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METHOD OF PRODUCING WET-STRENGTH PAPERS

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The present invention is concerned with a new and improved process for the production of papers having improved wet-strengths.

It has heretofore been proposed in McLaughlin United States Patent 2,765,229 to anchor linear polymers containing carboxylate units to the fibers in papers by cationic agents to improve various dry-strengths such as the burst, tear, and tensile-strength. One of the advantages of that procedure was that the wet-strength of the paper so treated was not appreciably increased so that "broke" recovery was possible.

It has now been found that the direct impregnation of certain papers in a substantially dry state and under certain conditions with aqueous solutions of certain polymers containing ammonium carboxylate units serves to produce an unexpected and surprising increase in wet-strength when the amount of polymer deposited is in the range of 2% to 8% based on the weight of the fiber.

The types of papers with which the present process is concerned are those having a basis weight between 10 and 60 lbs. for a 500 sheet ream in which the sheets are 24" x 36". The papers must also be highly beaten so that they have Canadian Freeness values in the range of 300 to 400. They may be sized papers and particularly those sized with rosin in conventional manner using alums such as the conventional papermakers' alum. The amount of rosin sizing may be that which is customary, namely from 0.2% to 2% by weight of the rosin based on the weight of fibers in the paper. These papers are adapted when finished to be employed as wrapping papers (when prepared from sized stock) or as tissue papers including toilet tissue, toweling, creped or not, diapers, and for other moisture-absorbent uses (when prepared from unsized stock).

The linear polymers the ammonium salts of which have been found to impart the wet-strength to such papers when the latter are impregnated in aqueous solutions of the polymer salts are those which contain 25% to 60% by weight of units derived from an acid selected from the group consisting of methacrylic acid, acrylic acid, and itaconic acid. The balance of the polymer is formed of polymerized units of acrylonitrile or esters of acrylic or methacrylic acid. For example, the polymer may contain up to 75% by weight of an ester of acrylic acid with a lower alcohol having from 1 to 4 carbon atoms, such as methyl acrylate, ethyl acrylate, or butyl acrylate. Besides the lower alkyl esters of acrylic acid (that is, instead thereof or in addition thereto), the copolymer may contain units of higher alcohol esters of acrylic acid such as cyclohexyl acrylate, n-hexyl acrylate, amyl acrylate, 2-ethyl-hexyl acrylate, t-octyl acrylate, decyl acrylate, dodecyl acrylate, hexadecyl acrylate, or octadecyl acrylate. Besides the ester of acrylic acid, the copolymer may contain units of acrylonitrile or of lower alkyl esters of methacrylic acid, such as methyl methacrylate, ethyl methacrylate, or butyl methacrylate, or even higher alkyl esters of acrylic acid such as the cyclohexyl and other alkyl methacrylates corresponding to the higher alkyl esters of acrylic acid mentioned hereinabove.

It is also essential that the copolymer have a high molecular weight. Since the molecular weights of copolymers containing a large proportion of acid units are

generally difficult to measure because of the viscosity effects produced by the carboxylate units, the most satisfactory way of expressing the range of molecular weights is by reference to a viscosity of the ammonium salt of the copolymer in solutions thereof in water at a concentration of 10% and at 25° C. Such viscosities when measured with a Brookfield viscometer at 60 r.p.m. are in the range of 12 to 40 poises. It is generally believed that the molecular weights of these polymers are at least 500,000 (viscosity average) and may even have a minimum viscosity average molecular weight of at least one million. Many of the polymers with which the present invention is concerned have molecular weights as high as several million. In order to produce such high molecular weight polymers, the process resorted to for their preparation may either be an emulsion or a suspension polymerization procedure. When the emulsion procedure is employed, the emulsifier may be used in a proportion of about ½% to 6% based on the weight of monomers (total). For suspension polymerization, a lesser amount of emulsifier and frequently a less effective emulsifier is generally employed. In either case conventional aqueous emulsion or suspension polymerization techniques are employed. Preferably, water-soluble initiators are used such as the alkali metal or ammonium persulfates in amounts from 0.10% to 3% on the weight of the monomers. Preferably, a redox system is used in which the persulfate or like initiator is used in conjunction with a reducing agent such as sodium metabisulfite in about the same proportion as the initiator. A promoter, such as small proportions of metal ions such as copper, iron, or the like, may be used. The polymerization may be effected as a batch system or by continuous addition of the monomers to the aqueous solution containing initiator, reducing agent and promoter. Generally, it is unnecessary to heat the polymerization system, and in many cases it may be desirable to cool the system to control the temperature and maintain it between room temperature and 85° C. Agitation during the polymerization is generally desirable but may be omitted. The amount of water may be selected at the beginning of the polymerization procedure with reference to the amount of comonomers to be copolymerized so that any desired concentration on the order of 25% to 50% or more of copolymer is obtained in dispersed condition in the reaction vessel when an emulsion procedure is employed. If the suspension procedure is employed, small granules or beads of the polymer form in the system.

When the emulsion technique is employed, it is merely necessary to add ammonia to the aqueous dispersion of the emulsion copolymer until a pH of 8 to 10 or more is reached. Such neutralization forms the ammonium salt of the copolymer and results in a colloidal solution of the ammonium salt thereby obtained within the water of the system. In the case of suspension polymerization, the granules may be separated from the polymerization medium and then neutralized with ammonia in a suitable solution or the ammonia may be added to the polymerization system containing the granules without the separation thereof. This results in neutralization to form the ammonium salt which dissolves in the water.

The solution of the ammonium salt of the polymer is originally prepared or diluted to a concentration of 2% to 10% by weight of the ammonium salt in the solution for application. The aqueous solution of the ammonium salt of the copolymer is applied to the paper by simply dipping or immersing the paper therein while the solution is at a temperature of 70° to 140° F. Advantageously, the paper may proceed continuously through such aqueous polymer salt solution. For example, it may be passed through such a solution in a size press immediately follow-

ing the normal paper drying drums. Of course, the paper proceeds from the size box into a final drier. When unsized papers pass through the polymer salt solution, there is approximately 125% wet pickup; whereas when a sized paper is employed, the wet pickup is generally about 20% to 50% cold or up to 80% if heated so that the concentration of the polymer salt solution employed with sized papers should be at least about 2% to 4%.

The paper may be formed from a wide variety of materials. Thus, it may be a kraft pulp, rag pulp, soda, sulfate, groundwood, sulfite pulp, or alpha pulp. Besides employing the normal wood pulp fibers, the paper may be formed of cotton-linters and, if desired, the wood or cotton fibers may be used in admixture with fibers from other sources such as jute, hemp, sisal, rags, strings, chopped canvas, and so on.

The finished paper products may be employed as filter papers, disposable diaper fillers, toilet tissue, paper toweling, bibs, and various wrapping materials.

One of the advantages of the procedure of the present invention is the fact that the normal drying equipment employed in conventional papermarking machinery is adequate for drying the paper after impregnation with the water-soluble copolymer salt. Hence, the process can be employed as an "on-machine" size press coating operation. However, if desired, the paper may be treated in an "off-machine" converting process by passing the paper through a saturating bath (size tub) and then dried and/or creped on a drum drier or other drying equipment. When the polymers are prepared by the suspension technique which is the preferred technique, relatively little emulsifier is present and the application of the copolymer salt actually serves not only to improve wet-strength but also sizes the paper when unsized paper is the initial starting material. In other words, the ammonium copolymer salt after drying down to the insoluble form on the impregnated sheet reduces the penetration of water and/or ink; whereas the presence of a large proportion of emulsifier as would be the case when an emulsion polymerization technique is employed would ordinarily not be capable of reducing the penetration by water. Most of the wet-strength resins conventionally employed require either a high temperature cure (in excess of the temperature available in the conventional paper-drying machinery) or require ageing for as much as one month in order to develop a full wet-strength obtainable therefrom. Such wet-strength resins of thermosetting aminoplast type also need a low pH on the acid side to facilitate the cure or development of the wet-strength on ageing. In contrast with this, the polymer salt solutions of the present invention are applied at a pH of about 8 to 10 where less likelihood of corrosion on the machinery is encountered.

Another advantage of the alkaline polymer salt solutions of the present invention is the fact that they need not be at higher temperatures than 140° F. or even above 70° F. to provide good impregnation and pickup, whereas the customary thermosetting aminoplast resins generally have to be at a temperature of 180° F. at the point of impregnation in order to provide efficient pickup by the paper.

In general, the copolymer salts of the present invention provide an improvement in wet-strength immediately on drying which is from 50% to 100% greater than the wet-strength obtained with conventionally employed thermosetting aminoplast resins even after 28 days of ageing required for the substantially full development of wet-strength with such aminoplast resins.

The conventional thermosetting aminoplast resins are applied at about 14% solids at about 180° F. at an acid pH of about 4.5 with alum or hydrochloric acid. They have a tendency to gel at this temperature and must be promptly used. Batches of as much as 200 gallons are made up at a time and any left over after a batch wet-strength paper run must be thrown out. In contrast with this, the aqueous polymer salt solutions of the present invention are stable and can be stored indefinitely so that they can be saved for the next wet-strength batch conversion operation.

Typical thermosetting aminoplast types of wet-strength resins when applied to sized papers either reduce or destroy the sizing effects. The compositions of the present invention either have no effect on the size of the sized paper in the case of an emulsion copolymer or, when a suspension type of polymer is employed for producing the copolymer salt solution, the sizing is increased.

In the following examples which are illustrative of the present invention, the parts and percentages are by weight unless otherwise noted.

EXAMPLE 1

An aqueous solution containing 5% of an ammonium salt of a copolymer of 50% by weight of ethyl acrylate, 17% of methyl methacrylate, and 33% of methacrylic acid (having a viscosity of 37 poises at 25° C. and 10% concentration) was applied at 135° F. to a rosin-sized bag paper obtained from a pulp having a Canadian freeness of 300 ml. by passing the paper through the solution and then through rubber squeeze rolls. The impregnated paper picked up 4% of copolymer (on fiber) and was dried at room temperature. Similarly a solution of the same polymer salt was applied at 2.5% concentration providing 1.9% copolymer on the fiber weight of the dried sheet. The wet strengths (machine direction) were measured after a 24-hour soak in water at room temperature. The results are given in the following Table I. A commercial cationic urea-formaldehyde condensate having a pH of 4.5 was also applied at 5% and 2.5% concentrations (giving 2.5% and 1.5% pickups) and tested after a 28-day ageing for comparisons.

Table I

Saturant	Concentration, percent	pH	Wet Tensile (MD), lbs./in. width
			2.6
Copolymer Salt	5.0	9.0	12.2
Copolymer Salt	2.5	9.0	9.6
U-F resin	5.0	4.5	7.5
U-F resin	2.5	4.5	6.2

EXAMPLE 2

An aqueous 5% solution of an ammonium salt of 75% methyl methacrylate and 25% of methacrylic acid (having a viscosity of 20 poises at 10% concentration and 25° C.) was applied to a rosin-sized bag paper as in Example 1. The polymer pickup was 3.95% on fiber. The wet strength after a 24-hour water-soak was 8.0 lbs. per inch width.

EXAMPLE 3

A saturating paper (unsized) having a basis weight of 32 pounds and obtained from a pulp having a Canadian freeness of 400 ml. was impregnated as in Example 1 with a 5% aqueous solution of the copolymer salt of Example 2. The wet strength was 4.9 lbs. per inch width. The untreated sheet disintegrates completely in the soak.

EXAMPLE 4

The procedure of Example 3 was repeated substituting for the copolymer salt the ammonium copolymer salt of Example 1. The wet-strength was 9.4 lbs. per inch width (measured after a 24-hour soak).

EXAMPLE 5

A saturating paper having a small amount of a cationic urea-formaldehyde wet-strength resin, obtained from a pulp having a Canadian freeness of 400, having a wet-strength of 1.9 lbs. per inch, and a basis weight of 36 pounds was passed through an aqueous 2.5% solution of an ammonium salt of a copolymer of 60% methyl meth-

acrylate and 40% of methacrylic acid (having a viscosity at 10% concentration and 25° C. of 36 poises). The paper after drying contained 3.65% of copolymer salt. The wet strength was raised to 7.2 lbs. per inch width.

EXAMPLE 6

The procedure of Example 5 was repeated substituting for the copolymer salt an ammonium salt of a copolymer of 40% methyl methacrylate and 60% of methacrylic acid at 5% concentration. The copolymer salt at 10% concentration and 25° C. had a viscosity of 20 poises. The pickup was 7.5% and the wet strength was 9.9 lbs. per inch width.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined by the appended claims.

We claim:

1. A method for producing a wet-strength paper which consists of the steps of impregnating a substantially dry paper prepared from fibers beaten to a Canadian freeness between 300 and 400 and having a basis weight of 10 to 60 lbs. per ream of 500 sheets having a size of 24" x 36" with an aqueous solution containing 2% to 10% by weight of an ammonium salt of a water-insoluble copolymer of a mixture of 25% to 60% by weight of an acid selected from the group consisting of methacrylic acid, acrylic acid, and itaconic acid, and at least one other comonomer selected from the group consisting of acrylonitrile, esters of acrylic acid with an alcohol selected from the group consisting of cyclohexanol and alkanols having from 1 to 18 carbon atoms, and esters of methacrylic acid with an alcohol selected from the group consisting of cyclohexanol and alkanols having from 1 to 18 carbon atoms, the ammonium salt having a viscosity from 12 to 40 poises at 10% concentration in water and at 25° C., the paper and aqueous solution being free of any cationic agent, and subsequently drying the impregnated paper.

2. A method for producing a wet-strength paper which consists of the steps of impregnating a substantially dry paper prepared from fibers beaten to a Canadian freeness between 300 and 400 and having a basis weight of 10 to 60 lbs. per ream of 500 sheets having a size of 24" x 36" with an aqueous solution containing 2% to 10% by weight of an ammonium salt of a water-insoluble copolymer of a mixture of methyl methacrylate, ethyl acrylate, and 25% to 60% by weight of methacrylic acid, the ammonium salt having a viscosity from 12 to 40 poises at 10% concentration in water and at 25° C., the paper and aqueous solution being free of any cationic agent, and subsequently drying the impregnated paper.

3. A method for producing a wet-strength paper which consists of the steps of impregnating a substantially dry paper prepared from fibers beaten to a Canadian freeness between 300 and 400 and having a basis weight of 10 to 60 lbs. per ream of 500 sheets having a size of 24" x 36" with an aqueous solution containing 2% to 10% by weight of an ammonium salt of a water-insoluble copolymer of a mixture of ethyl acrylate and 25% to 60% by weight of methacrylic acid, the ammonium salt having a viscosity from 12 to 40 poises at 10% concentration in water and at 25° C., the paper and aqueous solution being free of any cationic agent, and subsequently drying the impregnated paper.

4. A method for producing a wet-strength paper which consists of the steps of impregnating a substantially dry paper prepared from fibers beaten to a Canadian freeness between 300 and 400 and having a basis weight of 10 to 60 lbs. per ream of 500 sheets having a size of 24" x 36" with an aqueous solution containing 2% to 10% by weight of an ammonium salt of a water-insoluble copolymer of a mixture of methyl methacrylate and 25% to 60% by weight of methacrylic acid, the ammonium salt having a viscosity from 12 to 40 poises at 10% concentration in water and at 25° C., the paper and aqueous solution being free of any cationic agent, and subsequently drying the impregnated paper.

5. A method for producing a wet-strength paper which consists of the steps of impregnating a substantially dry, unsized paper prepared from fibers beaten to a Canadian freeness between 300 and 400 and having a basis weight of 10 to 60 lbs. per ream of 500 sheets having a size of 24" x 36" with an aqueous solution containing 2% to 10% by weight of an ammonium salt of a water-insoluble copolymer of a mixture of 25% to 60% by weight of an acid selected from the group consisting of methacrylic acid, acrylic acid, and itaconic acid, and at least one other comonomer selected from the group consisting of acrylonitrile, esters of acrylic acid with an alcohol selected from the group consisting of cyclohexanol and alkanols having from 1 to 18 carbon atoms, and esters of methacrylic acid with an alcohol selected from the group consisting of cyclohexanol and alkanols having from 1 to 18 carbon atoms, the ammonium salt having a viscosity from 12 to 40 poises at 10% concentration in water and at 25° C., the paper and aqueous solution being free of any cationic agent, and subsequently drying the impregnated paper.

6. A method for producing a wet-strength paper which consists of the steps of impregnating a substantially dry, rosin-sized paper prepared from fibers beaten to a Canadian freeness between 300 and 400 and having a basis weight of 10 to 60 lbs. per ream of 500 sheets having a size of 24" x 36" with an aqueous solution containing 2% to 10% by weight of an ammonium salt of a water-insoluble copolymer of a mixture of 25% to 60% by weight of an acid selected from the group consisting of methacrylic acid, acrylic acid, and itaconic acid, and at least one other comonomer selected from the group consisting of acrylonitrile, esters of acrylic acid with an alcohol selected from the group consisting of cyclohexanol and alkanols having from 1 to 18 carbon atoms, and esters of methacrylic acid with an alcohol selected from the group consisting of cyclohexanol and alkanols having from 1 to 18 carbon atoms, the ammonium salt having a viscosity from 12 to 40 poises at 10% concentration in water and at 25° C., the paper and aqueous solution being free of any cationic agent, and subsequently drying the impregnated paper.

7. A method for producing a wet-strength paper which consists of the steps of impregnating a substantially dry paper prepared from fibers beaten to a Canadian freeness between 300 and 400 and having a basis weight of 10 to 60 lbs. per ream of 500 sheets having a size of 24" x 36" with an aqueous solution containing 5 to 10% by weight of an ammonium salt of a water-insoluble copolymer of 25 to 60% by weight of an acid selected from the group consisting of methacrylic acid, acrylic acid, and itaconic acid, and at least one other comonomer selected from the group consisting of acrylonitrile, esters of acrylic acid with an alcohol selected from the group consisting of cyclohexanol and alkanols having from 1 to 18 carbon atoms, and esters of methacrylic acid with an alcohol selected from the group consisting of cyclohexanol and alkanols having from 1 to 18 carbon atoms, the ammonium salt having a viscosity from 12 to 40 poises at 10% concentration in water and at 25° C., the paper and aqueous solution being free of any cationic agent, and subsequently drying the impregnated paper.

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