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[54] **PROCESS OF IMPROVING WATER DRAINAGE FROM PAPER WEBS BY ADDITION OF A WATER SOLUBLE BLOCK POLYMER TO A CELLULOSIC PULP SLURRY**

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[51] **Int. Cl.**[2] **D21D 3/00**

[58] **Field of Search** 162/168, 164; 260/895, 260/885

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[57] **ABSTRACT**

The use of water-soluble block polymers of the A-B-A type wherein the A block is derived from a water-soluble monomer and the B block is derived from N-vinyl pyrrolidone as drainage and retention aids for paper webs wherein the polymer is added to a cellulosic pulp slurry.

8 Claims, No Drawings

PROCESS OF IMPROVING WATER DRAINAGE FROM PAPER WEBS BY ADDITION OF A WATER SOLUBLE BLOCK POLYMER TO A CELLULOSIC PULP SLURRY

This invention relates to the use of water-soluble, polymeric compositions as drainage and retention aids in the manufacture of paper and paper based products.

More particularly, this invention relates to the use, as drainage and retention aids in the manufacture of paper and paper based products, of water-soluble, polymeric compositions of the A-B-A type wherein the A block represents from 10 to 100,000 mer units of a water-soluble monomer and the B block represents from 10 to 5,000 mer units of N-vinyl pyrrolidone. As used herein, the term "paper" means a product formed from a wet-laid web of fibrous materials such as wood, bagasse, synthetic polymers as for example polypropylene, polyethylene and similar materials, and any combinations thereof.

For the formation of the web in a paper-making process, water in a pulp slurry is drained through a wire screen leaving the pulp fibers on top, and the rate of drainage has a direct concern with the efficiency of paper production. It has long been known that the addition of aluminum sulfate to pulp slurry facilitates the water drainage from the web on a wire screen. Various water-soluble polymers have been proposed as additives which impart more effective drainage to paper web than the aluminum sulfate. It is believed that these additivies bond pulp fibers so that water may pass through the bonded fibers. By this bonding action, however, these additives sometimes take up unwanted fillers and fine fibers within the web thereby depressing the drainage. Further, these additives may contaminate a wire screen, felt or dryers by adherence thereto, or may damage the texture of paper. Therefore, careful selection and control are required when these additives are used.

In this use, the polymers of the present invention are continuously added to a pulp slurry so that the mixture will contain from about 0.001 to about 1 percent, preferably from about 0.005 to about 0.25 percent, based on the dry weight of the pulp fibers therein, of the polymer. The pulp slurry is then fed to a wire screen belt or cylindrical screen of a sheeting machine where water in the slurry is drained through the screen leaving the pulp fibers as a paper web on the screen. The purpose of the polymer is to increase the rate of water drainage and/or to improve the formation of said sheet.

Many papers, except the absorbent types, filter papers, and most packaging papers, must have a finely ground filler added to them, the purpose of which is to occupy the spaces between the fibers, thus giving a smooth surface, a more brilliant whiteness, improved printability and improved opacity. The fillers are normally inorganic substances and may be either naturally occurring materials such as talc, agalite, pearl filler, barytes and certain clays such as china clay or artifical fillers such as suitably precipitated calcium carbonate, crown filler (pearl hardening), blanc fixe, and titanium dioxide pigments. These polymers may also be successfully used to enhance the retention of synthetic fillers.

The polymers of this invention may also be used to increase the retention of fillers, fiber fines, and/or other additives. For this purpose, the polymers are added to the paper-making system in the previously-described

manner. The polymer is added such that the pulp slurry will contain from about 0.001 to about 0.5 percent, preferably from about 0.005 to about 0.25 percent, based on the dry weight of the pulp fibers.

The polymers of this invention may also be used as wet strength or dry strength agents for paper and paper based products.

The ceric ion method taught by U.S. Pat. No. 2,922,768 and J. Macromolecular Science-Chemistry, A 7(8), 1581 (1973) has been found to be a convenient means of accomplishing the block copolymer synthesis of the polymers used in the instant invention.

Suitable water-soluble monomers include dimethyl diallyl ammonium chloride, 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, methacryloyloxy-2-hydroxypropyl trimethyl ammonium chloride, methacryloyloxyethyl trimethyl ammonium chloride, methacryloyloxyethyl trimethyl ammonium methosulfate, 2-acrylamido-2-methyl propane sulfonic acid, acrylic acid and salts thereof, methacrylic acid, 3-acrylamido-3-methyl butyl dimethylamine, acrylamide, methacrylamide, diacetone acrylamide, hydroxymethylated diacetone acrylamide, dimethyl-1-(2-hydroxypropyl) amine methacrylamide, and sodiuim styrene sulfonate. The preferred monomers, however, are 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, 2-acrylamido-2-methyl propane sulfonic acid, dimethyl dially ammonium chloride, methacryloyloxyethyl trimethyl ammonium chloride, methacryloyloxyethyl trimethyl ammonium methosulfate, and acrylamide.

The invention will be better understood by the following examples which illustrate the preparation and effectiveness of reprsentative polymers of this invention.

EXAMPLE 1

Preparation of Poly(Vinylpyrrolidone-b-Acrylamide)

A one liter, 4-neck flask fitted with a mechanical stirrer, condenser, nitrogen inlet and catalyst addition tube was charged with 16.00 g. acrylamide, 2.78 g. poly(vinylpyrrolidone), m.w. = 360,000 and 500 ml distilled water. After stirring the contents for an hour under a nitrogen purge, a solution of 0.123 g. ceric ammonium nitrate, 2.25 ml 1N HNO_3 and 10 ml water was added dropwise over a three hour period. The reaction solution became very viscous and wrapped around the stirrer shaft. After 16 hours at room temperature, the resulting polymer gel was precipitated into methanol in a blender. The solid product was isolated, washed with methanol and dried in vacuo. The product, obtained in 86% yield, exhibited an intrinsic viscosity in 1N $NaNO_3$ of 6.3 dl/g. The composition of the block polymer, determined by infrared analysis was 90 mole percent acrylamide, 10 mole percent vinylpyrrolidone. The following equation (Guilbault and Brooks, J. Macromolecular Science-Chemistry, A7(8), 1581 [1973]), was employed to calculate the molecular weight of the acrylamide end blocks:

$$G = \left(\frac{S}{C} - S\right)/N$$

Where

G = d.p. of the end blocks

S = d.p. of poly(vinylpyrrolidone) = 3200

N = no. of end blocks per poly(vinylpyrrolidone) block = 2

C = composition, as mole fraction vinylpyrrolidone

The block polymer structure calculated by this method was:

	(Polyacrylamide)	(Polyvinylpyrrolidone)	(Polyacrylamide)
Mol. Wt.	1×10^6	3.6×10^5	1×10^6

EXAMPLE 2

Preparation of Poly(Vinylpyrrolidone-b-Acrylamide)

A one liter, 4-neck flask fitted with a mechanical stirrer, condenser, nitrogen inlet and catalyst addition tube was charged with 6.75 g. acrylamide, 0.56 g. poly(vinylpyrrolidone), m.w. = 360,000 and 100 ml distilled water. After stirring the contents for an hour under a nitrogen purge, a solution of 0.052 g. ceric ammonium nitrate, 0.95 ml 1N HNO_3 and 10 ml water was added dropwise over a 3 hour period. The reaction solution became very viscous and wrapped around the stirrer shaft. After 16 hours at room temperature, the resulting polymer gel was precipitated into methanol in a blender. The solid product was isolated, washed with methanol and dried in vacuo. The product, obtained in 90% yield, exhibited an intrinsic viscosity in 1N $NaNO_3$ of 7.5 dl/g. The composition of the block polymer, determined by infrared analysis was 95 mole percent acrylamide, 5 mole percent vinylpyrrolidone.

The block polymer structure, calculated by the method of Example 1 was:

	(Polyacrylamide)	(Polyvinylpyrrolidone)	(Polyacrylamide)
Mol. Wt.	22×10^5	3.6×10^5	22×10^5

EXAMPLE 3

Preparation of Poly(Vinylpyrrolidone-b-Acrylamide)

A one liter, 4-neck flask fitted with a mechanical stirrer, condenser, nitrogen inlet and catalyst addition tube was charged with 13.33 g. acrylamide, 6.95 g. poly(vinylpyrrolidone), m.w. = 360,000 and 500 ml distilled water. After stirring the contents for an hour under a nitrogen purge, a solution of 0.103 g. ceric ammonium nitrate, 1.88 ml 1N HNO_3 and 10 ml water was added dropwise over a 3 hour period. The reaction solution became very viscous and wrapped around the stirrer shaft. After 16 hours at room temperature, the resulting polymer gel was precipitated into methanol in a blender. The solid product was isolated, washed with methanol and dried in vacuo. The product, obtained in 85% yield, exhibited an intrinsic viscosity in 1N $NaNO_3$ of 3.2 dl/g. The composition of the block polymer, determined by infrared analysis was 73 mole percent acrylamide, 27 mole percent vinylpyrrolidone.

The block polymer structure, calculated by the method of Example 1 was:

	(Polyacrylamide)	(Polyvinylpyrrolidone)	(Polyacrylamide)
Mol. Wt.	3.1×10^5	3.6×10^5	3.1×10^5

Extraction experiments demonstrated that the polyvinylpyrrolidone present in the product is incorporated into the block polymer structure. A sample (6.22 g.) of a 27.9 mole percent vinylpyrrolidone block polymer was extracted with refluxing methanol (a good solvent for polyvinylpyrrolidone) in a Soxhlet Thimble for 24 hours. The extracted sample weighed 6.20 g. and analyzed for 27.1 mole percent vinylpyrrolidone.

EXAMPLE 4

Preparation of Poly(Vinylpyrrolidone-b-Acrylamide)

A one liter, 4-neck flask fitted with a mechanical stirrer, condenser, nitrogen inlet and catalyst addition tube was charged with 8.88 g. acrylamide, 13.88 g. poly(vinylpyrrolidone), m.w. = 360,000 and 500 ml distilled water. After stirring the contents for an hour under a nitrogen purge, a solution of 0.069 g. ceric ammonium nitrate, 1.25 ml 1N HNO_3 and 10 ml water was added dropwise over a 3 hour period. The reaction solution became very viscous and wrapped around the stirrer shaft. After 16 hours at room temperature, the resulting polymer gel was precipitated into methanol in a blender. The solid product was isolated, washed with methanol and dried in vacuo. The product, obtained in 83% yield, exhibited an intrinsic viscosity in 1N $NaNO_3$ of 3.4 dl/g. The composition of the block polymer, determined by infrared analysis was 56 mole percent acrylamide, 44 mole percent vinylpyrrolidone.

The block structure, calculated by the method of Example 1 was:

	(Polyacrylamide)	(Polyvinylpyrrolidone)	(Polyacrylamide)
Mol. Wt.	1.4×10^5	3.6×10^5	1.4×10^5

EXAMPLE 5

Preparation of Poly(Vinylpyrrolidone-b-Acrylamide)

A one liter, 4-neck flask fitted with a mechanical stirrer, condenser, nitrogen inlet and catalyst addition tube was charged with 5.33 g. acrylamide, 19.43 g. poly(vinylpyrrolidone), m.w. = 360,000 and 500 ml distilled water. After stirring the contents for an hour under a nitrogen purge, a solution of 0.041 g. ceric ammonium nitrate, 0.75 ml 1N HNO_3 and 10 ml water was added dropwise over a 3 hour period. The reaction solution became very viscous and wrapped around the stirrer shaft. After 16 hours at room temperature, the resulting polymer gel was precipitated into methanol in a blender. The solid product was isolated, washed with methanol and dried in vacuo. The product, obtained in 54% yield, exibited an intrinsic viscosity in 1N $NaNO_3$ of 3.5 dl/g. The composition of the block polymer, determined by infrared analysis was 50 mole percent acrylamide, 50 mole percent vinylpyrrolidone.

The block polymer structure, calculated by the method of Example 1 was:

	(Polyacrylamide)	(Polyvinylpyrrolidone)	(Polyacrylamide)
Mol. Wt.	1.1×10^5	3.6×10^5	1.1×10^5

EXAMPLE 6

Preparation of
Poly(Vinylpyrrolidone-b-2-Acrylamido-2-Methyl Propane Sulfonic Acid)

This polymer was prepared in a manner analogous to Example 1, using 5.18 g. 2-acrylamido-2-methyl propane sulfonic acid, 8.33 g. poly(vinylpyrrolidone), m.w. = 360,000 and 100 ml water. The catalyst solution contained 0.25 ml 1N HNO_3, 0.014 g. ceric ammonium nitrate and 10 ml water. The product, obtained in 76% yield, was isolated from the reaction gel by precipitation into acetone. Utilizing the equation of Example 1, the molecular weight of each end block was found to be 1×10^5, and that of the poly(vinylpyrrolidone) center block, 3.6×10^5. The block polymer contained 24 mole percent anionic monomer units, as measured by infrared analysis.

EXAMPLE 7

Preparation of
Poly(Vinylpyrrolidone-b-2-Acrylamido-2-Methyl Propane Sulfonic Acid)

This polymer was prepared in a manner analogous to Example 1, using 15.53 g. 2-acrylamido-2-methyl propane sulfonic acid, 2.78 g. poly(vinylpyrrolidone), m.w. = 360,000 and 100 ml water. The catalyst solution contained 0.75 ml 1N HNO_3, 0.041 g. ceric ammonium nitrate and 10 ml water. The product, obtained in 54% yield, was isolated from the reaction gel by precipitation into acetone. Utilizing the equation of Example 1, the molecular weight of each end block was found to be 4.8×10^5, and that of the poly(vinylpyrrolidone) center block, 3.6×10^5. The block polymer contained 60 mole percent anionic monomer units, as measured by infrared analysis.

EXAMPLE 8

Preparation of
Poly(Vinylpyrrolidone-b-2-Acrylamido-2-Methyl Propane Sulfonic Acid)

This polymer was prepared in a manner analogous to Example 1, using 10.35 g. 2-acrylamido-2-methyl propane sulfonic acid, 5.55 g. poly(vinylpyrrolidone), m.w. = 360,000 and 100 ml water. The catalyst solution contained 0.50 ml 1N HNO_3, 0.027 g. ceric ammonium nitrate and 10 ml water. The product, obtained in 61% yield, was isolated from the reaction gel by precipitation into acetone. Utilizing the equation of Example 1, the molecular weight of each end block was found to be 2.1×10^5, and that of the poly(vinylpyrrolidone) center block, 3.6×10^5. The block polymer contained 39 mole percent anionic monomer units, as measured by infrared analysis.

EXAMPLE 9

Preparation of
Poly(Vinylpyrrolidone-b-Methacryloyloxyethyl Trimethyl Ammonium Chloride)

This polymer was prepared as in Example 1, using 10.86 g. of the cationic monomer, 5.55 g. poly(vinylpyrrolidone), m.w. = 360,000 and 100 ml water. The catalyst solution, comprised of 0.50 ml 1N HNO_3, 0.274 g. ceric ammonium nitrate and 10 ml water, was added at the beginning of the reaction. The product was obtained in 78% yield by precipitation of the reaction mixture into acetone. The block polymer contained 51 mole percent cationic monomer units, as measured by chloride titration. Utilizing the equation of Example 1, the molecular weight of each end block was found to be 3.4×10^5, and that of the poly(vinylpyrrolidone) center block 3.6×10^5.

EXAMPLE 10

Preparation of
Poly(Vinylpyrrolidone-b-Methacryloyloxyethyl Trimethyl Ammonium Chloride)

This polymer was prepared as in Example 1, using 16.30 g. of the cationic monomer, 2.78 g. poly(vinylpyrrolidone), m.w. = 360,000 and 100 ml water. The catalyst solution, comprised of 2.5 ml 1N HNO_3, 1.37 g. ceric ammonium nitrate and 10 ml water, was added at the beginning of the reaction. The product was obtained in 63% yield by precipitation of the reaction mixture with acetone. The block polymer contained 80 mole percent cationic monomer units, as measured by chloride titration. Utilizing the equation of Example 1, the molecular weight of each end block was found to be 13×10^5, and that of the poly(vinylpyrrolidone) center block 3.6×10^5.

EXAMPLE 11

Preparation of
Poly(Vinylpyrrolidone-b-Methacryloyloxyethyl Trimethyl Ammonium Chloride)

This polymer was prepared as in Example 1, using 5.44 g. of the cationic monomer, 8.33 poly(vinylpyrrolidone), m.w. = 360,000 and 100 ml water. The catalyst solution, comprised of 0.75 ml 1N HNO_3, 0.411 g. ceric ammonium nitrate and 10 ml water, was added at the beginning of the reaction. The product was obtained in 89% yield by precipitation of the reaction mixture into acetone. The block polymer contained 20 mole percent cationic monomer units, as measured by chloride titration. Utilizing the equation of Example 1, the molecular weight of each end block was found to be 0.8×10^5, and that of the poly(vinylpyrrolidone) center block 3.6×10^5.

EXAMPLE 12

The effectiveness of the polymers of the instant invention as drainage aids was evaluated on a lab-scale via use of a standard Schopper-Riegler Freeness Tester. Standard laboratory procedures were employed.

Generally, the furnish for evaluation is prepared by mixing the required amount of dry-lap pulp(s) and

water using a lightning mixer. Consistency at this point is usually ca. 1.5 and ca. 10 minutes mixing time is required. The furnish is then transferred to a Valley Beater and slurried without weights for 10–20 minutes. Weights are subsequently added and the furnish allowed to beat until the desired freeness is obtained. For example, after about 30 minutes beating, a Kraft furnish will have reached ca. 350 ml Schopper-Riegler Freeness.

The beaten pulp is transferred to a clean container and diluted to a suitable working consistency usually 0.2. If more than one pulp is employed in the furnish, mixing is accomplished. pH is adjusted to the desired value and any additives such as alum, etc. are added at this point and thoroughly mixed.

A one liter aliquot of the final stock slurry is collected into a graduated cylinder. The drainage aid is pipeted into the sample as a dilute aqueous solution to the desired feed rate and mixed thoroughly. The freeness of the stock and drainage aid is compared to that of stock only via use of the Schopper-Riegler Freeness Tester. Typical lab results are summarized in the following table.

TABLE I

Drainage Aid
50/50 News/Corrugated Stock
pH 4.5 and 6.9
Results Reported as % Increase
Over Control (No Treatment)

Polymer Sample	Feed Rate (lb./ton)	% Increase Over Blank pH = 4.5	pH = 6.9
2-AMPSA* Triblock Polymer	1	18%	6%
(60% 2-AMPSA)	2	18%	3%
2-AMPSA Triblock Polymer	1	—	—
(39% 2-AMPSA)	2	13%	9%
2-AMPSA Triblock Polymer	1	—	—
(24% 2-AMPSA	2	5%	9%
METAC* Triblock Polymer	1	—	38%
(75% METAC)	2	24%	56%
METAC Triblock Polymer	1	—	47%
(51% METAC)	2	34%	63%
METAC Triblock Polymer	1	—	38%
(20% METAC)	2	24%	41%

*2-AMPSA = 2-Acrylamido-2-Methyl Propane Sulfonic Acid
*METAC = Methacryloyloxyethyl Trimethyl Ammonium Chloride

EXAMPLE 13

The utility of the polymers described herein as retention aids was evaluated in the lab using a standard Noble-Wood Handsheet machine. Percent retention of such pigments as clay and/or TiO_2 is determined by ashing the handsheet to determine the amount of pigment retained in the sheet with respect to the amound fed. The efficiency of retention aid was determined via comparison of percent retention with the additive retention aid versus retention of a control wherein no retention aid was used.

Stock is prepared according to the general procedure outlined in Example 12. In the normal operating procedure, stock for evaluation of retention aids is beaten to 300 to 350 ml Schopper-Riegler Freeness and includes pigment (usually ca. 13% clay and 2% TiO_2 based on the consistency). An extra 10 minutes mixing is utilized to disperse the clay and TiO_2.

In evaluation of retention aids, the headbox of the Noble-Wood Handsheet machine is made up to 19 liters at a consistency of 0.4 (as opposed to the 0.2 used in drainage evaluation). The stock is drawn off at the rate of 500 ml per handsheet (2 g. per handsheet or 30 lbs./3,000 ft.^{2}). The retention aid (if any) is pipeted into the 500 ml sample at the desired feed rate and mixed for 30 seconds.

The stock sample is transferred to the deckle box which contains ca. 13 liters of water and dispersed. The handsheet is subsequently prepared by draining off the water and collecting the pulp on a standard 8 inch × 8 inch wire. The handsheet is pressed and drum dryed at 232°F. to reach ca. 5% moisture. The sheet is weighed and subsequently ashed at 900°C. Percent retention is calculated from the original weight of the handsheet, the percent of pigment in the furnish and the percent ash from the handsheet.

Table II

Pigment Retention Aid
Furnish - 50/50 Hard Wood/Soft Wood Kraft
13% Clay
2% TiO_2
2% Alum
10% Rosin
Acid
Adjust pH with N/2 H_2SO_4
30 lb/3,000 ft.^{2} sheet (2g)
250 milliliters Schopper-Riegler Freeness
Results Reported as % Increase
Over Blank (No Treatment)

Polymer Sample	Feed Rate (lb./ton)	% Increase Over Blank pH = 4.5	pH = 7.0
2-AMPSA* Triblock Polymer	.35	40%	38%
(60% 2-AMPSA)	.60	40%	—
METAC* Triblock Polymer	.35	40%	25%
(51% METAC)	.60	36%	33%

2-AMPSA* = 2-Acrylamido-2-Methyl Propane Sulfonic Acid
METAC* = Methacryloyloxyethyl Trimethyl Ammonium Chloride

We claim:

1. A process of improving water drainage from paper webs comprising adding to a cellulosic pulp slurry about 0.001 to about 1%, based on the dry weight of

pulp fibers, of a polymer of the formula A-B-A wherein the A block represents from 10 to 100,000 mer units of a water-soluble monomer selected from the group consisting of 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, 2-acrylamido-2-methyl propane sulfonic acid, dimethyl diallyl ammonium chloride, methacryloyloxyethyl trimethyl ammonium chloride, methacryloyloxyethyl trimethyl ammonium methosulfate and acrylamide and the B block represents from 10 to 5,000 mer units of N-vinylpyrrolidone, depositing the pulp onto a forming surface and draining the water from the fiber network.

2. A process as in claim **1** wherein the water-soluble monomer is acrylamide.

3. A process as in claim **1** wherein the water-soluble monomer is 2-acrylamido-2-methyl propane sulfonic acid.

4. A process as in claim **1** wherein the water-soluble monomer is methacryloyloxyethyl trimethyl ammonium chloride.

5. A process of improving the retention of inorganic fillers in the processing of paper which comprises the step of adding to an aqueous paper pulp suspension about 0.001 to about 1%, based on the dry weight of pulp fibers, of a polymer of the formula A-B-A wherein the A block represents from 10 to 100,000 mer units of a water-soluble monomer selected from the group consisting of 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, 2-acrylamido-2-methyl propane sulfonic acid, dimethyl diallyl ammonium chloride, methacryloyloxyethyl trimethyl ammonium chloride, methacryloyloxyethyl trimethyl ammonium methosulfate and acrylamide and the B block represents from 10 to 5,000 mer units of N-vinyl(pyrrolidone).

6. A process as in claim **5** wherein the water-soluble monomer is acrylamide.

7. A process as in claim **5** wherein the water-soluble monomer is 2-acrylamido-2-methyl propane sulfonic acid.

8. A process as in claim **5** wherein the water-soluble monomer is methacryloyloxyethyl trimethyl ammonium chloride.

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