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3,597,374

COATING PROCESS FOR FIBROUS SUBSTRATES

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2 Claims

ABSTRACT OF THE DISCLOSURE

A coating composition for paper and similar substances which comprises an aqueous solution of starch, a water-soluble cationic polymer and a water-soluble acrolein polymer.

This invention relates to an improved process for coating fibrous substrates. More particularly, this invention relates to a process whereby a hydrocolloid is first modified with a cationic polymer and an acrolein polymer prior to its use to coat fibrous substrates.

A substantial portion of the fibrous materials produced in the United States are coated with various substances. Asbestos and other mineral fibers, as well as cellulosic and synthetic fibers are employed in many different uses in which different types of coatings are applied. Of particular importance is the paper coating art which includes fiberboard, liner board, printing stock and many diverse grades of paper products.

In the coating of fibrous substrates such as paper there are two main types of coating processes, namely, off-machine and machine coating. Off-machine coating is carried out as a separate operation once the paper or other fibrous substrate has been made. This type of coating was the earliest method used due to the requirement that the coated solution had to be applied at much slower speeds than the rate at which paper machines normally operate. With improved technology, the process of coating paper directly on the paper machine was developed and this process is used to produce a substantial portion of the coated paper manufactured today. Likewise, other fibrous substrates such as asbestos and other inorganic materials are coated by these two basic methods.

There are about ten basic types of processes for coating fibrous substrates. These methods, all of which are conventional, may broadly be described as dip, knife, cast, rhone, brush, air-brush, spray, print, extrude and strip coating methods. Each of these various methods has its particular function in the coating art, depending upon the particular fibrous substrate, the use for which the coated product is intended and the like.

One class of compounds which are used to coat fibrous substrates may generically be defined by the term "hydrocolloid." These materials are hydrophilic substances of the gelatin sol type, as well as synthetic hydrophilic substances having properties similar to the gelatin sol. Both the natural and synthetic substances are colloidal or near colloidal solutions in water. Examples of hydrocolloids are gelatin, glue, starch, dextrin, albumin, casein, wood products such as tannin and lignin, and synthetic materials such as polyvinylalcohol, polyvinylacetate and polyacrylamide.

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While it is true that a large amount of paper and other fibrous products are coated with hydrocolloids, there are certain drawbacks or disadvantages in the use of these coating materials. For example, oftentimes the coated paper does not have sufficiently low porosity and therefore the paper does not have sufficient strength. It has been found that lower porosity has a direct correlation with paper strength, since a more densely packed paper (less porous), has greater strength. Still another disadvantage in the use of hydrocolloid coatings for fibrous substrates is the lack of smoothness of the coating. Smoothness is, of course, directly related to the appearance of the paper, with a smoother paper being obviously more attractive. Coated fibrous substrates which are later used in printing processes require a high degree of smoothness to properly apply printing inks uniformly. Further, when other materials are pasted or glued to a coated fibrous substrate, smoothness directly effects the ability of the material to bond to the pasted or adhesive or glued surface.

A further important criteria of coated materials is the resistance to abrasion. Coatings which rub off or are easily penetrated through physical wear are less desirable than the sturdier, more resistant coating. Improvement in the resistance to abrasion of the coated fibrous substrates would permit the use of lesser amounts of hydrocolloid, and would make suitable a wider variety of materials for each application.

It would therefore be of great advantage to the coating art if a process could be derived which would permit fibrous substrates to be coated with a hydrocolloid which has superior porosity, smoothness and abrasion resistance characteristics.

Accordingly, it is an object of this invention to provide a composition which is useful in coating fibrous substrates.

Another object of this invention is to provide a process whereby hydrocolloid materials may be modified to increase their efficiency as coating additives.

It is a specific object of this invention to provide a process for improving the porosity, smoothness and abrasion resistance characteristics of hydrocolloid coatings which are applied to fibrous substrates.

Other objects will appear hereinafter.

It has now been discovered that an insoluble hydrocolloid coating may be applied to fibrous substrates by modifying the hydrocolloid in the following manner. Specifically, the addition of a cationic polymer to an aqueous suspension, solution or dispersion of the hydrocolloid followed by the addition of an acrolein polymer to the pretreated hydrocolloid has been found to result in a superior treated hydrocolloid which may be employed as a coating material for fibrous substrates.

Examples of the hydrocolloids which have been found to be suitable for the purposes of the present invention include the following:

Carbohydrates, Starches, modified Starches and Gums: Starch, dextrin, karaya gum, guar gum, locust bean gum, gum arabic, gum tragacanth, hydroxyethyl starch, hydroxyethyl cellulose, methyl cellulose, sodium carboxymethyl cellulose, sodium alginate, Chinese vegetable gelatin;

Proteins: gelatin, glue, zein, egg albumin, blood albumin, soy bean flower, soy bean protein (alpha protein), casein;

Wood Hydrocolloids: lignin, Goulac (calcium lignin sulfonate), tannin;

Synthetic Hydrocolloids: polyvinyl alcohol, polyacrylamide, partially degraded polyacrylamide (Hofmann reaction), polyvinyl pyrrolidone, polyvinyl methyl ether/maleic anhydride copolymer, styrene/maleic anhydride copolymer, sodium polymethylsiliconate.

A preferred hydrocolloid which has been found to be suitable for use in this invention is starch. The term "starch," as used herein, is intended to mean any of the natural starches as well as dextrines and the various modified starches and starch derivatives. Examples of natural starches are cornstarch, potato, tapioca, waxy maize, rice, wheat and so on. Modified starches and starch derivatives include acid modified, hypochlorite-oxidized, and enzyme-converted starch and the acetates and ethers of starch. Hydrocolloids falling within the generic class of gums are also preferred.

It is a preferred practice of this invention to first prepare an aqueous solution of the hydrocolloid. Of course, the term solution is intended to mean any solution dispersion or suspension of the hydrocolloid which is conventionally employed as a coating composition. While the concentration of the hydrocolloid is normally determined by the amount of hydrocolloid which is desired to be coated on the paper, a broad range of this concentration is from about 1% to 40% by weight of the hydrocolloid in water. A preferred range is from 2% to 15% by weight hydrocolloid. Natural materials such as starches and gums normally have a higher concentration than more costly synthetic materials such as polyvinyl-alcohol.

The second component which is used to modify the hydrocolloid for use in the process of this invention is broadly defined as a cationic polymer. Only very minor amounts of the cationic polymer are necessary to achieve the surprising efficiency of the process of this invention. In fact, notable results are obtained while employing substantially less cationic polymer than was thought possible prior to the discovery herein. Normally, it is only necessary to employ approximately 0.01% to 2.0% by weight of the cationic polymer, based on the dry weight of the hydrocolloid. A preferred range for this additive ranges from about 0.1% to 1.0%.

CATIONIC POLYMERS

As is discerned from the discussion above, a wide variety of cationic polymers may be suitably employed in the invention. Generally, such materials usually have sufficient strength of ionization to form salts with alkali cations in aqueous media. The following materials are just a few of the typical cationic polymers which may be suitably employed in practice of the invention.

The most preferred cationic class of materials is a polymeric polyamine substance. Generally, these polymers have molecular weight in excess of 1,000 and more preferably in excess of 2,000. The most preferred polymers of this type have molecular weight ranges of 2,000-50,000. Such above polymeric polyamines may be formed by a wide variety of reactions such as by the reaction of alkylene polyamines or ammonia and difunctional alkyl materials such as ethylene dichloride.

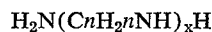
One class of polyamine polymers are condensation polymers of alkylene polyamines and halohydrins. Exemplary polymers of this type are those disclosed in Green U.S. Pat. 2,969,302, the disclosure of which is incorporated herein by reference.

A preferred polyamine condensation polymer of the type described in Green U.S. Pat. 2,969,302, is generically defined as an aqueous solution containing 5-40% by weight of a high molecular weight epihalohydrin-alkylene polyamine condensation copolymer, said aqueous solution being further characterized as having a viscosity of at least 10 cps., when measured as an aqueous solution containing 20% by weight of said condensation copolymer at 75° F. Preferred materials falling within this class have

a viscosity of at least 50 cps. when measured as just described. The upper limit of the viscosity is anything short of gel formation. Most preferred products have viscosities of from about 50 to about 800 cps. In order to form the preferred polymers of the invention, it is only necessary to polymerize the epihalohydrin and alkylene polyamine at temperatures ranging from about 105° F. to 185° F. at a mole ratio of epihalohydrin to alkylene polyamine falling within the range of 1.4:1 to 2.2:1. For best results the polymerization reaction is generally carried out in dilute aqueous solutions at reactant concentrations ranging from about 10 to about 30% by weight.

As mentioned above, the two classes of monomeric reactants involved in the condensation polymerization are epihalohydrins and alkylene polyamines. The epihalohydrins that may be employed include such materials as epichlorohydrin, epibromohydrin, and epiiodohydrin. Of these, the most preferred, due to cost and ready availability, is epichlorohydrin.

The alkylene polyamines which are reacted with the polyfunctional halohydrin for the purpose of the invention are well-known compounds having the general formula:



where n is an integer from 1 to 4 and x is one or more. Preferably, n is 2 and x ranges from 1 to 5 to give the preferred polyethylene polyamine class. Examples of alkylene polyamines useful in the invention are the alkylene diamines, such as ethylene-diamine, 1,2-propylene diamine, 1,3-propylene diamine and the polyalkylene polyamines, such as, for example, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, dipropylene triamine, and the similar polypropylene polyamines and polybutylene polyamines. Mixtures of any of the above may also be used and often-times commercial sources of these compounds contain two or more of any of the above alkylene polyamines. Some commercial amine products may contain mixtures of as many as five separate compounds.

Yet another species of polyamines falling within the above class is formed by reaction of an alkylene dihalide and an amine. Preferred amine reactants include ammonia, ethylene diamine, diethylene triamine, tetraethylene pentamine and triethylene pentamine. Of these, the most preferable due to excellent reactivity, low cost and availability is ammonia. The alkylene dihalide reactant may be chosen from a wide variety of difunctional organics including ethylene dichloride and 1,2-propylene dichloride. Of these the most preferred is ethylene dichloride. One excellent cationic polymer for use in the instant invention is formed by reaction of ammonia and ethylene dichloride under super-atmospheric pressures and with heating.

In addition to the above preferred condensation type polymers, many other condensation polymeric cationics are also admirably suited for use in the invention. Effective water-soluble cationic polymers or resins are to be found among the class consisting of amine-aldehyde resins and amide-aldehyde resins, preferably hydrophilic melamine-formaldehyde resins. Such colloidal cationic resin solutions may be prepared by dissolving ordinary melamine-aldehyde condensation products, such as methylol melamines, in acids such as hydrochloric, to form acidified or acid-type resin solutions having a glass electrode pH value within the range of about 0.5 to about 3.5 when measured at 15% solids, or pH values up to 4.5 when measured in more dilute solutions, followed by aging to the colloidal condition, as described in U.S. Pat. 2,345,543.

Another class of cationic melamine-aldehyde resins that may be used in practicing the present invention are the resinous polymers of melamine, urea and aldehydes such as formaldehyde containing at least 0.7 mole of melamine for each 4 moles of urea and about 1 to 4 moles

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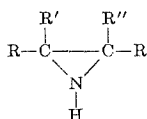
of combined formaldehyde for each mole of melamine plus urea. Such resins are described in U.S. Pat. 2,485,079. These cationic melamine resin copolymers are obtained by first preparing an acidified aqueous solution of an aldehyde condensation product of melamine and urea containing 1 to 70 mole percent of urea and 30 to 99% of melamine and about 0.2 to 1.5 moles of acid per mole of melamine, depending on the strength of the acid, and aging the solution until the colloidal cationic condition is reached.

Another suitable class of cationic polymers are those of the polyimine type. The polyimines are derived, for example, by the homopolymerization of monomers containing the imine radical,



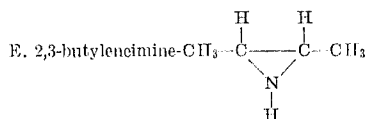
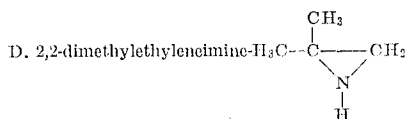
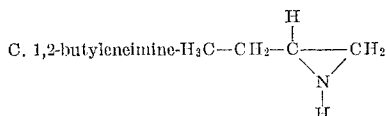
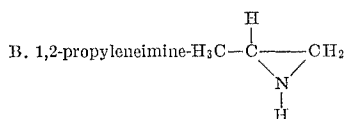
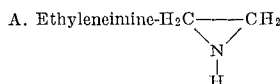
and have a molecular weight of at least 1000.

The imine monomers preferably employed contain not more than 7 carbon atoms. Of the monomers employed for making polyimines, some of those best suited for the purpose of the invention are classified as substituted ethyleneimines and have the structural formula:

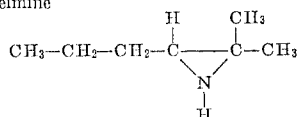


wherein R, R', R'' are either hydrogen or acyclic hydrocarbon radicals containing from 1 to 3 carbon atoms.

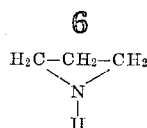
Examples of such monomers are the following:



F. 1,1-dimethyl,2-n-propylethyleneimine



Other monomers capable of producing cationic polymers suitable for the practice of this invention are tri-methyleneimine which has the structural formula:



and its lower alkyl substituted derivatives in which one or more of the hydrogen atoms attached to a carbon atom is substituted by an alkyl group containing not more than 3 carbon atoms, i.e., methyl, ethyl, and propyl.

Ethyleneimine, as well as many of its derivatives, may be prepared by any of several well-known methods such as are described in the "Journal of American Chemical Society," vol. 57, p. 2328 (1935) and Ber. 21 1094 (1888).

The polymerization of ethyleneimine and its derivatives is usually conducted at reduced temperatures using acid catalysts such as HCl and the like. The polymerization of the various monomers listed above is described in detail in the "Journal of Organic Chemistry," vol. 9, p. 500 (1944).

The linear polyimines are characterized by a long acyclic chain structure in which nitrogen atoms of imine groups are connected at intervals to carbon atoms. It will be recognized, therefore, that linear polyimines can be prepared not only by homopolymerization but also by condensation reactions with the elimination of a hydrohalide. Thus, ethylene dibromide or propylene dibromide can be condensed with diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and/or dipropylenetriamine to produce polyimines, and the present invention contemplates the employment of such materials.

In general, the polyimines employed in the practice of the invention can be described as water-soluble polyimines in which imino (--NH--) groups are attached to carbon atoms and recur every two to three atoms in a main linear chain, preferably containing not more than 6 carbon atoms in any side chain. Where imino groups are separated from each other by ethylene groups, the linear polyimines are referred to as polyethyleneimines. Where the imino groups are separated from each other by propylene groups, the linear polyimines are referred to as polypropyleneimines.

The molecular weight of the useful imine polymers should be at least 1,000 and is preferably from 5,000 to 50,000. If the condensation reactions from which these polymers are derived are allowed to continue for too long a period of time or the conditions are not suitable, infusible, water-insoluble resins may result. In the case of 2,2-dimethylethyleneimine, care must be used to control the reaction so that the materials produced are sufficiently water-soluble so that they can be employed at effective concentrations. Similarly, long chain water-soluble cationic polymers may be prepared by condensing formaldehyde with a polyalkylene polyamine such as tetraethylenepentamine to link the polyamines with a plurality of methylene bridges.

The above type condensation polymers may be generally described as water-soluble cationic polymers containing a plurality of cationic sites in a straight or branched chain configuration. In addition to these cationic polymers, other suitable organic cationic polymers may be used in practicing the invention.

Yet another class of cationic polymers include addition-type polymers which in aqueous medium will form organic cations having a substantial number of positive charge distributed at a plurality of positions on the polymer. Generally, these materials have a molecular weight in excess of 100,000 and contain in a side chain a hydrophilic group possessing the ability to form the above described positive charge. Typical members of this group are polyvinyl pyridine or other similar monomers having nitrogen-containing nuclei. Another specific material of this type is polyvinyl pyrrolidone. Salts of the above may also be employed.

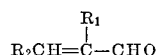
Still other suitable cationics include the well-known vinyl benzyl quaternary ammonium compounds such as the homopolymers of vinyl benzyl quaternary ammonium salts or copolymers thereof formed by a copolymerization reaction with acrylamide, methacrylamide, etc. The vinyl benzyl quaternary materials are generally formed by chloromethylating polystyrene and subsequently substituting the chloro group with a tertiary amine to produce the corresponding nitrogen quaternary.

Other examples of cationic polymers suitable as a treating agent in the last step of formation of useful additives of the invention includes homopolymers and water-soluble copolymers of aminoethyl acrylate hydrochloride, aminoethyl methacrylate hydrochloride, or substituted ammonium alkyl acrylates or methacrylates such as N-methyl or N,N-dimethyl-aminoalkyl acrylate or methacrylate wherein the alkyl groups contain 2-3 carbons or suitable materials. Other cationic polymers may be formed when the cationic monomer of the type just described in copolymerized with any one or more monoethylenically unsaturated monomers capable of vinyl polymerization such that the resulting copolymer is water-soluble or water dispersible. Suitable monomers of this type which may be copolymerized with the cationic monomers include acrylamide, methacrylamide, acrylonitrile, the lower alkyl esters of acrylic and methacrylic acids, vinyl methyl ether, etc.

The above list of materials are just a few of the available cationic polymers which may be suitably employed in the practice of the instant invention. It is understood, of course, that cationic polymer substances may be used other than those listed above without departing from the scope of the invention.

The last component of the novel composition of this invention may be generically defined as an acrolein polymer. By the term "acrolein polymer," it is meant a synthetic polymer which is prepared from a monomer mixture containing at least 30% by weight of an acrolein monomer. Preferred acrolein polymers contain at least 50% of acrolein monomers. It is a most preferred embodiment of this invention to use the homopolymer of acrolein.

The acrolein monomers useful in the invention may be represented by the general formula:



where R₁ and R₂ may be either hydrogen, lower alkyl radicals or halogen. When the backbone of the aldehyde molecule contains attached thereto an alkyl radical, it is preferred that these radicals contain less than 6 carbon atoms and more preferably 3 carbon atoms or less. Useful alpha-beta-unsaturated aldehydes may be chosen from among acrolein, alpha-methyl acrolein, alpha-ethyl acrolein, alpha-n-hexyl acrolein, alpha-bromo acrolein, etc. Other representative aldehyde monomers are crotonaldehyde, alpha chlorocrotonaldehyde, beta-chlorocrotonaldehyde, alpha-bromocrotonaldehyde, alpha-beta-dichlorocrotonaldehyde, alpha-beta-dimethyl acrolein, alpha-methyl-beta-ethyl acrolein, alpha-methyl-beta-isopropyl acrolein, alpha-ethyl-beta-propyl acrolein, etc. These monomers may be used alone to obtain polymers or they may be copolymerized with one or more other monomers. It is a preferred practice to employ the homopolymer of acrolein in the process of this invention.

Comonomers which are suitable for copolymerization may be broadly defined as any ethylenically unsaturated monomer which will copolymerize with acrolein monomers. Examples of suitable comonomers are acrylamide, acrylic acid, alkyl esters of acrylic acid such as methyl acrylate, etc., and salts of acrylic acid. Likewise, compounds such as maleic acid, and derivatives thereof, such as esters, salts, etc., vinyl sulfonic, and vinyl phosphonic acids, methyl isopropentyl ketone, dimethylaminoethyl methacrylate, diethylmethylene succinate, ethyl vinyl

ketone, vinyl acetate, vinyl pyrrolidone, allyl alcohol, sulfonated styrene, vinyl pyridine, and N-allyl amines may be used, as well as other compounds such as aconitic acid, itaconic acid, and the like.

The compounds which may be used in making the interpolymers of this invention such as copolymers and terpolymers also include the ethylenically unsaturated carboxylic acids and their anhydrides such as methacrylic acid, crotonic acid, alpha-phenylacrylic acid, alpha-chloromaleic acid, beta-phenylacrylic acid, alpha-cyclohexacrylic acid, tetrahydrophthalic acid, methyltetrahydrophthalic acid, chloromaleic acid, 7,9-dodecadienoic acid, 10,12-eicosadienoic acid, cyanoacrylic acid and methoxyacrylic acid.

Other monomers which can be included in the synthesis of acrolein polymers of the invention are styrene, acrylonitrile, methacrylonitrile, N-ethylacrylamide, mono-olefins and diolefins, such as ethylene, propylene, butylene, octylene, butadiene, isoprene, and the like.

It is preferred that any comonomer or monomers employed with acrolein comprise no more than 70 mole percent of the polymer and most preferably no more than 50 mole percent.

The monomer or monomers may be polymerized by a wide variety of synthetic techniques including bulk, solution, emulsion, suspension, etc., polymerization. One preferred method is polymerization by emulsion techniques. In its broadest aspect this procedure involves adding of the monomer or monomers to an aqueous solution containing a catalyst and suitable amount of an emulsifying agent. Preferably, the reaction flask has been previously purged with an inert gas such as nitrogen. Almost any type of known emulsifier may be employed, but preferred are oxyalkylated alkyl phenols, such as the well-known "Triton" materials, ethylene oxide condensates of fatty acid amides such as "Ethomide-15, 0-15, and HT-15," as well as "Arlacel 80" and "Span," which are sorbitan monooleates. Other suitable emulsifying agents are sorbitan mono-stearate, sodium dodecyl benzene sulfonate, aluminum stearates, aluminum oleates, etc. Only minute amounts of these emulsifiers are necessary, say from about 10 to about 1000 p.p.m. The concentration of the active monomer ingredients in the reaction mixture may be as low as about 1.0% and as highly concentrated as an emulsion containing 50.0% monomer. The reaction itself may be run in the presence of air, but it is preferred that the reaction vessel be first purged with an inert gas such as nitrogen, carbon dioxide, etc., in order to rid the system of oxygen having somewhat of a tendency to inhibit polymerization and provide lower product molecular weight.

The catalysts that are employed in the process include conventional peroxidic oxidizing agents such as potassium persulfate, hydrogen peroxide, and ammonium persulfate. It is preferred that water-soluble compounds be used for this purpose. The amount of catalyst used in the process can vary from 0.003% to about 5.0% by weight based on the weight of the monomers. The preferred range is from about 0.003% to about 2.0%. In a preferred embodiment, the polymerization reaction is carried out using a redox type catalytic system. In this method it is particularly preferred to remove oxygen from the system and introduce an inert gas therein in order to permit the catalyst to form free radicals. In a redox system, the catalyst is activated by means of reducing agent which, in the absence of oxygen, immediately produces free radicals without the use of heat. One of the reducing agents most commonly used is sodium metabisulfite. Other suitable agents include water-soluble thiosulfates, hydrosulfites and reducing salts, such as the sulfates of metals which are capable of existing in more than one valence state. The metals include cobalt, iron, nickel and copper. Another excellent reducing agent is silver nitrate. The use of a redox initiator system has several advantages, the most important of which is that it is possible to carry out the polymerization at lower temperatures since it is not required to de-

compose the catalyst. The catalyst and the activator may, if desired, be dissolved in a small amount of water and then added to the reaction mixture containing the emulsified monomers. Also, the catalyst initiator may be added directly to the emulsion and dissolved therein with mild agitation.

The polymerization itself is carried out at rather low temperatures, and preferably below about 80° C. More preferably, the reaction is carried out at a temperature range of 20–60° C. for a period of time of at least one hour. Excellent polymers have been formed in from about 1 to about 3 hours reaction time.

The products formed in the process described above, generally gel after a period of time and may become completely water-insoluble. However, these products may be reacted with an aqueous solution of an alkali metal bisulfite or ammonium bisulfite or an aqueous solution of sulfur dioxide wherein water-soluble derivatives are obtained. It is preferred therefore that the acrolein polymers of this invention be solubilized by use of the above solubilizing agents.

One simple technique for preparing these water-soluble derivatives is to simply add the solid copolymer, or reaction mixtures thereof, to a dilute aqueous solution of alkali metal or ammonium bisulfite or aqueous SO₂ solution. With mild heat, the polymer is easily reacted to form the water-soluble derivative thereof.

The amount of acrolein polymer used in this invention may vary from 0.1% to 10% by weight, based on the dry weight of the hydrocolloid. Preferably, the amount of acrolein polymer present will range from 0.2% to 5% by weight, based on the hydrocolloid.

Broadly speaking, the process of this invention comprises coating at least one side of a fibrous substrate with an aqueous solution of a treated hydrocolloid. The coating solution may be applied either by an off-machine process or a machine coating process, depending upon the type of fibrous substrate, the particular hydrocolloid which is to be employed, and other factors which normally determine the selection of one of these two processes. Any of the above described basic types of coating processes such as spray, brush, etc., may be employed where they would normally be used to coat the fibrous substrate with the particular hydrocolloid which has been chosen. It is preferred to coat the substrate with from 0.1% to about 15% by weight of the hydrocolloid, based on the weight of the dry substrate. More, or less coating may also be employed if desired.

The procedure for preparing the treated hydrocolloid which is to be used in the process of this invention is as follows. First, approximately 0.01% to about 2.0% by weight of a cationic polymer is added to a solution of hydrocolloid to form a pretreated hydrocolloid. Next, from 0.1% to 10.0% of an acrolein polymer is added to the pretreated hydrocolloid, based on the dry weight of the hydrocolloid, to form a treated hydrocolloid. Once the treated hydrocolloid is prepared, normal coating procedures for coating fibrous substrates may be employed using this treated material. Fibrous substrates which have been coated using the process of this invention have been found to have superior porosity, smoothness and abrasion resistance characteristics. It is not contemplated that any additional procedures or modifications will be necessary to accomplish the objects of this invention.

The following examples are presented by way of illustration to demonstrate the efficacy of this invention. Of course, the examples are merely illustrative and are not to be considered limiting upon the scope of the invention.

EXAMPLES

A number of field tests were run in a paper mill in the midwest part of the United States. In this mill, paper was coated with a starch solution by means of a dip coating device. In all cases during this mill trial, 60 pounds of starch per ton dry pulp was applied. The starch

used in this mill trial was an oxidized cornstarch at a concentration of 6% by weight in water.

Paper produced during this mill trial was evaluated to determine the porosity of the coated paper with a Gurley Densometer. In this test, sheets of paper are clamped together and air is forced through the surface of the paper. The amount of time, in seconds, which is required to displace 100 cc. of air is measured. Lower porosity is shown by a longer time period for displacement of the standard volume of air.

Similarly, during the mill trial, the smoothness of the paper therein produced was evaluated. The smoothness was measured by a Gurley Smoothness Tester which measures the amount of time required for 25 cc. of air to be displaced between sheets of coated paper clamped together. Smoother paper is capable of fitting closer together with fewer voids between the sheets. Therefore, a longer period of time will be necessary to displace the standard volume of air when smoother sheets are employed.

Lastly, the paper produced in this mill trial was subjected to a Taber Abrasion Test. The Taber Abrasion Test, a standard test method in the industry, consists of measuring the amount of weight loss which results from 200 cycles of abrasion. Each cycle is determined by a full revolution of the weighted wheel which rubs against or abrades the surface of the paper.

During this mill trial, four different hydrocolloid solutions were employed as the coating additive. The first run, Run A, represents paper produced using a simple solution of the starch as the coating solution. Run B represents the use of a hydrocolloid containing 0.2%, based on the weight of the starch, of a cationic polymer. In this case, a polyamine was employed. Run C represents the use of 4.5% based on the weight of the starch, of an acrolein polymer as a hydrocolloid additive. Finally, Run D, representing the process of this invention, was made using a hydrocolloid containing 0.2% by weight of the polyamine of Run B plus 4.5% of the acrolein polymer of Run C, based on the weight of the starch. Presented below in Table I are the results of the porosity, smoothness and abrasion tests which were made on the four mill trial runs.

It is readily apparent that Run D, corresponding to the process of this invention, produced paper of substantially superior quality. Specifically, the paper produced during Run D had noticeably lower porosity, thereby indicating that the strength of the paper was materially increased. Further, the improvement in smoothness was to great as to allow the use of this paper as a substitute for higher grades of coated papers, thereby resulting in substantial savings for the consumer. Lastly, it is to be noted that the improvement in abrasion was remarkably unexpected and superior. In point of fact, the improvement found in Run D was more than three times greater than the sum of the improvements over unmodified stock achieved by the same additives employed in Runs B and C when used as the sole additive.

TABLE I

Run No.	Porosity, sec./100 cc. displacement	Smoothness, sec./25 cc. displacement	Abrasion 200 cycles, gram weight loss $\times 1,000$
A.....	10.7	39.1	163
B.....	11.0	38.5	157
C.....	12.0	37.2	157
D.....	14.1	47.5	125

While particular emphasis has been placed upon the improvements in porosity, smoothness and abrasion resistance, it should be pointed out that other properties such as insolubility of the coating, increased wet strength, water holdout or sizing efficiency and dimensional stability and the like are improved as well. Papers produced by the process of this invention are highly

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suitable for use as key punch cards, "easy erase" paper, and other specialty paper products.

What is claimed is:

1. A coating composition suitable for coating fibrous substrates comprising an aqueous solution containing 1.0% to 40% by weight of starch, based on the weight of the system, 0.01% to 2.0% by weight of a water-soluble cationic polymer selected from the group consisting of alkylene polyamines and condensation polymers of alkylene polyamines and halohydrins, based on the weight of the starch, and 0.1% to 10.0% of a water-soluble acrolein polymer by weight, based on the weight of the starch.

2. The coating composition of claim 1 where the water-soluble cationic polymer is a condensation polymer of an alkylene polyamine and the water-soluble acrolein polymer is a polyacrolein bisulfite.

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117—155, 161; 260—8, 17.5