to neutralize anionic dissolved materials, generally higher amounts are desirable, in the normal case from 1,000 grams to 50,000, especially from 1,500 to 15,000 grams, per tonne fibre depending on the process by which the fibres are produced (see, for example, Progr. Colloid & Polymer Sci. 65, 251-264 (1978) for a discussion of the amounts of anionic material likely to be present). Fibres produced by a mechanical process generally require a higher addition than fibre prepared by a chemical process. It is, of course, also possible to only partly neutralize the total amount of dissolved anionic materials. In such cases amounts from as little as, say, 10 grams per tonne of paper may be effective.

Sometimes it can be preferred to spray the reaction product used in this invention onto a particular part of the pulp-or paper-making machinery such as the wire or press felts. In such cases, the polymer is preferably pre-diluted with water, generally to a concentration below 10% by weight and preferably 1 to 5% by weight.

In some instances, it will be convenient to add the polymer together with a biocide, in particular a slimicide used in the paper making industry. Examples of suitable biocides include those in the following classes:

(i) a substituted 5-or 6-membered ring heterocyclic compound in which the hetero atom or atoms are one or more of nitrogen, oxygen or sulphur and the substituent is an alkyl group, a keto group or a hydroxyl group or a halogen atom, such compounds include isothiazolones, and in particular, those having the formula:



wherein R represents hydrogen or chlorine. A blend of these two isothiazolones is commercially available, the weight ratio of the chloro-substituted compound to the unsubstituted compound being about 2.66:1;

- (ii) an amine or amide including 2,2-dibromo-3-nitrilopropionamide;
- (iii) an organic cyanide or thiocyanate, particularly methylene bis(thiocyanates);
- (iv) a sulphone including halosulphones, particularly hexachlorodimethylsulphone;
- (v) a straight chain aliphatic aldehyde, particularly glutaraldehyde;
- (vi) a triazine, particularly thio and/or amino-substituted alkyl triazines;
- (vii) bis bromo acetoxy butene; and
- (viii) a dithiocarbamate, especially the monomethyl, dimethyl, monoethyl and diethyl derivatives, typically in the form of sodium salts.

Other agents can optionally be added particularly when the composition is used as a spray, including corrosion inhibitors to protect metal substrates, thickening agents to increase contact times between the composition and the equipment, and surfactants such as amine oxides to improve the wetting of equipment. Suitable corrosion inhibitors for use in this manner include alkanolamine salts of aryl sulphonamide carboxylic acids, such as the product Hostacor KS1-X available commercially from Hoechst. Preferred surfactants for use in this manner include n-alkyl ethoxy dimethylamine oxides where the alkyl has between about 12 and about 18 carbons, such as the product Empigen OY (25% active) available commercially from Albright and Wilson; and lauryl/myristyl dimethylamine oxides, such as the product Empigen OB (30% active) commercially available from Albright and Wilson.

The polymer is generally compatible with the usual pulp and paper making additives including starch, for example potato or corn starch, titanium dioxide, a de foamer such as a fatty acid alcohol, a size, for example a rosin size based on abietic acid, a neutral size based on alkyl ketene dimer or a succinic acid anhydride based size and a wet strength resin such as, if neutral, an epichlorohydrin polyamide or, if acid, a melamine-or urea-formaldehyde resin.

The precise nature of the pH of the system is unimportant since the effectiveness of the polymer is substantially unaffected by changes in pH.

Some of the polymers used in the present invention are commercially available, typically as aqueous

solutions containing a concentration of 40 to 50 %, especially about 45%, by weight. Typically, the compositions used in the present invention will possess from 1 to 70%, especially 10 to 30%, by weight of the polymer.

The following Examples further illustrate the present invention.

EXAMPLES

A polyallyl amine hydrochloride was evaluated together with commercially available pitch control agents using essentially the method described in 1977 TAPPI paper makers conference p 23-32 by Ch E Farley. This method is built on TAPPI Standard Method RC324 which is a recognised method for evaluating depositability of pitch. The standard pitch solution was prepared as described in the above references. A synthetic pitch emulsion/dispersion was prepared by adding one litre volume of various back waters from commercial paper makers at 50°C to the synthetic pitch to reach a 1200 ppm concentration.

A solution of calcium chloride was added to reach a hardness of 377 ppm expressed as calcium carbonate. The pH was adjusted to 8.0. To evaluate the products as pitch control agents, the products were added to obtain a concentration of polymer as specified in Table I. The depositability of the pitch was evaluated according to the procedure in the above references. The test duration was always five minutes. The results are presented in the following Table (mg deposited pitch).

<u>Products</u>	<u>Concentration</u> <u>(active) ppm</u>	<u>Pitch Deposit mg</u>
(In Back Water 1)		
Blank	-	180
Polymer 1	10	30
	20	12

5		30	2
10	Polymer 2	10	84
		20	50
		30	36
15			
	Polymer 3	10	106
		20	57
20		30	20
	(In Back Water 2)		
25	Blank	-	200
	Polymer 1	10	32
		20	8
30		30	6
35	Polymer 2	10	180
		20	80
		30	56
40			
	Polymer 4	10	100
		20	116
45			
	(In Back Water 3)		
50	Blank	-	230
	Polymer 1	10	160
		30	80
55			

5	Polymer 2	10	224
		30	164
10	(In Back Water 4)		
	Blank	-	175
15	Polymer 1	10	18
		20	14
		30	2
20			
	Polymer 2	10	122
25		20	70
		30	44
30			
	Polymer 4	10	164
		20	148
35		30	120
	(In Back Water 5)		
40	Blank	-	210
	Polymer	10	160
		20	78
45		30	36
50	Polymer 2	10	205
		20	198
		30	122
55			

5	Polymer 4	10	205
		20	200
		30	98

10

(In Back Water 6)

15	Blank	-	150
	Polymer 5	10	20
		20	3
20		30	2

25	Polymer 2	10	76
		20	27
		30	5

30

35	Polymer 4	10	140
		20	75
		30	15

(In Back Water 7)

40	Blank	-	185
	Polymer 5	10	15
45		20	12
		30	10

50	Polymer 2	10	48
		20	16
55		30	12

Polymer 4 10 120

5 20 52

30 15

10 Polymer 1 = Polyallylamine hydrochloride - Molecular weight
50,000 - 83,000

15 Polymer 2 = Commercial product based on dicyandiamide/
formaldehyde/formic acid reaction product

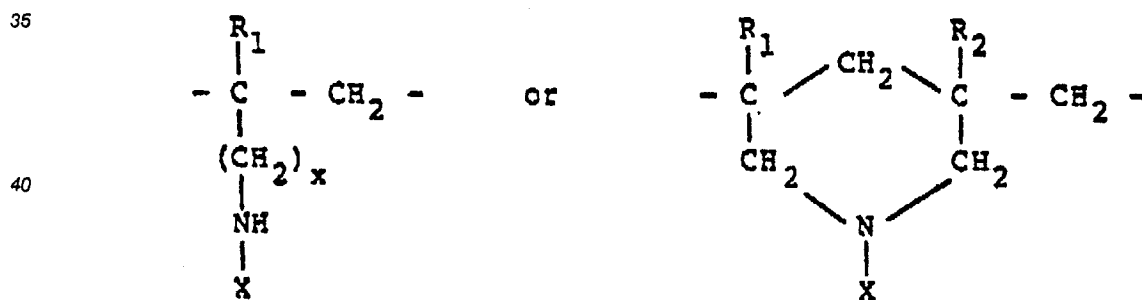
Polymer 3 = Commercial product based on epichlorohydrin/
dimethylamine/ethylene diamine reaction product

20 Polymer 4 = Commercial product based on dicyandiamide/
formaldehyde/formic acid/phosphoric acid reaction product.

25 Polymer 5 = Polyallylamine hydrochloride - Molecular weight
7,500 - 11,000.

Claims

30 1. A method for the control of pitch in an aqueous system used in pulp or paper making characterised by adding to the system, or to the pulp making or paper making machinery, a substantially linear water soluble polymer or copolymer possessing recurring units of the formula:

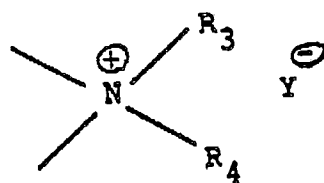


45 where each of R_1 and R_2 independently represents hydrogen or methyl, X represents hydrogen, $-(CH_2CH_2NH)_nH$ or $-(CH_2CH_2CH_2NH)_nH$, x represents 0 or 1, and n represents 1 to 3, or an acid addition salt or quaternary ammonium salt thereof.

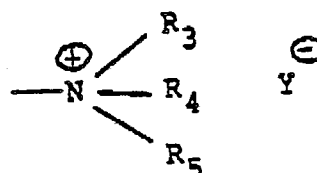
2. A method according to claim 1 characterised in the X represents hydrogen.

50 3. A method according to claim 1 or 2 characterised in that the polymer is at least partially quaternised or at least partially in the form of an acid addition salt, the, or the terminal, amino group being in the form

55



or



wherein each of R_3 , R_4 and R_5 independently represents hydrogen, a straight or branched chain alkyl or hydroxyalkyl group containing 1 to 5 carbon atoms, an optionally nuclear substituted benzyl group or a cyclohexyl group, or R_3 and R_4 together with the nitrogen atom form a morpholino or piperidino ring, and Y represents an anion.

4. A method according to claim 3 characterised in the R_3 , R_4 and R_5 represent methyl.

5. A method according to claim 3 characterised in that R_3 , R_4 and R_5 represent hydrogen and Y^- represents a chloride anion.

6. A method according to any one of the preceding claims characterised in that the polymer is a poly-(allylamine)hydrochloride.

7. A method according to any one of claims 1 to 5 characterised in that the polymer is a copolymer of allylamine and diallylamine, of diallylamine and acrylamide or of diallylamine and sulphur dioxide.

8. A method according to any one of the preceding claims characterised in that the polymer has a molecular weight of 5,000 to 100,000.

9. A method according to claim 8 characterised in that the polymer has a molecular weight of 50,000 to 85,000 or of 7,500 to 11,000.

10. A method according to any one of the preceding claims characterised in that the polymer is added to the aqueous system with the furnish containing the paper pulp.

11. A method according to any one of the preceding claims characterised in that the polymer is added in an amount from 1,000 to 50,000 grams per tonne of fibre.

12. A method according to any one of claims 1 to 9 characterised in that the polymer is sprayed onto at least a part of the pulp or paper making machinery.

13. A method according to any one of the preceding claims characterised in that a slimicide is also added to the aqueous system.

14. A composition suitable for use in pulp or paper making characterised by comprising a polymer as defined in any one of claims 1 to 9 and a slimicide.

15. A composition according to claim 14 characterised in that it contains 1 to 70% by weight of the polymer.

16. A composition according to claim 15 characterised in that it contains 10 to 30% by weight of the polymer.

17. A composition according to any one of claims 14 to 16 characterised in that the slimicide is a substituted 5-membered ring heterocyclic compound in which the heteroatoms are nitrogen and sulphur, an amine, 2,2-dibromo-3-nitrilopropionamide, a thiocyanate or a straight chain aliphatic aldehyde.



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.4)
X	EP-A-0 058 621 (CALGON CORP.) * Whole document * ---	1,3,7,8 ,10	D 21 H 3/38 A 01 N 25/10
X	EP-A-0 069 573 (MERCK & CO.) * Claims 1,7 * ---	1,3,7,8 ,10,13- 15,17	
X	CA-A-1 194 254 (ALCHEM) * Whole document * ---	1,3,8- 11	
A	EP-A-0 131 306 (NITTO BOSEKI CO., LTD) * Abstract * ---	1-3,6,7 ,8,10	
A	US-A-4 021 484 (H. TODA et al.) * Column 1, lines 27-68; column 2, line 47 - column 3, line 2; column 7, lines 33-55; column 8, lines 14-18; examples 1,5,8,10,26; column 20 * -----	1-6,8, 10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			D 21 H
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-05-1988	Examiner NESTBY K.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			