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Vaughn et al.

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[54] **CELLULOSIC MATERIALS INTERNALLY SIZED WITH COPOLYMERS OF ALPHA BETA-ETHYLENICALLY UNSATURATED HYDROPHOBIC MONOMERS AND AMMONIATED CARBOXYLIC ACID COMONOMERS**

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[51] **Int. Cl.** **C08g 45/18**

[58] **Field of Search** ..... 260/17.4 CL, 17.4 ST; 162/164, 168, 175, 185, 169

[56] **References Cited**

UNITED STATES PATENTS

3,575,796	4/1971	Brown et al.	162/158
3,655,506	4/1972	Baggett	162/164
3,674,896	7/1972	Purcell	260/897

OTHER PUBLICATIONS

Union Carbide Brochure–F–42958; Products for Paper; PC4–300 – An Alkali Dispersible Ethylene Copolymer, Printed 10/70; pp. 1–2, 11–12 and 14.

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[57] **ABSTRACT**

Cellulosic materials such as paper are internally sized by treating fibers of the cellulosic material, e.g., paper pulp, with a copolymer of an α,β-ethylenically unsaturated hydrophobic monomer and an ammoniated α,β-ethylenically unsaturated carboxylic acid and a reaction product of epihalohydrin and ammonia. Internal sizing of the cellulosic material by this method can be carried out under acidic, neutral or basic conditions.

21 Claims, No Drawings

CELLULOSIC MATERIALS INTERNALLY SIZED WITH COPOLYMERS OF ALPHA BETA-ETHYLENICALLY UNSATURATED HYDROPHOBIC MONOMERS AND AMMONIATED CARBOXYLIC ACID COMONOMERS

BACKGROUND OF THE INVENTION

This invention relates to internal sizing of cellulosic material over the complete range of pH conditions which are normally encountered in the cellulosic manufacturing arts.

Cellulosic materials such as paper and paperboard, are often sized with various materials with the purpose of increasing their resistance to water penetration as well as to penetration by other types of aqueous solutions. These materials are referred to as sizes or sizing agents and they may be introduced during the actual manufacture of the cellulosic material, e.g., paper making operation, wherein the process is known as internal sizing, often called beater sizing, wet end sizing or engine sizing. Surface sizing cellulosic materials by applying sizing agent to fabricated sheet or web is also well known; but is usually considered to be substantially different from internal sizing.

The basis of present internal sizing methods is the intimate coating of the individual fibers of the cellulosic material with a material which is insoluble in most materials and is repellant to water. For example, in manufacture of paper, the substance originally and still most widely used for this purpose is rosin or fatty acid. In order to insure the most intimate contact between the rosin and the pulp fiber, the former is added in either the dissolved state or as a finely dispersed emulsion. It is followed by a precipitating agent, usually aluminum sulfate, known to the paper maker as "alum." The alum coagulates the rosin, i.e., throws it out of solution or emulsion as a gelatinous precipitate. Since the rosin or emulsion is first mixed thoroughly with the pulp in the beater, the precipitate has a maximum chance of adhering to and being subsequently retained by the pulp. When the pulp is made into paper, the rosin in contact with the pulp adheres to the pulp as small particles, e.g., particles having diameters of one micron or less. The paper having the small particles of rosin adhered to the fibers exhibits the desired strength and ink and water resistance.

In addition to rosins, various water-repellant or hydrophobic materials have been utilized as internal sizing agents. These include fortified rosin, mixtures or rosins with waxes, wax emulsions, ketene dimer emulsions, fluorocarbons, fatty acid complexes of chromium or aluminum chlorides, long chain thermoplastic copolymers, as well as thermosetting condensation-type resins. Although all of these materials are effective under certain conditions, their use is nonetheless subject to one or more limitations.

For example, in the case of rosin, it is only useful as sizing agent in acidic solutions and therefore cannot be used for the sizing of neutral or alkaline pulps. Rosin is inoperable with the latter since it must ordinarily be used in combination with alum, or an acidic aluminum ion donor which is present for the purpose of precipatating and setting the metal rosinate onto the fibers. The use of alum for this purpose is, however, precluded under neutral or alkaline stock conditions. This is a definite disadvantage in paper making since paper produced from neutral or alkaline pulp has been found to have higher strength, greater stability and superior aging characteristics in comparison with paper prepared from acidic pulp. Also, the internal use of alkaline pigments such as calcium carbonate is precluded. This limitation also applies to most wax emulsions which cannot be used on the alkaline side since they are usually combined with small quantities of alum for the purpose of breaking the emulsions. On the other hand, it may be noted that certain sizing agents will not tolerate acidic conditions. In addition to the above described pH limitations, the water resistance or water holdout which is obtainable with many of the heretofore employed sizing agents is often inadequate for many applications which require paper or paperboard displaying an exceptionally high degree of water-resistance. Some sizing agents provide complete water repellancy as opposed to the desired limited amount of water-resistance. Many sizing agents have been found to be incompatible with pigments, fillers or other ingredients which are often added to the paper. A further disadvantage of some sizing agents is that a considerable degree of heat curing is required in order to develop full effectiveness.

For these and other reasons, it would be highly desirable to provide an internal sizing agent which can be effectively employed under acidic, neutral or alkaline conditions and which can be cured to a size having the desired limited water resistance under normal drying conditions used in the early stages of manufacturing paper and other cellulosic materials.

SUMMARY OF THE INVENTION

In the present invention, paper and other cellulosic materials are internally sized under pH conditions ranging from moderately acidic through strongly alkaline by an improved internal sizing method. In this improved method for internally sizing the cellulosic material wherein an internal sizing agent is applied to the fibers of the cellulosic material, the improvement comprises the use of a copolymer of an α,β-ethylenically unsaturated hydrophobic monomer and an ammoniated α,β-ethylenically unsaturated carboxylic acid as an internal sizing agent and as a retention aid, a reaction product of epihalohydrin and ammonia, or an aliphatic polyamine having at least two amine hydrogens per molecule or mixture of ammonia and polyamine. In another aspect, this invention is an internal sizing composition for a cellulosic material comprising a sizing amount of the aforementioned copolymer and an amount of the aforementioned retention aid which is effective to retain the copolymer on the cellulosic material. In a further aspect, this invention is a cellulosic material internally sized with the aforementioned composition. The resultant internally sized cellulosic material displays a very desirable degree of water-resistance along with resistance to acidic and alkaline solutions. Of prime importance is the fact that the successful use of the aforementioned copolymers as sizing agents in combination with the aforementioned cationic retention aid is not restricted to acidic pH which thus allows utilization of such sizing agents in the treatment of neutral and alkaline pulp as well as acidic pulp. Furthermore, it is found that only mild drying and curing conditions are needed to develop the full sizing value of such internal sizing agents.

DETAILED DESCRIPTION OF THE INVENTION

For the purposes of this invention, the term "cellulosic material" is meant to include paper, paper board and other fibrous, sheet-like or molded masses derived from wood, wood pulp, or cotton or other sources of cellulosic fibers. This term also includes sheet-like or molded masses prepared from combination of cellulosic materials and non-cellulosic materials such as polyamides, polyesters, polyacrylic acid resin fibers and mineral fibers such as asbestos, glass and the like.

By the term "internal-sizing" is meant a method of sizing in which the cellulosic material in raw form, e.g., fibrous stock such as paper pulp, is contacted with the sizing agent under conditions effective to size the cellulosic material, i.e., deposit the sizing agent on the fibers and cure it to full sizing effectiveness. Accordingly, it is understood that the term internal sizing is generic, and therefore includes such terms as "beater-sizing," "engine-sizing," "internal wet end sizing" and the like.

The internal sizing agents suitably employed in the practice of this invention are copolymers of α,β-ethylenically unsaturated hydrophobic monomer and ammoniated α,β-ethylenically unsaturated carboxylic acid, i.e., α,β-ethylenically unsaturated carboxylic acid in the ammonium salt form. Generally, such copolymers are water-dispersible, semi-solid or solid materials. Such copolymers have molecular weights which give melt flow viscosities in the range from about 0.2 decigram/minute as measured by ASTM D–1238-65T(E) to about 50 decigrams/minute as measured using the procedure of ASTM D–1238-65T(B) except that in said procedure the orifice of the extrusion plastometer is 0.020 inch. Preferably, the copolymer has a number average molecular weight, as determined by ebulliometry, in the range from about 1,000 to about 10,000 and a melt flow viscosity in the range from about 0.5 to about 50 decigrams/minute as determined by ASTM D–1238-65T(B) using the plastomer with a 0.020 inch orifice. Preferred copolymers are also film-forming at temperatures used in the sizing operation. By "water-dispersible" is meant a material which can exist in the form of a stable aqueous colloidal dispersion in the absence of a surface active agent. In addition, the copolymers in the form of aqueous dispersions preferably form films under ambient conditions which films dry to form water-insoluble coatings. By α,β-ethylenically unsaturated hydrophobic monomer is meant any water-immiscible monomer containing a terminal double bond capable of polymerization under normal conditions of addition polymerization to form a water-insoluble homopolymer having a polyethylenic backbone. By α,β-ethylenically unsaturated carboxylic acid is meant an α,β-ethylenically unsaturated carboxylic acid which is capable of addition copolymerization through the ethylenically unsaturated group with the α,β-ethylenically unsaturated hydrophobic monomer. By ammoniated α,β-ethylenically unsaturated carboxylic acid is meant that in the copolymer the carboxylic acid groups are neutralized with ammonia.

Preferably, the internal sizing agent is a normally solid, water- and alkali-insoluble thermoplastic addition copolymer in the form of a fluid aqueous colloidal dispersion. The occurrence of ammoniated acid groups in the polymer should be general throughout the macromolecules thereof so that each macromolecule contains a minimum number of active salt groups sufficient to render the polymer water-dispersible as defined hereinbefore. The maximum number of ammoniated acid groups which may be present in the macromolecules is fixed by the requirement that the molecule be substantially water-insoluble. Generally speaking, such copolymers contain from about 6 to about 40 weight percent of ammoniated acid comonomer, with preferred copolymers containing from about 10 to about 20 weight percent of ammoniated acid comonomer and especially preferred copolymers containing from about 15 to about 18 weight percent.

Exemplary preferred copolymers are the random copolymer products of copolymerization of mixtures of one or more polymerizable ethylenically unsaturated carboxylic acids having 3 to 8 carbon atoms inclusive of anhydrides and alkyl half esters of ethylenically unsaturated acids such as acrylic acid, methacrylic acid, maleic acid and anhydride, itaconic acid, fumaric acid, crotonic acid and citraconic acid and anhydride, methyl hydrogen maleate, ethyl hydrogen maleate, and one or more α,β-ethylenically unsaturated hydrocarbon monomers such as the aliphatic α-olefin monomers, e.g, ethylene, propylene, butene-1 and isobutene; conjugated dienes, e.g., butadiene and isoprene; and monovinylidene aromatic carbocyclic monomers, e.g., styrene, α-methylstyrene, toluene, and t-butylstyrene. In addition, other ethylenically unsaturated hydrophobic monomers which are not entirely hydrocarbon are copolymerized with the aforementioned acid comonomers. Examples of such suitable monomers which are not entirely hydrocarbon include esters of α,β-ethylenically unsaturated carboxylic acids such as ethyl acrylate, methyl methacrylate, ethyl methacrylate, methyl acrylate, isobutyl acrylate, and methyl fumarate; unsaturated esters of non-polymerizable carboxylic acids such as vinyl acetate, vinyl propionate, and vinyl benzoate; vinyl halides such as vinyl and vinylidene chloride; vinyl ethers; α,β-ethylenically unsaturated amides and nitriles such as acrylamide, acrylonitrile, methacrylonitrile and fumaronitrile. It is understood that the aforementioned suitable hydrophobic monomers may be copolymerized with preferred hydrocarbon monomer and the acid comonomer in proportions such that a water- and alkali-insoluble polymer is provided. Preferred copolymers include copolymers from about 70 to about 90 weight percent of ethylene, from about 10 to about 20 weight percent of one or more ammoniated ethylenically unsaturated acids such as acrylic acid and methacrylic acid and from 0 to about 20 weight percent of suitable ethylenically unsaturated hydrophobic monomer as described hereinbefore such as acrylonitrile, ethyl acrylate and vinyl acetate.

Other copolymers which are suitable are made from pre-formed, non-acid polymers by subsequent chemical reactions carried out thereon. For example, the carboxylic acid group may be supplied by grafting a monomer such as acrylic acid or maleic acid onto a polymer substrate such as polyethylene. Additionally, copolymers containing carboxylic anhydride, ester, amide, acylhalide and nitrile groups can be hydrolyzed to carboxylic acid groups which can then be neutralized to form the ammoniated carboxylic acid.

It is further understood that the α,β-ethylenically unsaturated carboxylic acid in ammonium salt form may be copolymerized with the hydrophobic monomer in order to prepare a suitable copolymer.

Specified procedures and means for making the polymers are known to the art as exemplified by U.S. Pat. No. 3,520,861 to Thomson et al. and U.S. Pat. No. 3,426,363 to Helin. Preferred low molecular weight copolymers are prepared according to methods disclosed in the foregoing references except that a telogen such as propylene is employed in the reaction mixture. In instances wherein the acid copolymer is obtained in mass form, the copolymer may be converted to aqueous colloidal dispersion in accordance with the methods of U.S. Pat. No. 3,389,109 to Harmon et al. which is subsequently concentrated and ammoniated by the method described in U.S. Pat. No. 3,644,258 to Moore et al. Generally methods of producing the aqueous colloidal dispersion of a copolymer which require the use of little or no emulsifier or other surface active agents are preferred. Preferably, the aqueous colloidal dispersion of copolymer has a polymer solids content from about 5 to about 60 weight percent and sufficient stabilizing ammonia to give the dispersion a pH of at least about 7.5. High solids dispersions are suitably prepared from lower solids dispersions by the method disclosed in the aforementioned patent to Moore et al.

In order to obtain a degree of sizing which is useful in manufacture of sized paper (including highly sized paper), it is necessary to utilize the copolymer sizing agent of the present invention in conjunction with a reaction product of epihalohydrin and ammonia, or an aliphatic polyamine having at least two amine hydrogens per molecule or a mixture of the polyamine and ammonia, hereinafter collectively referred to as epihalohydrin/amine reaction product. These epihalohydrin/amine reaction products are useful as co-additives which enhance the retention of the copolymer sizing agent and which bring the copolymer sizing agent in closer proximity to the fibers of the cellulosic materials during the sizing operation. Suitable epihalohydrin/amine reaction products are water dispersible, preferably water-soluble. Generally such water dispersible reaction products have molecular weights in the range from about 1000 to about 80,000. Preferred reaction products comprise from about 0.9 to about 2.1, especially from about 1.5 to about 1.7, mole of epihalohydrin per mole of amine, i.e., ammonia, polyamine or mixture thereof. Generally, such preferred reaction products have one or more molecular weight peaks as determined by gel permeation chromatography and such peaks normally occur in the range from about 2,000 to about 70,000. Especially preferred reaction products are those exhibiting at least one peak in the molecular weight range from about 40,000 to about 70,000. Such reaction products, including their method of preparation, are further described in U.S. 3,655,506 to Baggett which is hereby incorporated by reference in its entirety.

In the internal sizing of paper and other cellulosic materials using the above-described copolymers as internal sizing agents, a number of variations and techniques may be employed. It is critical however, that all of the techniques employed achieve uniform dispersal of the sizing agent throughout the cellulosic fiber during internal sizing. Uniform dispersal may be obtained by adding the ammoniated copolymer sizing agent in a fuller dispersed form such as an aqueous colloidal dispersion.

In order to achieve maximum distribution of the copolymer sizing agent on the fiber stock and to avoid flocculation of the copolymer sizing agent, it is desirable, particularly when the epihalohydrin/amine reaction product is highly cationic, to add the copolymer sizing agent to the fiber stock prior to the addition of the reaction product or simultaneously therewith or shortly thereafter, e.g., usually within 30 minutes. Preferably the copolymer sizing agent is added to the fiber stock slurry prior to addition of the reaction product. Whichever technique is chosen for the addition of the ammoniated copolymer and epihalohydrin/amine reaction product to the fiber stock, care must be taken to avoid contact of the ammoniated copolymer and the reaction product prior to contacting the fiber stock.

The actual addition to the cellulosic material fiber of either the reaction product or the sizing agent may take place at any point in the cellulosic material manufacturing process prior to the ultimate conversion of wet-fibrous material into web, sheet or molded article. Thus, for example, in paper manufacture, the sizing agent may be added to the pulp while the latter is in the head box, beater, hydropulper or stock chest.

In order to obtain good internal sizing, it is desirable that the ammoniated copolymer sizing agents be uniformly dispersed throughout the fiber in as small a particle size as is possible to obtain. One method for providing such uniform dispersions is to disperse the sizing agent in aqueous media prior to its addition to stock using, for example, a method as described hereinbefore. While it is generally desirable to use the ammoniated copolymer sizing agent in aqueous colloidal dispersion which is free of emulsifiers and surface active agents, such agents can be suitably employed in the practice of the invention provided that such agents are fugitive during sizing or otherwise do not impair the effectiveness of the copolymer sizing agent.

The sizing agents of this invention are most successfully utilized for the sizing of paper prepared from all types of both cellulosic and combination of cellulosic with non-cellulosic fibers. The cellulosic fibers which may most advantageously be used include the bleached and unbleached sulfate (kraft), bleached and unbleached sulfite, bleached and unbleached soda, neutral sulfite, semi-chemical, chemi-ground wood, ground wood and any combination of these fibers. These designations refer to wood pulp fibers which have been prepared by means of a variety of processes which are known in the pulp and paper industries.

It is understood that all types of additives such as pigments, fillers, stabilizers, retention aids, wet strength additives and dry strength additives, additional sizing agents, and the like may be employed in combination with the copolymer sizing agents of the present invention. Such additaments include kaolin clay, talc, titanium dioxide, calcium carbonate, diatomaceous earth, plastic pigments, aluminum trihydrate, and precipitated silica.

The ammoniated copolymer sizing agents are suitably employed in amounts effective to achieve the purposes of the sizing such as water-resistance, i.e., an amount effective to size the cellulosic material. Generally, amounts ranging from about 0.03 to about 20 weight percent based on dry weight of the cellulosic material in the finished sheet or article are suitable, with preferred amounts being in the range from about 0.05 to about 2 weight percent and especially preferred amounts being in the range from about 0.2 to about 1 weight percent. It is understood that within this numeri-

cal range, the precise amount which is used will depend for the most part on the type of cellulosic material which is being employed, the specific operating conditions, as well as the particular end use for which the cellulosic material is destined. For example, paper which will require good water-resistance or ink holdout will necessitate the use of a higher concentration or sizing agent than a paper having characteristics which necessitate the use of only small amounts of sizing. Accordingly, any amount which is suitable to effect the desired end result of the sizing is suitable for the purpose of this invention.

These same factors also apply in relation to the amount of epihalohydrin/amine reaction product which is used as a retention aid in conjunction with ammoniated copolymer sizing agent. Thus, the skilled artisan will be able to use the reaction product and the sizing agent in any concentrations which is found to be applicable to the specific operating conditions of internally sizing cellulosic material as defined hereinbefore. However, as a general rule, the epihalohydrin/amine reaction product is usually employed in amount in the range from about 0.5 to about 5 weight parts per 1 weight part of copolymer sizing agent, preferably from about 1.5 to about 3 weight parts of the reaction product per 1 weight part of copolymer sizing agent.

tained at 16°–20°C., 925 g. (10 g. moles) of epichlorohydrin is added over a period of 4 hours. At the end of the addition, the reaction mixture is stirred for another 16 hours at the same temperature, then 330 g. of water is added and the mixture is heated to 100°C. and cooled to room temperature over a 2-hour period. A mixture of 200 parts by weight of this prepolymer resin with 100 parts of epichlorohydrin and 200 parts of water is stirred at 95°–98°C. for 2 hours and cooled to room temperature. The aqueous dispersion of copolymer and reaction product solution are added separately to 236 parts of a 0.33 percent solids aqueous slurry of bleached kraft pulp slurry having a pH of 7.8 which is adjusted to pH 4.5 by adding H_2SO_4. Handsheets are formed and dried in accordance with TAPPI T–205m-53. Surface wettability by water (angle of contact) and ink penetration of the handsheets is determined and recorded in Table I.

As an additional illustration of this embodiment, a sizing composition containing different amounts of the aqueous dispersion of the copolymer and the reaction product is used for internal sizing of the aforementioned pulp. In the foregoing manner, the treated pulp is converted to handsheets and tested for surface wettability and ink penetration. The results are also recorded in Table I.

TABLE I

Sample No.	Copolymer Concentration lb/ton (1)	Reaction Product Type	Reaction Product Concentration lb/ton (1)	Ink Penetration, % Reflectance at 120 sec. (2)	Contact Angle (3), precured
1	6	NH_3/EPCH*	15	93	103°
2	4	NH_3/EPCH*	15	70	105°

*Reaction product of epichlorohydrin/ammonia in the mole ratio of 1.7:1, said reaction product having molecular weight peaks at 5000 and 50,000 as measured by gel permeation chromatography.

(1) Measured in dry weight as pounds of specified additive per ton of pulp.

(2) A photometric determination of black ink penetration through white or light-colored paper by measuring light reflectance on the side of the paper opposite to which a pool of the black ink is applied. The paper tested prior to inking using a black background of 0% reflectance has a 100% reflectance.

(3) Surface wettability by water (Contact Angle) before curing as determined by TAPPI-458m-48.

The following examples are given to illustrate the preferred embodiment of the invention and should not be construed as limiting its scope. In these examples, all parts and percentages are by weight unless otherwise noted.

EXAMPLE 1

A 500-g portion of ethylene/acrylic acid (87.3/**12.7**) copolymer having a molecular weight peak of 6950 as determined by gel permeation chromatography and a melt flow viscosity [ASTM D–1238-65T(B) using a plastometer having a 0.020 inch orifice] of 2 decigrams/minute is added to 240 ml of aqueous ammonia (28 percent NH_3) in a 4 liter kettle containing 2.94 liters of water. The foregoing ingredients are stirred for 8 hours at 100°C, and the resulting dispersion is allowed to cool to room temperature. The dispersion is passed through gauze to remove flocculated material. The resulting filtrate is an aqueous dispersion containing 13.6 percent ethylene/ammonium acrylate copolymer solids and having pH of about 8.

A 5-liter reaction flask equipped with reflux condenser, stirrer, thermometer, and feeding funnel is charged with 431 g. (7 g. moles) of 28–30 percent aqueous ammonia and partially immersed in a cooling bath. With the reaction mixture temperature main-

EXAMPLE 2

A 7.3-lb. portion of ethylene/acrylic acid (86/**14**) copolymer having a melt flow viscosity (ASTM D–1238-65T(B) with a 0.020 inch orifice) of 2 decig./min. (number average molecular weight of 4,450) is added to 7.5 gallons of water and 0.617 gallons of aqueous ammonia (28 percent NH_3) in a 10 gallon stirred kettle. The kettle is heated and stirred for 3 hours at 100°C and 45 psi. The product is drained and filtered through a 100 mesh stainless steel screen. A good amber colored dispersion having 10 percent copolymer solids is obtained.

A 4-part portion of the epichlorohydrin/ammonia reaction product as used in Example 1 is diluted with 27 parts of water. A 2.9-part portion of the foregoing copolymer dispersion is diluted with 4.8 parts of water. The two dilutions are added separately to a bleached kraft pulp slurry. The mixture is adjusted to a pH of 3.5 with sulfuric acid. The pulp slurry is formed into a handsheet and tested for ink penetration and water contact angle. The foregoing procedure is repeated using pulp slurries adjusted to pH values of 4.8, 6.1, **7.1, 7.9, 9.1,** and 10.2. The results of the foregoing tests which are recorded in Table II show the copolymer sizing agent to be effective over a wide range of pH.

TABLE II

Sample No.	Additive Concentration (1), lbs/ton Ethylene/Ammoniated Acrylic Acid Copolymer	Ammonia/Epichlorohydrin Reaction Product	Ink Penetration, % Reflectance at 120 sec. (2)	Contact Angle, precured (3)	pH (4)
1	10	15	98	115°	3.5
2	10	15	98	120°	4.8
3	10	15	99	117°	6.1
4	10	15	99	118°	7.1
5	10	15	100	122°	7.9
6	10	15	95	120°	9.1
7	10	15	98	118°	10.2

(1) Same as in Table I.
(2) Same as in Table I.
(3) Same as in Table I.
(4) pH of pulp slurry before processing into handsheets.

EXAMPLE 3

A 40-g. portion of ethylene/acrylic acid (89/**11**) copolymer having a melt flow viscosity [ASTM D–1238-65T(B) with a 0.20 inch orifice] of 43 decig./min. (number average molecular weight of 4,075) is added to 27 g. of aqueous ammonia (28 percent of NH_3) and 200 g. of water in a 0.5 liter stainless steel bomb reactor. The bomb is sealed and the reaction mixture is shaken for 3 hours at 95°C. The resulting dispersion contains 15 percent copolymer solids.

A 0.18-part portion of epichlorohydrin/ammonia reaction product as used in Example 1 is diluted with 6 parts of water. The resulting solution is added to a bleached kraft pulp slurry in the proportion set forth in Table III and is stirred for one minute. A 0.19-part portion of the foregoing ethylene copolymer dispersion is diluted with 7.7 parts of water and is then added to the pulp slurry as an internal size in the proportion specified in Table III. The pH of the resulting pulp slurry is adjusted to 4.5 with sulfuric acid. The pulp is formed into a handsheet and is tested for ink penetration and water contact angle. The results are listed in Table III.

TABLE III

Sample No.	Additive Concentration (1), lbs/ton Ethylene Copolymer	Ammonia/Epichlorohydrin Reaction Product	Ink Penetration, % Reflectance at 120 sec. (2)	Contact Angle, precured (3)
1	10	15	91	112°

(1)-(3) Same as in Table I.

EXAMPLE 4

Following the procedure of Example 1, an aqueous dispersion (11 percent copolymer solids) of ammoniated ethylene/acrylic acid (86/**14**) copolymer having a number average molecular weight of 4,500 is prepared.

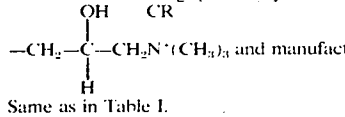
An aqueous solution of a retention aid as specified in Table IV is added in proportions specified in Table IV to a bleached kraft pulp slurry (0.3 percent solids in water) while stirring. The ammoniated copolymer dispersion is then added to the stirred pulp slurry in the amount indicated in Table IV. The pulp slurry is converted to handsheets and dried in accordance with TAPPI T–205m-53. Surface wettability by water (angle of contact) and ink penetration of the dried handsheets are then determined. The results are recorded in Table IV.

For the purpose of comparison, the foregoing procedure is followed except that a cationic starch is employed as a retention aid. The resultant handsheets are likewise tested for surface wettability and ink penetration. These results are also recorded in Table IV.

TABLE IV

Sample No.	Size Type	Size Concentration lb/ton (1)	Retention Aid Type	Retention Aid Concentration lb/ton (1)	Beater pH	Contact Angle(3)	Ink Penetration, (2), sec.
1	Et/AA(NH_3)(a)	5	NH_3/EPCH(d)	9	6.4	117°	3614
2	Et/AA(NH_3)(b)	5	"	9	6.65	60°	0.9
A*	Et/AA(NH_3)(a)	10	Sta-lok 400(3)	20	6.25	84°	6.0
B*	Et/AA(NH_3)(c)	10	"	20	6.2	<20°	0.1

*Not an example of the invention.
(a) Ammoniated ethylene/acrylic acid (86/14) copolymer having a number average molecular weight of 4500.
(b) Ammoniated ethylene/acrylic acid (80.5/19.5) copolymer having a number average molecular weight of 30,000.
(c) Ammoniated ethylene/acrylic acid (80/20) copolymer having a melt flow viscosity [ASTM-D-1238-65 T(E)] of 250 decig/min which approximately corresponds to a number average molecular weight of 18,300.
(d) Reaction product of epichlorohydrin/ammonia in the mole ratio of 1.61:1, said reaction product having molecular weight peaks at 2500 and 65,000 as measured by gel permeation chromatography.
(e) Potato starch bearing quaternary amine groups as follows:



and manufactured by A. E. Staley Manufacturing.
(1) Same as in Table I.
(2) Time in seconds taken for paper to have an 80% reflectance using test method (2) in Table I.
(3) Same as in Table I.

EXAMPLE 5

A 50-pound portion of ethylene/acrylic acid (85/15) copolymer having a melt flow viscosity of 5 decig./min. (ASTM D-1238-65T(E) is added to 75 pounds of aqueous ammonia (28 percent NH_3) and 75 pounds of water in a 25-gallon stirred kettle. The kettle is heated at 140°C for five hours. The excess ammonia is stripped at 85°C and then the product is drained from the kettle. The resulting dispersion contains 24 percent copolymer solids.

A 4.0-part portion of an epichlorohydrin/ammonia reaction product as used in Example 1 (25 percent solids) is diluted with 27 parts of water. A 0.12-part portion of the foregoing ethylene copolymer dispersion is diluted with 7.7 parts of water. The two dilutions are added to a bleached kraft pulp slurry in the proportions set forth in Table V. The resulting slurry is adjusted to a pH of 4.5 with sulfuric acid and formed into a handsheet. The handsheet is tested for ink penetration and water contact angle and the results are recorded in Table V.

TABLE V

Sample No.	Additive Concentration (1), lbs/ton Ethylene Copolymer	Ammonia/Epichlorohydrin Reaction Product	Ink Penetration, % Reflectance at 120 sec. (2)	Contact Angle, precured (3)
1	10	15	89	92°

(1)-(3) Same as in Table I.

What is claimed is:

1. In a method for internal sizing of a cellulosic material wherein an internal sizing agent and a retention aid are applied to the fibers of the cellulosic material, the improvement wherein the internal sizing agent is a water-dispersible, water- and alkali-insoluble copolymer of an α,β-ethylenically unsaturated hydrophobic monomer and an ammoniated α,β-ethylenically unsaturated carboxylic acid and the retention aid is a water dispersible reaction product of epihalohydrin and ammonia, or an aliphatic polyamine having at least two amine hydrogens per molecule or a mixture of ammonia and aliphatic polyamine.

2. The improvement of claim **1** wherein the reaction product has at least one molecular weight peak as determined by gel permeation chromatography in the range from about 2,000 to about 70,000.

3. The improvement according to claim **1** wherein the reaction product is water soluble and the mole ratio of epihalohydrin to amine is from about 0.9 to about 2.1 mole of epihalohydrin to 1 mole of amine.

4. The improvement according to claim **1** wherein the cellulosic material is pulp.

5. The improvement according to claim **1** wherein the hydrophobic monomer is an α,β-ethylenically unsaturated hydrocarbon.

6. The improvement according to claim **5** wherein the hydrocarbon is an aliphatic α-monoolefin having 2 to 14 carbon atoms.

7. The improvement according to claim **6** wherein the aliphatic α-monoolefin is ethylene.

8. The improvement according to claim **7** wherein the carboxylic acid is acrylic acid.

9. The improvement according to claim **7** wherein the carboxylic acid is methacrylic acid.

10. The improvement according to claim **7** wherein the copolymer is film-forming under the conditions of internal sizing.

11. The improvement of claim **10** wherein the copolymer has a number average molecular weight peak in the range from about 1,000 to about 10,000 and contains from about 10 to about 20 weight percent of α,β-ethylenically unsaturated carboxylic acid.

12. The improvement according to claim **1** wherein the cellulosic material is internally sized under conditions of pH of at least 7.

13. An internal sizing composition for a cellulosic material comprising a sizing amount of a water-dispersible, water- and alkali-insoluble copolymer of an α,β-ethylenically unsaturated hydrophobic monomer and an ammoniated α,β-ethylenically unsaturated carboxylic acid, said copolymer containing from about 6 to about 40 weight percent of the ammoniated carboxylic acid and a water dispersible reaction product of epihalohydrin and ammonia, or aliphatic polyamine having at least two amine hydrogens per molecule or mixture of ammonia and the polyamine in an amount effective to retain the copolymer on the cellulosic material.

14. The composition according to claim **13** wherein the reaction product has at least one molecular weight peak as determined by gel permeation chromatography in the range from about 2,000 to about 70,000.

15. The composition of claim **14** wherein the reaction product is water soluble and the mole ratio of epihalohydrin to amine is from about 0.9 to about 2.1 mole of epihalohydrin to 1 mole of amine.

16. The composition according to claim **13** wherein the hydrophobic monomer is ethylene and the carboxylic acid is acrylic acid.

17. The composition of claim **13** wherein the hydrophobic monomer of the copolymer is ethylene.

18. A cellulosic material internally sized with water-dispersible, water- and alkali-insoluble copolymer of an α,β-ethylenically unsaturated hydrophobic monomer and an ammoniated α,β-ethylenically unsaturated carboxylic acid, and a water-dispersible reaction product of epihalohydrin and ammonia, aliphatic polyamine having at least two amine hydrogens per molecule or mixture thereof.

19. The cellulosic material of claim **18** wherein the copolymer contains from about 10 to about 20 weight percent of the carboxylic acid.

20. The cellulosic material of claim **18** wherein the cellulosic material is paper.

21. The cellulosic material of claim **18** wherein the reaction product is water-soluble and the mole ratio of epihalohydrin to amine is from about 0.9 to about 2.1 mole of epihalohydrin to one mole of amine.

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