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(54) **process for control of pitch deposition from pulps in papermaking systems.**

(57) An improved process for controlling natural pitch deposition in pulp and papermaking aqueous systems involves the use of ampholytic polymers containing diallyl dimethyl ammonium quaternary salts and also containing (meth) acrylic acid salts and optionally containing (alkyl) acrylic acid esters or hydroxy esters. These ampholytic polymers give improved results in terms of control of natural pitch in the manufacture of pulp and paper.

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This invention relates to a process for controlling natural pitch deposition obtained from the processing of various wood pulps which are then used to manufacture paper products. These natural pitch depositions are detrimental to efficient operations of paper mills. Pitch deposits on process equipment used in the paper making systems result in operational problems related to the accumulation of pitch deposits on consistency regulators and other instrumental probes used to monitor the process of manufacturing paper from various types of pulp and paper furnishes.

In addition pitch deposits can form on screens and can reduce throughput as well as upset the operation of the paper manufacturing process. The deposition of natural pitch can occur not only on the metal surfaces in the system but also on plastic and synthetic surfaces such as machinery wires, felts, foils, UHLE boxes, and head box components. These pitch deposits may also break off resulting in spots and defects in the final paper product which thereby decreases the paper quality.

Surfactants, anionic polymers and co-polymers of anionic monomers and hydrophobic monomers have been used extensively to prevent pitch deposition. For example, in the text "Pulp and Paper" by James B. Casey, volume II, second edition, pages 1096-7, the above types of polymers are described for this purpose.

In addition, bentonite, talc, diatomaceous earth, silica, starch, animal glue, gelatin and alum have also been used to reduce pitch deposits. U.S. Patent 3,081,219, Drennen et al., discloses the use of polymeric N-vinyl lactam to control pitch in making paper from sulfite pulps.

In addition the following patents have disclosed the use of various kinds of chemicals both polymeric and nonpolymeric for pitch control.

U.S. Patent 3,154,466, Nothum
U.S. Patent 3,582,461, Lipowski et al.,
U.S. Patent 3,619,351, Kolosh
U.S. Patent 3,748,220, Gard
U.S. Patent 3,992,249, Farley
U.S. Patent 4,184,912, Payton
U.S. Patent 4,190,491, Drennen et al.,
U.S. Patent 4,253,912, Becker et al.,
U.S. Patent 4,871,424, Dreisbach, et al.,
U.S. Patent 4,765,867, Dreisbach et al.,
U.S. Patent 4,744,865, Dreisback et al.,
Canadian Patent 1,194,254, Molnar
Canadian Patent 1,150,914, Molnar
U.S. Patent 4,313,790, Pelton et al.,

All of the above patents disclose certain processes and formulations, including cationic polymers and specifically, for example, in Canadian 1,194,254, certain cationic polymers formed by polymerization of diallyl dimethyl ammonium chloride, which polymers are useful for pitch control.

In addition, an article appearing in a publication by the Institute of Paper Science and Technology in Atlanta, Georgia, authored by Weigel, et al., and entitled "Resin Deposits and Their Control in Paper-making" and translated from Papier 40(10A): V52-62 (October 1986), also described pitch deposits and their control in various paper mills.

An article, "Unusual Applications of Dual Polymer Systems" by Dykstra, et al., published in the 1987 TAPPI Advanced Topics in Wet End Chemistry Seminar, speaks of the use of anionic polymers in combination with charged condensation polymers having cationic charge for use in pitch control.

Another article entitled "Pitch and Stickies Control in Pulp and Paper Mills" by Pamela J. Allison published in Paper Southern Africa, Volume 8, No. 3, 1988, talks of pitch and stickies deposits and techniques for their control. Another paper by Dykstra et al., entitled, "A New Method for Measuring Depositable Pitch and Stickies and Evaluating Control Agents", published in 1988 TAPPI Papermakers Conference Proceedings, page 327, also talks of pitch and stickies control. This paper also talks of dual polymer treatment.

Finally in the June, 1988, Tappi Journal, on page 195, an article by Hassler, entitled, "Pitch Deposition in Papermaking and the Function of Pitch-control Agents," speaks of various pitch control agents and techniques to assist in pitch deposition and control.

All of the above patent and literature references are incorporated herein by reference.

In none of the references, including the specific Canadian patent to Molnar referring to the use of a homopolymer of DADMAC, i.e., diallyl dimethyl ammonium chloride, is there any mention of the use of ampholytic polymers containing diallyl dimethyl ammonium halide monomers.

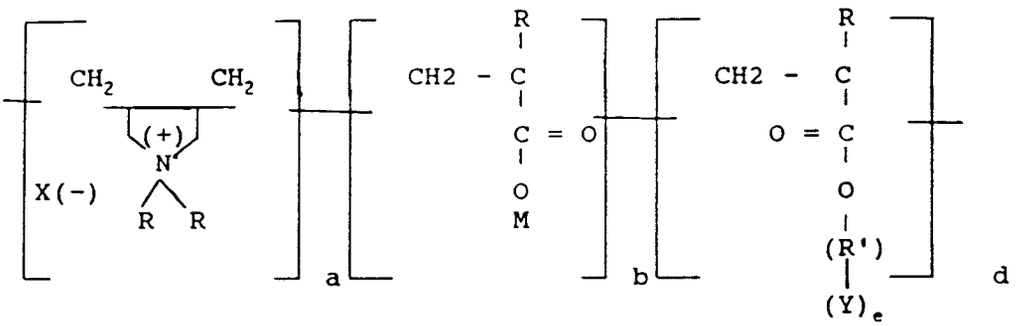
The present invention provides an improved process of pitch control which process uses as a pitch

control agent, water soluble co-polymers or terpolymers which are formed by polymerization of diallyl dimethyl ammonium salts with acrylic acid or methacrylic acid or their salts, and optionally using various alkyl acrylate esters or hydroxy substituted alkyl esters of acrylic acid or methacrylic acid.

Another object of the invention is to eliminate or minimize the effect of natural pitch deposits in the manufacture of paper by adding to a pitch contaminated paper furnish prior to sheet formation, an improved pitch control agent which agent is a co-polymer or terpolymer containing diallyl dimethyl ammonium salts, acrylic acid or methacrylic acid and its salts, and, optionally, alkyl acrylate or hydroxy alkyl acrylates.

Another object of the invention is to provide a specific co-polymer and/or terpolymer which is useful as a pitch control agent which polymer has a molecular weight ranging from about 10,000 to about 1,000,000 and contains from 75 - 95 mole per cent of diallyl dimethyl ammonium chloride; contains from about 2 to about 25 mole per cent of acrylic acid, methyacrylic acid, or their salts, or mixtures thereof; and from about 0 to about 10 mole per cent of an alkyl acrylate or a hydroxy alkyl acrylate or mixtures thereof.

We have determined that an improved process for controlling natural pitch deposition onto paper machine surfaces and into the paper sheet can be demonstrated, which process includes the addition of an effective pitch deposit controlling amount of pitch control agents to the pitch contaminated paper furnish prior to paper sheet formulation, the improvement comprising using as a pitch control agent a water soluble co-polymer comprising a combination of monomers chosen from the group consisting of diallyl dimethyl ammonium salts, (meth)acrylic acids and salts thereof, and alkyl or hydroxyalkyl acrylates, thereby forming polymers having the structure:



wherein R is individually chosen, at each occurrence, from hydrogen, methyl groups, and ethyl groups, provided that if R is covalently bonded to a nitrogen, R is chosen, at each occurrence, only from methyl groups and ethyl groups; and

M is chosen, at each occurrence, from hydrogen, alkali metal cations, equivalent amounts of alkaline earth metal cations, ammonium cations, protonated amine or quaternary ammonium cations and mixtures thereof; and

R' is a multivalent hydrocarbonaceous linear or branched alkyl group containing from 1-24 carbon atoms; and

X is an anion present in electroneutral amounts relative to positively charged nitrogen in the polymer backbone;

Y is chosen from -H, -OH, and mixtures thereof;

wherein the sum of a + b + d is sufficient to provide for a weight average molecular weight ranging between about 10,000 and about 1,000,000;

e is from 0 to 6; and the following relationships exist:

a:b is at least 3:1

a:(b + d) is at least 75:25, and

d:(a + b) ranges from 0 to 1:9, and further

d, but not a or b, can be zero.

THE POLYMER STRUCTURE

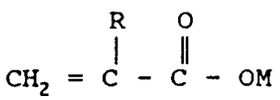
The polymer structure is as that described above. In this structure each monomer unit is essentially randomly distributed along the polymer chain and the polymer is ampholytic in nature, i.e. it can carry both a positive and a negative charge.

In addition the polymer optionally contains from 0 to about 10 mole per cent of a monomer which is oleophillic in character. This oleophillic monomer is preferably an ester or hydroxyester of acrylic acid,

methacrylic acid, ethacrylic acid, or mixture thereof.

The cationic character of the polymers described above are provided by inclusion of from about 75 to about 95 mole per cent of diallyl dimethyl ammonium salts. These salts may be chlorides, bromides, iodides, sulfates, nitrates, phosphates, and the like. Preferably, these quaternary di-vinyllic salts are in the form of diallyl dimethyl ammonium chloride (known in abbreviation as DADMAC). The diallyl dimethyl ammonium chloride (DADMAC) monomer is contained in the polymer at from about 75 to about 95 mole per cent, preferably from about 80 to about 90 mole per cent, and most preferably between 85 to about 90 mole per cent. This provides for an overwhelming positive charge on the backbone polymer.

However, it has been demonstrated that improvements in the use of these materials as pitch control agents are provided by the inclusion in the backbone of the polymers described above of from 2 to about 25 mole per cent of an anionic monomer unit. The preferred anionic monomer is chosen from acrylic acid, methacrylic acid, ethacrylic acid, and their common salts, or mixtures thereof. Preferably the salts are in the form of alkali metal salts, equivalent amounts of alkaline earth metal salts, or salts of ammonium cations, quaternary amine cations, or protonated amine cations. Most preferably the anionic monomer is acrylic acid, or methacrylic acid, or mixtures thereof, used either as the free acid or as the sodium, potassium, and/or ammonium salts. Of course any mixtures of the salts are also included in the concept of using these anionic monomer units and incorporating them in the monomer structures above. These anionic monomers can be represented by the term (meth)acrylic acid, but this term is used herein to represent any vinylic acid, or vinylic acid salt having the structure:



where R is H, CH_3, C_2H_5, and mixtures therof; and M is as defined above.

As above, the polymer can be improved by the incorporation, optionally, of certain oleophillic monomers such as (meth) acrylic acid esters, or (meth)acrylic acid hydroxy esters. These compounds provide some oleophillic character to the polymer and can assist in accumulating and dispersing pitch particles and attaching these pitch particles to cellulosic fibers so they do not accumulate disadvantageously on paper machine surfaces or cause difficulties otherwise in the manufacture of paper. These vinylic acid esters and vinylic acid hydroxy esters are primarily those materials chosen from acrylic acid esters, methacrylic acid esters, or ethacrylic acid esters. By the term acrylic acid ester, methacrylic acid ester, or ethacrylic acid ester we mean to also include the hydroxy esters that contain one or more hydroxyl groups on the alkyl unit attached to the ester oxygen.

The polymer that is preferred is a polymer that has a molecular weight ranging from about 10,000 to about 1,000,000 and most preferably has a molecular weight ranging from about 50,000 to about 500,000. These molecular weights are weight average molecular weights. The most preferred polymer contains from about 80 to about 90 mole per cent of diallyl dimethyl ammonium chloride, from about 5 to about 20 mole per cent of acrylic acid or methacrylic acid or mixtures thereof, (or salts thereof) and from about 0 to about 10 mole per cent of acrylic acid esters chosen from the group consisting of hydroxy alkyl acrylates and alkyl acrylates, or mixtures thereof, where the alkyl group of the ester functionality has from about 1 to about 24 carbon atoms, preferably from about 2 to about 14 carbon atoms.

The ampholytic polymers of this invention do not necessarily have to contain the (meth)acrylate esters or hydroxy alkyl (meth) acrylate esters, but can be formed merely as co-polymers of diallyl dimethyl ammonium chloride (or other salt) and either acrylic acid, methacrylic acid, ethacrylic acid, their salts, or mixtures thereof. When co-polymers are used, it is preferred that DADMAC is present between about 80 to about 95 mole per cent and the anionic (meth)acrylic acid units are present at between about 5 to about 20 mole per cent. Most preferably these co-polymers contains about 80 to 90 mole per cent DADMAC and from about 10 to about 20 mole per cent (meth)acrylic acid, or its salts.

DOSAGES

Typically, dosages of products containing the pitch control agents described above normally range from about 0.05 to about 20 pounds of formulated product per ton of paper product, on a dry fiber basis. The pitch control agents normally are provided as liquid dispersions or solutions of the polymers described in water which products normally range from about 1 to about 40 weight per cent active polymer. The polymer may also be provided as a water-in-oil latex emulsion containing a dispersed aqueous phase in which the

polymer described above has been dissolved. This emulsion normally also contains a controlled HLB surfactant system such that when the water-in-oil emulsion is added to the paper making system, inversion of phases occurs, and the polymer is rapidly dissolved and dispersed in the aqueous paper making media. When the product is supplied as a water-in-oil emulsion, the polymer content of the emulsion product can range from about 5 to about 55 weight per cent of the product. On an active polymer basis, the polymer dosage for the polymers of this invention, and described above, normally ranges from about 0.05 to about 2.0 pounds per ton, on the basis of active polymer per ton of dry fiber. To further exemplify and demonstrate our invention the following examples are provided:

EXAMPLES

Laboratory trials of products meeting the descriptions provided above were tested by the following procedure:

Example 1.

Approximately 7,000 ml of a hardwood kraft paper stock was prepared. This hardwood kraft stock contained 2.27 weight per cent fiber. This paper stock material was diluted with water until it contained approximately 1.5 weight per cent hardwood kraft stock fiber. The pH of this stock was adjusted to about 10.6 with sodium hydroxide solution. Approximately 100 ml of a 1 per cent dispersion of a laboratory pitch mixture was added to 700 ml of the 1.5 per cent hardwood kraft stock. The pH dropped to a pH of approximately 7.4-7.5. To this pitch containing slurry of hardwood kraft fibers was added 5 ml of a 0.5 molar calcium chloride dihydrate solution. This mixture was gently stirred and the pH checked. The pH had dropped to approximately 6.5. The pH of this test preferably ranges somewhere between 5.5 and 7.0 during the testing sequence for pitch deposition control.

The mixture of hardwood kraft stock, which mixture contains synthetic pitch dispersion and calcium chloride as described above is then poured into an laboratory blender. To this slurry is added a preweighed poly tetrafluoro ethylene plastic (PTFE) coupon which acts as a surface on which pitch is accumulated. This PTFE coupon is added to the pitch contaminated hardwood kraft stock in the blender. The blender used had 14 buttons controlling agitation blade speed. After addition of the preweighed PTFE plastic coupon, button number 4 is pushed and the stock is agitated for three minutes. Other blender speeds are also operable. A pitch deposit is obtained on the PTFE coupon, and after the coupon is removed, rinsed with distilled water from a wash bottle and dried in air, the coupon is then weighed. Drying time can range from about 4 hours to about 24 hours. The amount of deposited pitch is calculated by the difference from the original weight of the coupon.

By using this technique for each test sample, the following results were obtained.

TABLE I

Pitch Deposition Test

Inhibition of Pitch Deposition by Polymers #1, and Polymer #3

Treatment	Dosage (lb/ ton) Actives Basis	Product Basis	Pitch Deposit Weight (mg)	Percent Decrease in Pitch Deposit Weight*
Control-1	0	0	290	--
Polymer #1	0.1	0.5	10	97
Polymer #3	0.1	0.5	9	97
Control-2	0	0	288	--
Polymer #1	0.2	1.0	5	98
Polymer #3	0.2	1.0	2	99
Control-3	0	0	309	--
Polymer #1	0.5	2.5	3	99
Polymer #3	0.5	2.5	2	99

Average control (untreated) pitch deposit weight = 296 mg

1 standard deviation = 12 mg

* Percent decrease in pitch deposit weight = $\frac{\text{weight (control) - weight (treated) x 100}}{\text{weight (control)}}$

Polymer #1 — polyDADMAC; MW ~ 150,000, 20% polymer solids
6.19 meq charge/g polymer

Polymer #3 — polyampholyte coagulant; 20% polymer solids
DADMAC:Acrylate:Hydroxypropylacrylate terpolymer
87:10:3 mole ratio
4.92 meq charge/g polymer (pH >8.0)
5.57 meq charge/g polymer (pH <4.5)

Example II.

In addition, various tests were also performed on a trial and experimental basis, on a machine chest stock obtained from an active producing paper mill. The pH of the machine chest stock was measured at 7.95 and samples of this stock were treated in the laboratory with a homopolymer of diallyl dimethyl ammonium chloride, as taught by Molnar, and was simultaneously treated with the polymers of this invention. Results are shown in Table II.

TABLE II

Reduction in Colloidal Pitch and Anionic "Trash" Content of Machine Chest Stock from a South eastern U.S. paper mill

Product	Treatment Dosage (lb/ton)	Percent Transmittance (PTU)	Percent Decrease in Filtrate Turbidity*
Control	0	44	-
Polymer #1	3.1	44	0
Polymer #1	6.2	54	23
Polymer #1	9.3	69	57
Polymer #2	3.1	44	0
Polymer #2	6.2	48	9
Polymer #2	9.3	62	41
Polymer #3	3.4	46	4
Polymer #3	6.8	69	57
Polymer #3	10.2	84	91

* Percent Reduction in Filtrate Turbidity = $\frac{\text{turbidity (treated) - turbidity (control)} \times 100}{\text{turbidity (control)}}$

Polymer #1 = polyDADMAC homopolymer

Polymer #2 = a polyDADMAC solution polymer (different manufacturer)

Polymer #3 = Ampholyte polymer of invention
87 mole % DADMAC
10 mole % acrylic acid (Na salt)
3 mole % hydroxypropyl acrylate

Success in Table II is measured by the percent decrease in filtrate turbidity which is a measure of the amount of pitch which has been suspended and attached to the fiber so that it does not contribute to filtrate turbidity.

In addition to the Polymer #3 described above which polymer is a polyampholyte containing DADMAC/acrylic acid, salts, and hydroxypropylacrylate in a terpolymer, as described above, the following data is also presented which describes other co-polymers and terpolymers which fall within the claims of our invention and the use of these experimental polymers for pitch deposition control.

Examples III. (A - L)

The following test polymers were treated in the laboratory using the procedures set forth in Example I, except that a modified synthetic laboratory pitch was used.

TABLE III

Other ampholyte polymers

Polymer	Monomer Type & Mole Ratio *%	Solids	Intrinsic Viscosity (dl/g)
Polymer 1	DADMAC (100%)	20	0.63
poly Ampholyte (A)	DADMAC:AA:HPA (87:10:3)	20	1.08
poly Ampholyte (B)	DADMAC:AA (90:10)	20	0.92
poly Ampholyte (C)	DADMAC:AA (95:5)	22.6	0.93
poly Ampholyte (D)	DADMAC:AA (85:15)	23.3	0.80
poly Ampholyte (E)	DADMAC:AA (80:20)	23	0.72
poly Ampholyte (F)	DADMAC:MAA (98:2)	21	0.74
poly Ampholyte (G)	DADMAC:MAA (95:5)	22.8	0.70
poly Ampholyte (H)	DADMAC:MAA (85:15)	22.5	0.37
poly Ampholyte (J)	DADMAC:2-EHA (97:3)	21.9	0.86
poly Ampholyte (K)	DADMAC:2-EHA (95:5)	22.5	0.74
DADMAC copolymer (L)	DADMAC:a-MS (97:3)	13.9	0.21

*DADMAC = diallyl dimethyl ammonium chloride
AA = acrylic acid
MAA = methacylic acid
2-EHA = 2-ethylhexyl acrylate
a-MS = alpha-methylstyrene
HPA = hydroxypropylacrylate

The results of the testing of the polymers described in Table III are set forth below:

TABLE IV

Pitch Deposition
PolyDADMAC Versus Polyampholytes A - K and
DADMAC copolymer L

Treatment	Dosage (lb/ton) Actives Basis	Dosage (lb/ton) Product Basis	Pitch Deposit Weight (mg)	Percent Decrease in Pitch Deposit Weight*
Control-1	0	0	78	--
p-DADMAC	0.01	0.05	64	12
p-Amphol. A	0.01	0.05	71	3
p-Amphol. B	0.01	0.05	63	14
p-Amphol. C	0.01	0.04	68	7
p-Amphol. D	0.01	0.04	66	10
p-Amphol. E	0.01	0.04	70	4
Control-2	0	0	73	--
p-DADMAC	0.05	0.25	42	42
p-Amphol. A	0.05	0.25	47	36
p-Amphol. B	0.05	0.25	19	74
p-Amphol. C	0.05	0.22	31	58
p-Amphol. D	0.05	0.22	24	67
p-Amphol. E	0.05	0.22	39	47
Control-3	0	0	57	--
p-DADMAC	0.10	0.50	18	75
p-Amphol. A	0.10	0.50	20	73
p-Amphol. B	0.10	0.50	11	85
p-Amphol. C	0.10	0.44	12	84
p-Amphol. D	0.10	0.43	20	73
p-Amphol. E	0.10	0.44	17	77
Control-4	0	0	85	--

TABLE IV (cont.)

Pitch Deposition
PolyDADMAC Versus Polyampholytes A - K and
DADMAC copolymer L

Treatment	Dosage (lb/ton) Actives Basis	Dosage (lb/ton) Product Basis	Pitch Deposit Weight (mg)	Percent Decrease in Pitch Deposit Weight*
Control-1	0	0	72	--
p-DADMAC	0.01	0.05	73	9
p-Amphol. F	0.01	0.05	72	10
p-Amphol. G	0.01	0.04	77	38
p-Amphol. H	0.01	0.04	80	0
p-Amphol. J	0.01	0.05	70	13
p-Amphol. K	0.01	0.04	73	9
DAD/Cop. L	0.01	0.07	68	15
Control-2	0	0	89	--
p-DADMAC	0.05	0.25	60	25
p-Amphol. F	0.05	0.24	24	70
p-Amphol. G	0.05	0.22	35	56
p-Amphol. H	0.05	0.22	53	34
p-Amphol. J	0.05	0.23	34	58
p-Amphol. K	0.05	0.22	35	56
DAD/Cop. L	0.05	0.36	52	35
Control-3	0	0	83	--
p-DADMAC	0.10	0.50	35	56
p-Amphol. F	0.10	0.48	18	78
p-Amphol. G	0.10	0.44	13	84
p-Amphol. H	0.10	0.44	27	66
p-Amphol. J	0.10	0.46	18	78
p-Amphol. K	0.10	0.44	20	75
DAD/Cop. L	0.10	0.72	50	38

TABLE IV (cont.)

Pitch Deposition
PolyDADMAC Versus Polyampholytes A - K and
DADMAC copolymer L

Treatment	Dosage (lb/ton) Actives Basis	Dosage (lb/ton) Product Basis	Pitch Deposit Weight (mg)	Percent Decrease in Pitch Deposit Weight*
Control-4	0	0	84	--
Control-5	0	0	74	--

Average control (untreated) pitch deposit weight = 80 mg

1 standard deviation = 7 mg

* Percent decrease in pitch deposit weight = $\frac{\text{weight (control)} - \text{weight (treated)} \times 100}{\text{weight (control)}}$

In all the tests above using the procedures set forth in Example I, the pitch dispersion used is a synthetic laboratory pitch comprising a mixture of fatty and resin acids and esters, sterols, sterol esters and fatty alcohols, which is representative of actual softwood and/or hardwood pitch. This synthetic pitch is used to form the 1% dispersion described in Example I, and ranges in content as described in Table V.

TABLE V

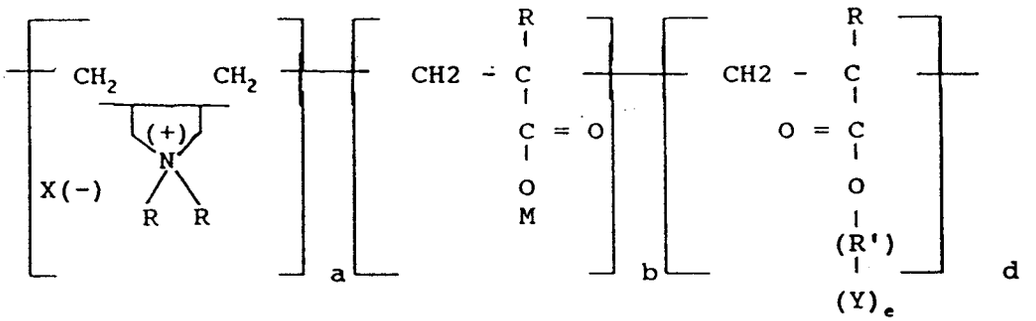
Synthetic Laboratory Ptch

%	Chemical Composition
5-50	Abietic acid (resin acid)
10-25	Oleic acid
5-10	Palmitic acid
10-35	Corn oil
5-15	Methyl stearate
2.5-7.5	Beta-sitosterol
2.5-7.5	Cholesteryl caproate
2.5-7.5	Oleyl alchol

This synthetic laboratory pitch is dispersed in isopropanol to form a
1% dispersion used as in Example I.

Claims

1. The process of controlling pitch deposition on paper machine surfaces by the addition of pitch control agents to a paper furnish prior to sheet formation, characterized in that the pitch control agent is a polymer having the structure:



wherein R is chosen, at each occurrence, from H, CH_3 and C_2H_5;

R' is a multivalent hydrocarbonaceous bridging group containing from 1 - 24 carbon atoms and chosen from linear and branched alkyl groups, cyclic groups, aromatic groups, alkaryl and aralkyl groups, and mixtures thereof;

M is chosen, at each occurrence, from H, alkali metals, alkaline earth metals in equivalent amount, ammonium, protonated amine and quaternary amine cations, and mixtures thereof;

X is an anion present in electroneutral amounts relative to positively charged nitrogen in the polymer backbone;

Y is chosen from -H, -OH, and mixtures thereof; and the sum of a + b + d is sufficient to provide a weight average molecular weight ranging between about 10,000 and about 1,000,000;

e is from 0 to 6; and

the following ratios exist:

a:b is at least 3:1,

a:(b + d) is at least 75:25,

d:(a + b) ranges from 0 to 1:9; and

d, but not a or b, can be zero.

2. The process of claim 1 wherein the pitch control agent is a terpolymer having a weight average molecular weight ranging between about 50,000 to about 500,000, and R, when attached to nitrogen in the polymer structure is - CH_3, and when attached to carbon in the polymer structure is from the group H, CH_3, or mixtures thereof; R' is a linear or branched alkylene group having from 1 to 16 atoms; and

e is from 0 to 4; and

the following ratios exist:

a: b is at least 4:1,

a: (b + d) is at least 80:20, and

d: (a + b) ranges from 0 to 1:9, and the effective pitch deposit controlling amont of the copolymer ranges from about 0.01 to about 2.0 pounds active copolymer per ton of dry fiber.

3. The process of claim 1 wherein R is chosen at each occurrence from H and CH_3;

R' is linear or branched alkyl group having from 1 to about 14 carbon atoms;

X is Cl

M is H, Na, K, Li, NH_4, or mixture thereof;

Y is from H and -OH, and mixtures thereof;

e is from 0 to 2; and

the sum a + b + d is sufficient to obtain a weight average molecular weight from about 50,000 to 500,000; d, but neither a or b can be zero; and the ratio a:b is at least 4:1; and the ratio, d:(a + b) never exceeds 1:9.

4. The process according to any one of the preceding claims wherein the polymer is added to the paper

stock at a dosage of from about 0.05 to about 1.5 pounds active polymer per ton paper, on a dry fiber basis.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 4199

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-0 058 622 (CALGON) * claims 1-3 * – – – – –	1	D 21 H 17/43 D 21 H 17/45 D 21 H 17/37

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 21 H
D 21 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	19 September 91	FOUQUIER J.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
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