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PROCESS FOR IMPREGNATING PAPER WITH pH CONTROLLED LATEX

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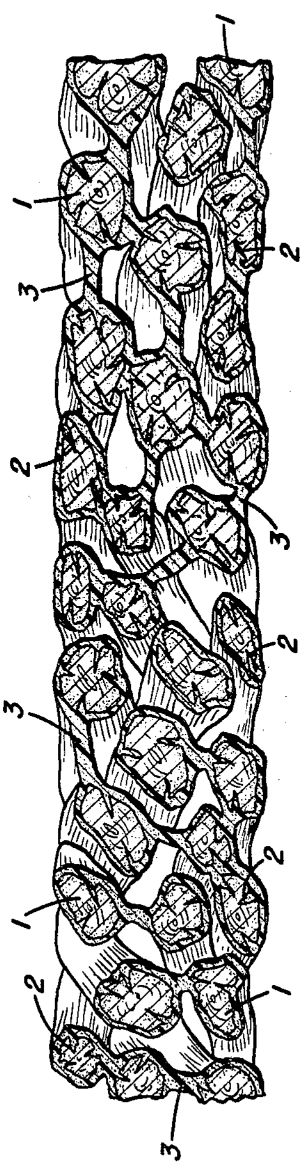

FIG. 1.
PRIOR ART

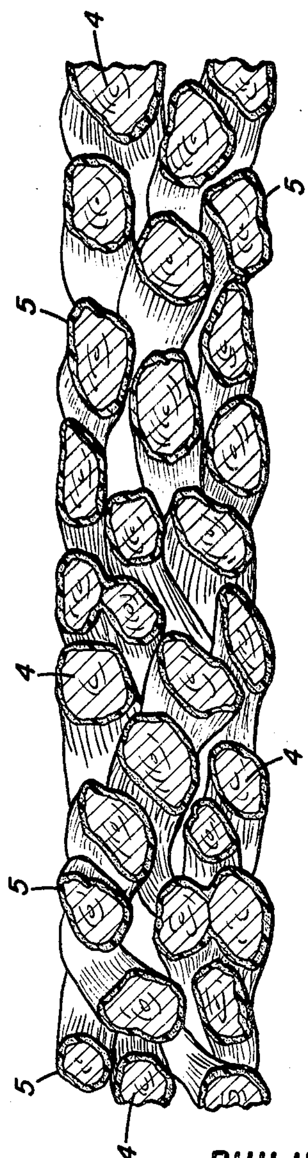

FIG. 2.

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3,483,014
PROCESS FOR IMPREGNATING PAPER WITH pH CONTROLLED LATEX

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ABSTRACT OF THE DISCLOSURE

The invention disclosed is directed to a process for impregnating paper with a synthetic polymer latex having a pH value below about 2.4. The pH value of the latex may be adjusted with a mineral acid.

The present invention relates to a novel and useful process for preparing a product. More particularly, it relates to a process for impregnating paper.

It is known in the art that various latex impregnated papers may be used in the manufacture of pressure sensitive tapes, shoe insoles, artificial leather bases and the like. In the preparation of the latex for paper impregnation, two distinct systems are utilized. The first system utilizes a monomer, water, soap and an initiator which are mixed with heat and pressure. The second system utilizes the polymer, water, a quite large quantity of surfactant and energy which is generally imparted in the form of mixing to disperse the particles. The latex resulting from each of these systems, when applied to a paper, usually results in a bridging of polymer strings between the paper fibers and some actual penetration of the polymer into the fibers. The bridging results in a waste of polymer since the bridges add little, if any, to the strength of the paper. The penetration of the polymer into the fibers also results in a loss of polymer since it actually detracts from the strength of the fibers it has penetrated. In a copending application, one of the inventors of the present invention has discovered that an improved impregnated paper results if the latex is deionized prior to impregnation. The only drawback to this process is that in order to deionize the latex ion exchange resin must be used which requires regeneration periodically. Thus, the improved process adds costs over the old method. Quite obviously, if a process could be developed which added very little to the cost, it would receive widespread acceptance in the art.

It is an object of the present invention to provide a process for preparing an improved impregnated paper. A further object is to provide an inexpensive process for impregnating cellulosic pulp paper. A still further object is to provide a uniformly impregnated cellulosic pulp paper. Other objects will become apparent as the description of the invention proceeds.

These objects are accomplished by the present invention which provides a process for impregnating paper which comprises adjusting the pH of a synthetic polymer latex to a value below about 2.4 with a mineral acid and thereafter applying the latex to a cellulosic pulp paper.

In a preferred embodiment of the present invention the latex contains from about 5% to about 70% synthetic polymer and more preferably from about 15% to about 50%.

In the preferred embodiment, the pH is adjusted to a value of from about 1.7 to about 2.4 with a mineral acid selected from the group consisting of sulfuric acid and nitric acid.

In a still more prefered embodiment, the pH is adjusted to a value of from about 2.0 to about 2.4 and

the impregnated cellulosic pulp paper is at least partially dried to allow the latex to gel and then the acid is neutralized, preferably with sodium bicarbonate, before the final drying operation.

The term "latex" is used in its conventional sense to mean a dispersion of solid synthetic polymer particles in water which is capable of forming a film from the dispersion. The synthetic polymers which can be utilized in the latex include, without limitation, polymers and copolymers of butadiene, isoprene, chloroprene, acrylates, vinyl halides, vinyl esters and the like. Specific examples include the homopolymers polyethyl acrylate, plasticized polyvinyl chloride and the copolymers styrene-butadiene (40%–60%) and styrene-acrylonitrile-butadiene-acrylic acid (35%–14%–50%–1%). Other polymers are likewise suitable.

The term "mineral acid" is used to signify any inorganic acid. It includes sulfuric acid, nitric acid, phosphoric acid, sulfurous acid, nitrous acid and the like. Preferably, the acid is used in a dilute form since concentrated acid will sometimes cause coagulation. If a concentrated acid is to be used the latex should be thoroughly agitated to prevent coagulation. The pH is generally adjusted using an automatic pH meter although indicators may be used or the required quantity of acid calculated beforehand. The two preferred acids are nitric acid and sulfuric acid in that order.

The terminology "cellulosic pulp paper" is used to mean any conventional paper such as that made from wood pulp, cotton linters and the like. It also includes paper which contains some synthetic filaments as reinforcement.

The invention will now be described by reference to the drawings. In the drawings:

FIGURE 1 is an artist's conception of an enlarged cross sectional view of a sheet of impregnated paper produced in accordance with the prior art; and

FIGURE 2 is an artist's conception of an enlarged cross sectional view of a sheet of impregnated paper produced in accordance with the present invention.

In FIGURE 1 the paper fibers **1** have been penetrated by the polymer **2** and strings of the polymer **3** bridge the individual filaments. The figure demonstrates that the prior art procedures result in a waste of polymer by the bridges being formed and by the polymer penetrating into the fibers.

In FIGURE 2 the paper fibers **4** are substantially uniformly coated with the polymer **5**. The figure demonstrates that very little polymer is wasted when the impregnated paper is made in accordance with the present invention since the polymer is quite uniformly coated onto the filaments.

The following examples are given to illustrate the invention and are not intended to limit it in any manner. All parts are given in parts by weight unless otherwise expressed.

In the following examples, the tests are carried out as follows.

The pH of the solutions are measured using an automatiic pH meter (Beckmann Zeromatic).

The percent total solids in the latex is determined by accurately weighing a sample of the latex, drying said sample to constant weight and reweighing. The total solids are then calculated from the following formula:

$$\frac{\text{Dry weight}}{\text{wet weight}} \times 100 = \text{percent total solids}$$

Tensile properties, i.e., tensile strength at failure, percent elongation at failure and 1% tensile modulus are measured in accord with ASTM–D–412–64T. The copolymer latex is dried in film form (3 mils thick), cut to 1/4" sample strips, placed in the jaws (2" apart) of a tensile strength tester (Instron, Model TT, available from Instron Engineering Inc., Quincy Mass.) and separated at a rate of 0.5" per minute and a strain rate of 50% per minute at 23° C. and 50% relative humidity.

The delamination resistance is measured by preparing test specimens which are cut to a length of approximately 4½ inches in machine direction and a width of approximately 2 inches in the cross direction of the paper. The test specimens are conditioned 48 hours at 23° C. and 50% relative humidity. A 5 inch long strip of rug binding tape is placed on each side of the paper specimen so that the tape extends beyond the ends of the paper. The specimen is then placed on the bottom platen of a press so that approximately 0.5 inch of the tape extends beyond the end of the platen. The specimens are pressed for 30 seconds at 275° F. at a pressure of 5.12 pounds per square inch on the binding tape. The specimens are cooled to room temperature. The specimens are cut in strips approximately 1 inch wide. The two ends of the rug binding tape are pulled apart into two approximately equal plies. The ends of the binding tape are put into the jaws of the Instron tensile tester and, after the first inch of separation, the average force required to separate the paper is recorded at a crosshead speed to 10 inches/min. The delamination resistance of the paper is reported in pounds based on the average values of 3 specimens.

EXAMPLES 1–5

To 1000 grams of a latex containing 50% of solids (a copolymer containing 35% styrene, 14% acrylonitrile, 50% butadiene and 1% acrylic acid) is mixed 5% nitric acid until the pH has dropped from an initial value of 5 to a value of 2. The final solids content is 35–40%. A standard size sheet (8½ inches by 11 inches) of cotton linters paper (12 mils thick) is impregnated with the latex by dipping the paper into the latex to give an impregnated paper having 40% polymer solids (dry weight). The sheet is air dried at room temperature. A control is also carried out using no acid whatsoever.

In Examples 2–4 the same procedure is repeated employing respectively 5% sulfuric acid, 5% hydrochloric acid and 5% phosphoric acid. In Example 5, the same procedure as Example 1 is carried out with the exception that after drying the sheet at room temperature the sheet is washed with 1% sodium bicarbonate and then redried at room temperature. Example 5 represents a particularly preferred embodiment of the present invention. The properties of the resulting products are given in the table below:

Example	pH	Acid used	Polymer uptake, percent	Tensile strength, p.s.i.	Elongation, percent	Delamination resistance
Control	5	None	40	941	12	0.81
1	2	Nitric	40	1,250	18	1.59
2	2	Sulfuric	40	1,203	18	1.43
3	2	Hydrochloric	40	1,124	13	1.29
4	2	Phosphoric	40	900	15	1.20

When the impregnated sheets of the present invention are examined under a high powered microscope, it can be seen that the fibers have been quite uniformly coated with the latex solids with the substantial absence of any strings or bridges connecting the fibers. By taking ½ of the paper sheet before drying, the latex on the exterior of the sheet can be removed by washing with water leaving only that latex which has penetrated into the fibers. A comparison of the weight of the washed dried sheet with the weight of the original sheets, shows that substantially no latex has penetrated into the fibers. In contrast, when a control latex is carried through the same procedure without adjusting the pH with the exchange resin, a great deal of bridging takes place between the fibers of the paper. Also, by the removal of the latex solids from the sheet, it can be determined that about 15% of the latex solids has penetrated into the interior of the fibers.

EXAMPLE 6

The procedure of Example 1 is repeated employing for the latex solids a polyethyl acrylate homopolymer. A control is also run as in Example 1.

The properties of the resulting products are given in the table below:

Example	pH	Acid used	Polymer uptake, percent	Tensile strength, p.s.i.	Elongation, percent	Delamination resistance
Control	6	None	40	2,054	12	1.90
6	2	Nitric	40	2,400	10	2.20

When the sheets are examined under the microscope, as in Examples 1–5, substantially the same structure is nited. Also when the sheets are tested by removing the latex from the exterior of the paper, substantially the same results are noted. When the control is examined, it is found that its structure and properties are essentially that of the control utilized above.

EXAMPLE 7

The procedure of Example 1 is repeated employing for the latex solid a copolymer of 60% butadiene and 40% styrene. A control is also run as in Example 1. The properties of the resulting products are given in the table below:

Example	pH	Acid used	Polymer uptake, percent	Tensile strength, p.s.i.	Elongation, percent	Delamination resistance
Control	5	None	40	850	12	1.80
7	2	Nitric	40	1,100	15	1.09

When the sheets are examined under the microscope as in Examples 1–5, substantially the same structure is noted. Also when the sheets are tested by removing the latex from the exterior of the paper, substantially the same results are noted. When the control is examined, it is found that its structure and properties are essentially that of the control utilized above.

EXAMPLES 7 AND 8

The procedure of Example 1 is repeated employing for the latex solids a copolymer of 60% butadiene and 40% acrylonitrile in Example 8. A control is also run as in Example 1. In Example 9, the procedure of Example 8 is carried out with the added wash with sodium bicarbonate as described in Example 5.

The properties of the resulting products are given in the table below:

Example	pH	Acid used	Polymer uptake	Delamination resistance
Control	5	None	60	1.30
8	2	Nitric	60	3.07
9	2	do	60	2.95

When the sheets are examined under the microscope as in Examples 1–5, substantially the same structure is noted. Also when the sheets are tested by removing the latex from the exterior of the paper, substantially the same results are noted. When the control is examined, it is found that its structure and properties are essentially that of the control utilized above.

The use of sodium bicarbonate (or any other neutralizing agent) in the above examples destroys any residual acids which if left in causes degradation and loss of tear strength. Accordingly, the procedure employing a basic rinse to remove the acid is a preferred embodiment of the present invention. Also, the paper may be washed with a considerable amount of water which substantially lessens the effect of the residual acid.

While in the above examples unmodified latex systems are utilized, it is obvious that latex systems containing anti-oxidants, fillers, pigments, oils, thickeners and the like can be employed.

Many equivalent modifications will be apparent to those skilled in the art from a reading of the foregoing without a departure from the inventive concept.

What is claimed is:

1. A process for coating fibers of paper which comprises, adding a mineral acid to a synthetic polymer latex and adjusting the pH thereof to a value below about pH 2.4 without coagulation, applying the acid treated uncoagulated latex having a pH value below about pH 2.4 to a cellulosic pulp paper, partially drying the acid treated latex to form a gel coating on the fibers, neutralizing any acid remaining on the latex coated fibers of the paper, and thereafter drying said fiber coated paper whereby the interior of the fibers is substantially free of said synthetic polymer.

2. The process of claim **1** wherein the mineral acid is sulfuric acid.

3. The process of claim **1** wherein the mineral acid is nitric acid.

4. The process of claim **1** wherein the acid is neutralized with aqueous $NaHCO_3$.

5. A process for coating fibers of paper which comprises, adding a mineral acid selected from the group consisting of sulfuric acid and nitric acid to a synthetic polymer latex and adjusting the pH thereof to a value of from about pH 1.7 to about pH 2.4 without coagulation, applying the acid treated uncoagulated latex having said pH value to a cellulosic pulp paper, partially drying the acid treated latex to form a gel coating on the fibers, neutralizing any acid remaining on the latex coated fibers of the paper, and thereafter drying said fiber coated paper whereby the interior of the fibers is substantially free of said synthetic polymer.

6. The process of claim **5** wherein the acid is neutralized with aqueous $NaHCO_3$.

7. The process of claim **5** wherein the pH value is from about pH 2.0 to about pH 2.4.

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