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PAPER IMPREGNATING COMPOSITIONS, IMPREGNATED PAPERS AND THE PROCESS OF IMPREGNATING PAPER

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The present invention is concerned with the impregnation of paper for the purpose of producing improved paper sheets having increased flexibility, extensibility and strength.

Heretofore, impregnation of paper sheets with synthetic linear polymers having high T_i values in the neighborhood of 0° to 15° C. has been found to increase the tensile strength substantially but the increase in edge tear resistance was far from what was desired. Attempts to employ polymers of low T_i in place of those of the high T_i values above resulted in providing a great increase in the edge tear resistance but the improvement in tensile strength in this case was well below what was desired.

The T_i value referred to is the transition temperature or inflection temperature which is found by plotting the modulus of rigidity against temperature. A convenient method for determining modulus of rigidity and transition temperature is described by I. Williamson, British Plastics, 23, 87-90, 102 (September 1950). The T_i value here used is that determined at 300 kg./cm.².

Applicants have discovered that excellent increases in both edge-tear and tensile strengths as well as in extensibility can be obtained by the employment of certain synthetic linear polymers of esters of acrylic acid or methacrylic acid.

These results have been found to be obtainable by the employment of dispersions of water-insoluble linear polymers of esters of acrylic acid or methacrylic acid provided the polymer or copolymer has a T_i between -17° C. and $+17^\circ$ C. In addition it is essential that the molecular weight of the polymer be reduced so that it does not exceed about 950,000 and in most cases is from about 20,000 to 300,00 viscosity average molecular weight as determined from a solution in benzene at 25° C. It is essential that the T_i and molecular weight be correlated within the ranges specified in order to provide the desired combination of high increases in both edge tear and tensile strengths.

The paper which is used as the starting material for the present invention is of the class called "impregnating" or "saturating" papers which are of porous character and have a thickness of about 5 to 250 mils. Their basis weight may be from 10 on up by which is meant the weight in pounds of 500 sheets having a dimension of 24" x 36". In general, the pulp used in making the paper will not have been beaten beyond a Canadian freeness of about 450. Generally, the paper will have been obtained from pulp beaten to a Canadian freeness of about 675 to 500. The paper may be made from all types of fiber stocks, especially those of poor quality, such as oak, poplar, and yellow birch, and those of extremely short fiber length, as well as those of long fiber length and of good quality derivation, such as from spruce and hemlock. A wide variety of fibrous cellulosic material used in the preparation of paper, board, moulded resin fillers, and the like may be used, such as kraft pulp, rag pulp, soda, sulfate, ground-wood, sulfite pulp and alpha pulp. Similarly, other forms of fibrous cellulose such as cotton linters, and the like may be employed. These materials may be used alone or in ad-

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mixture with fibers from other sources, such as jute, hemp, sisal, strings, chopped canvas, and other material, either cellulosic or non-cellulosic, that may improve the impact resistance, mechanical strength or other properties of the formed or moulded impregnated material. The process of the invention is also adapted to improve the extensibility, edge tear strength and tensile strength of papers formed from synthetic fibers, such as nylon and related polyamide fibers, polyethylene glycol terephthalate and related polyester fibers, and polymers of acrylonitrile, such as copolymers containing at least 75 to 90% by weight of acrylonitrile with other comonomers, such as vinyl acetate, vinyl chloride, vinyl pyridine, and esters of acrylic and methacrylic acid such as methyl methacrylate.

It is to be noted that the starting paper may be that obtained from bleached or unbleached kraft, bleached or unbleached sulfite, or bleached or unbleached semi-chemical pulps. In addition, the paper may be made from mixtures of cellulosic pulps with up to 10% and preferably containing 1 to 5% of other fibers, such as glass fibers or the synthetic fibers mentioned above.

For most purposes it is preferred that the starting paper be unsized and generally free of resins. However, for some purposes, it may be desirable to employ as the starting paper sheet a porous high wet strength paper such as may be obtained by the use of 0.5 to 5% by weight, on the weight of the fibers, of a thermosetting aminoplast, such as a urea-formaldehyde resin, and melamine-formaldehyde resin or methylolated ureido polymers, such as those obtained by the reaction of formaldehyde with polymers and copolymers of N-vinyl oxethyl-N,N'-ethyleneurea. Such wet strength papers are obtained in the conventional way by the use of one of the resins just cited applied to the pulp suspensions followed by sheeting and baking at temperatures of 210° to 400° F. for periods of about one-half or an hour to five or ten minutes respectively.

The composition of the polymers applied by way of their aqueous dispersions may simply be that obtained by homopolymerization of methyl acrylate or ethyl acrylate or by the copolymerization of acrylates of alcohols having one to four carbon atoms with each other or other comonomers, including comonomers which tend to raise the T_i value provided that value in the final copolymer does not exceed $+17^\circ$ C., such as the methyl, ethyl, propyl, and butyl methacrylates, styrene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, vinylidene chloride, and the like.

The polymers may also contain adhesion-promoting units, such as carboxylic groups in the form of free acid or salts, or amide units and substituted amide units. Thus, the copolymer may contain from 0.5 to 7% by weight (preferably about 1 to 4%) of acrylic acid, methacrylic acid, itaconic acid, aconitic acid, maleic acid, fumaric acid, the dimer of methacrylic acid and the trimer of methacrylic acid, acrylamide, methacrylamide, N-methylacrylamide, N-methylolacrylamide, N-ethylacrylamide. These adhesion-promoting units impart better internal bonding strength, improved wet-strength (if heated), and, whether or not heated on the paper, they provide even greater tensile strength than that obtainable by the use of polymers which do not contain such adhesion-promoting units.

Except for the inclusion of about 0.2 to 5%, and preferably 0.2 to 1.5% by weight, based on the weight of monomers of a chain-transfer agent, the copolymer dispersion may be made by any of the conventional emulsion polymerization procedures. For example, the polymerization procedures disclosed in the passage of McLaughlin et al., United States Patent 2,790,736, column 4, lines 8 to 74, may be employed provided the proportion

of a chain-transfer agent or chain regulator just specified above be included within the polymerization mixture in addition to the other ingredients. The passage of that patent just referred to is incorporated herein by reference. The chain-transfer agents which serve to reduce the molecular weight of the polymer obtained by the emulsion polymerization procedure in proportion to the amount of chain-transfer agents used may be any one of the following: long-chain alkyl mercaptans, e.g., t-dodecyl mercaptan, isopropanol, isobutanol, long-chain alcohols, e.g., lauryl alcohol, t-octyl alcohol, CCl_4 , C_2Cl_4 , and CBrCl_3 .

When the starting paper is of high-wet-strength cellulosic type obtained by the use of an aminoplast as mentioned hereinabove the molecular weight of the dispersed polymer used for impregnation should be between 20,000 and 300,000 viscosity average. However, when the starting paper is made of cellulose and is not of high-wet-strength type, the viscosity average molecular weight may be as high as 950,000 but, in this case, optimum results are obtained using the polymers of the lower molecular weight range just mentioned.

The amount of synthetic polymer applied to the paper may be within the range of 10 to 130% on the weight of fibers. The impregnation may be effected by dipping the sheet within the aqueous dispersion of the polymer, by spraying the aqueous dispersion on the sheet, by passing the sheet over a suction box above which the dispersion may be sprayed, by means of rollers, or by floating the sheet over the aqueous dispersion. Depending upon the thickness of the sheet being impregnated or saturated and upon the particular manner of application to the sheet, the concentration of the dispersion may be in the range of 5 to 60% by weight of polymer. Preferably the aqueous dispersion contains about 15 to 50% by weight of polymer. The impregnation may be effected in a period of time varying from about 7 to 10 seconds to several minutes in duration.

After impregnation to distribute the polymer substantially uniformly throughout the sheet, the latter may be subjected to drying. The temperature of drying may be from room temperature to 400° F. and the time may vary inversely with respect to the temperature such as from 10 seconds at the high temperature mentioned to 4 to 8 hours at the lower temperature. Preferably drying is effected at 180° to 212° F. The drying may be effected by means of infra-red lamps, radio frequency-induced currents, circulating air ovens, festoon driers, and in the latter two systems temperatures in the range of 140 to 300° F. are frequently employed.

The impregnated sheet obtained has markedly improved tensile and tear-strengths including both edge-tear and trapezoidal tear as well as increased extensibility. When the amount of polymer applied is in the lower portion of the range, e.g., about 10 to 60% by weight of the fibers, and the sheet has not been pressed after the impregnation, the product is a permeable, water-resistant sheet in which the characteristics of paper have not been completely suppressed. However, if about 40% or more of polymer is applied to the sheet and the sheet is pressed as in calendering, the product is essentially a continuous plastic film or sheet formed by the polymer with the fibers reinforcing the polymer and embedded in it. If desired, a pigment or dye may be included in the impregnated dispersion to modify the color of the product.

The impregnated sheets may be used as backing for sandpaper, masking tape backing, washable book covers (in which they may be used with or without an additional finish), as decorative papers, map-making papers, as lamina in floor covering laminates, as imitation leather, as a gasketing material, as shelving papers, as interliners for shoes, shirts, and other garments, as tablecloths or doilies, as "high-energy" papers, as in wrapping papers or

bags for packaging and shipping, as filter papers; electrical insulation papers.

In the following examples which are illustrative of the invention, the parts and percentages are by weight unless otherwise noted. In all examples, the Scott IP-4 tensile tester was used for measurement of tensile strength. The Finch attachment was used for edge tear resistance measurements. All values for both tensile and edge tear are in lbs./inch width. The "pickup" value given is the weight percent of polymer based on the dry weight of the saturating paper before impregnation. The abbreviations MD and CD refer to machine direction and cross direction (or transverse direction) respectively. All of the high molecular weight polymers prepared for comparative purposes without the use of a chain-transfer agent have average molecular weights of at least about two million.

EXAMPLE 1

An aqueous dispersion of a polymer is prepared by the emulsion copolymerization of a mixture of 87 parts of ethyl acrylate, 10.5 parts of methyl methacrylate, 2.5 parts by weight of itaconic acid, and 0.5 part of bromotrichloromethane in about 100 parts of water in the presence of 6 parts of a t-octylphenoxypolyethoxyethylene containing about 30 oxyethylene units, 0.2 part of ammonium persulfate and 0.25 part of sodium hydrosulfite. After polymerization sodium hydroxide was added to adjust the composition to a pH of 9 and the dispersion was then diluted to 30% solids concentration. The copolymer, referred to as polymer B in Table I, had a viscosity average molecular weight of about 170,000 and a T_g of about -4° C.

An impregnating paper obtained from a pulp beaten to a Canadian freeness of 630 cc. having a low wet tensile strength (0.52 lb./inch width in machine direction and 0.38 lb./inch width in cross direction) and having a basis weight of 32 pounds was immersed in the 30% dispersion prepared above. After thorough impregnation, the sheet was passed between squeeze rollers to remove excess impregnant and dried in contact with a chromium-plated surface heated to a temperature of 210° F. It was then conditioned overnight at 74° F. and 50% relative humidity.

Another sheet was obtained in the same manner except that the bromotrichloromethane was omitted from the polymerization mixture and the copolymer, designated polymer A in Table I, had a viscosity average molecular weight of about two million, the T_g being the same as that of polymer B.

Table I

Saturant	Pickup, percent	Tensile strength		Edge- tear resistance		Elongation at failure, percent of original length	
		MD	CD	MD	CD	MD	CD
Control (untreated).....	-----	10.6	6.2	3.3	2.3	-----	-----
Polymer A.....	45	23	18	17	20	5	8
Polymer B.....	45	20	15	27	23	7.5	17

EXAMPLE 2

An impregnating paper containing a small amount of wet strength resin, so that it has a wet tensile strength of 1.2 lbs./in. width in the machine direction and 0.75 lb./inch width in the cross direction, and having a basis weight of 36 pounds (3,000 square feet) is treated with the same two polymer dispersions mentioned in Example 1 and in the same manner therein described. Sheet A is that obtained from the dispersion made without the chain regulator and Sheet B with.

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Table II

Saturant	Pickup, percent	Tensile strength		Edge-tearing resistance	
		MD	CD	MD	CD
Control		16.3	8.1	5.9	4.4
Polymer A	45	30	18	18	13
Polymer B	45	28	19	26	26

EXAMPLE 3

The paper used in Example 2 was saturated with a pair of aqueous dispersions of polymers produced by the procedure of Example 1 except that the monomer charge was 88% ethyl acrylate and 12% methyl methacrylate (T_1 of about -4° C.). Polymer A was produced in the usual way to give the usual average molecular weight of two million or so; polymer B was identical except for the introduction of 0.5% chain-transfer agent, BrCCl_3 , during polymerization to reduce the average molecular weight to about 170,000. The properties of the saturated papers were as follows:

Table III

Saturant	Pickup, percent	Tensile strength		Edge-tearing resistance	
		MD	CD	MD	CD
A	45	26	16	16	19
B	45	24	10	28	22

The T_1 of both A and B was approximately -5° C.

EXAMPLE 4

Using the paper of Example 1, saturation was effected with a pair of aqueous dispersions of polymers produced by the procedure of Example 1, but with a monomer charge as follows: ethyl acrylate: 97.5%, itaconic acid: 2.5% (T_1 about -15° C.) were used as saturants. Polymer A was produced in the usual way and had a high average molecular weight of about two million; polymer B was produced in the presence of 0.05% chain-transfer agent, BrCCl_3 , and had, therefore, an estimated viscosity-average molecular weight of 950,000. The treated papers had the following properties:

Table IV

Saturant	Pickup, percent	Tensile strength		Edge-tearing resistance	
		MD	CD	MD	CD
A	45	22	16	20	23
B	45	22	16	24	25

EXAMPLE 5

Using the paper of Example 2 and a pair of aqueous dispersions of polymers identical to those of Example 4 except that polymer B was prepared in the presence of 0.5% BrCCl_3 , the following saturated paper properties were measured:

Table V

Saturant	Pickup, percent	Tensile strength		Edge-tearing resistance	
		MD	CD	MD	CD
A	45	29	18	10	16
B	45	23	15	21	19

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Polymer B has a viscosity-average molecular weight of about 170,000.

EXAMPLE 6

The pair of aqueous polymer dispersions used as saturants in Example 5 (composition: 97.5% ethyl acrylate, 2.5% itaconic acid) were incorporated into a paper comprising 90% by weight of fibers of about 90% of acrylonitrile (Du Pont papermaker's Orlon $\frac{1}{4}$ " 2 denier per filament) and 10% bleached sulfite wood pulp, 460 cc. Canadian freeness. This paper was prepared on Noble-Wood sheetmaking equipment in the laboratory and therefore was not "directional." In this case, improvement in edge-tearing was not observed but a remarkable increase in stretch (elongation at failure) and in the "tensile \times stretch" product was obtained. The tensile \times stretch product is an important property indicating the capacity of the paper to absorb energy as for example when dropped in a loaded condition. This product, therefore, measures the suitability of the paper for use in wrapping and packaging, e.g., multi-wall shipping bags. The saturated paper properties are as follows:

Table VI

Saturant	Pickup, percent	Tensile strength	Edge- tearing- resistance	Elonga- tion at failure, percent of original length	Product of tensile strength and stretch
A	25	7	11	5	35
B	25	7	10	23	161

As in Example 5, polymer B has a viscosity-average molecular weight of about 170,000. The untreated paper had the following properties:

Tensile strength ----- 0.5 lb./inch width.
Edge-tearing resistance ----- 0.5 lb./inch width.
Basis weight ----- 35 lbs. (3,000 square feet).
Stretch ----- 2% (elongation at failure).

EXAMPLE 7

The pair of aqueous polymer dispersions used as saturants in Examples 1 and 2 were incorporated into a non-"directional" paper predominantly based on Orlon exactly like that of Example 6. The properties obtained were as follows for two levels of pickup:

Table VII

Saturant	Pickup, percent	Tensile strength	Edge- tearing- resistance	Percent stretch	Product of tensile strength and stretch
Polymer A ¹	15	8	11	8	64
Polymer B ²	15	8	15	15	120
Polymer A	50	13	30	18	234
Polymer B	50	15	28	40	600

¹ Acrylic polymer produced in the usual way; viscosity-average molecular weight of at least two million.

² Polymer of reduced molecular weight as in Examples 1 and 2; viscosity-average molecular weight of about 170,000.

EXAMPLE 8

An aqueous copolymer dispersion was prepared by the procedure of Example 1 substituting for the monomers a mixture of 68.8 parts of ethyl acrylate, 28.7 parts of methyl methacrylate, and 2.5 parts of α -methylene- δ -methyl-adipic acid (dimer of methacrylic acid). T_1 equals about 16° C. In Table VIII following, the resulting polymer is called polymer A. Another aqueous dispersion of polymer (B) was prepared from the same mixture of monomers in the same way except the amount of BrCCl_3 was increased to 1.5 parts. The viscosity-average molecular weight (\bar{M}_v) is about 57,000.

The same base paper as that used in Example 1 was saturated as in that example by polymers A and B just described giving properties as in Table VIII.

Table VIII

Saturant	Pickup	Tensile strength		Edge-tearing resistance	
		MD	CD	MD	CD
A-----	Ca. 45%---	31	17	4	6
B-----	do-----	28	15	6	12

EXAMPLE 9

A paper composed of about equal parts of Du Pont papermakers' Dacron fibers and of bleached wood pulp (kraft) fibers had a basis weight of about 56 pounds (3,000 square feet) and the properties indicated below. Aqueous dispersions of three polymers having the composition: ethyl acrylate: 87; methyl methacrylate: 10.5; itaconic acid: 2.5; (T_1 equals about -4.0° C.) were applied to this base paper. The first (A) was produced in the way described in Example 1 but without any chain-transfer agent. Polymer B was produced in the same way but in the presence of 0.5% t-dodecylmercaptan. Polymer C was produced in the same way but in the presence of 0.5% BrCCl_3 . B and C both have approximate molecular weights (\bar{M}_v) of 288,000.

Table IX

Saturant	Pickup	Tensile strength		Edge-tearing resistance		Elongation at failure—percent of original length		Tensile strength—stretch product	
		MD	CD	MD	CD	MD	CD	MD	CD
A-----	Ca. 46%---	24	12	35	20	10	13	240	156
B-----	do-----	23	12	32	20	18	26	414	312
C-----	do-----	23	12	34	21	15	17	345	204
None.	0.0-----	15	6	5	4	3	4	42	24

EXAMPLE 10

Using the base paper of Example 2, a pair of aqueous dispersions of polymers having the composition: ethyl acrylate: 87; methyl methacrylate: 8; methacrylamide: 5; (T_1 equals -2° C.) were used as saturants. Polymer A was produced by the process of Example 1 but without using the chain-transfer agent; polymer B was produced in the same way but in the presence of 0.5% BrCCl_3 and has an \bar{M}_v of about 209,000. The T_1 is about -2° C.

Table X

Saturant	Pickup	Tensile strength		Edge-tearing resistance	
		MD	CD	MD	CD
A-----	Ca. 45%---	23	16	7	10
B-----	do-----	23	15	9	12

EXAMPLE 11

The paper of Example 1 was saturated with aqueous dispersions of polymers prepared as in Example 1 having the composition: ethyl acrylate: 68.8; methyl methacrylate: 28.7; fumaric acid: 2.5. T_1 equals about 16° C. The polymer of reduced molecular weight (B) was produced in the presence of 3.0% BrCCl_3 and has an \bar{M}_v of about 28,300 and a T_1 value of about 16° C. Polymer A of high molecular weight was prepared without a chain-transfer agent.

Table XI

Saturant	Pickup	Tensile strength		Edge-tearing resistance	
		MD	CD	MD	CD
A-----	Ca. 45%---	29	17	5	7
B-----	do-----	25	15	10	13

EXAMPLE 12

The paper of Example 1 was saturated with aqueous dispersions of polymers of the composition: ethyl acrylate: 68.8; methyl methacrylate: 31.2; T_1 equals about 14° C.; the polymer of reduced molecular weight (B) was prepared in presence of 3.0% BrCCl_3 by the procedure of Example 1 and has an \bar{M}_v of about 55,100. Polymer A was of high molecular weight obtained without a chain-transfer agent.

Table XII

Saturant	Pickup	Tensile strength		Edge-tearing resistance	
		MD	CD	MD	CD
A-----	Ca. 45%---	29	16	5	9
B-----	do-----	25	13	9	15

EXAMPLE 13

The paper of Example 1 was saturated with aqueous dispersions of polymers of the composition: ethyl acrylate: 68; methyl methacrylate: 28; methacrylamide: 4. T_1 equals about 17° C. The polymer (B) of reduced molecular weight was prepared in presence of 3.0% BrCCl_3 and has an \bar{M}_v of about 28,300. Polymer A was of high molecular weight obtained without a chain-transfer agent.

Table XIII

Saturant	Pickup	Tensile strength		Edge-tearing resistance	
		MD	CD	MD	CD
A-----	Ca. 45%---	29	17	5	5
B-----	do-----	26	16	8	9

EXAMPLE 14

A paper composed of Du Pont papermakers' nylon fibers and of bleached kraft pulp (approximately 50:50) was saturated with the pair of polymer dispersions described in Example 13. The polymer of reduced molecular weight (B) had an \bar{M}_v of about 28,300. Polymer A had high molecular weight obtained without a chain-transfer agent. The properties of the base paper are given in Table XIV.

Table XIV

Saturant	Pickup	Tensile strength		Edge-tearing resistance		Elongation at failure—percent of original length		Tensile strength—stretch product	
		MD	CD	MD	CD	MD	CD	MD	CD
A-----	Ca. 66%---	45	18	83	35	11	17	495	306
B-----	do-----	39	16	75	31	14	23	546	368
None.	-----	10	4	2	4	2	8	20	32

EXAMPLE 15

The base paper used in Example 14 (50:50 nylon: bleached kraft) was saturated by the procedure of Example 1 with a pair of aqueous dispersions of polymers

of the composition: ethyl acrylate: 97.5; aconitic acid: 2.5. T_1 equals about -5°C . Polymer A was prepared by the process of Example 1 but omitting the chain-transfer agent and had a molecular weight (\bar{M}_v) of about at least two million. Polymer B was produced in the presence of 0.5% chain-transfer agent (BrCCl_3) and had an \bar{M}_v of 132,000. The properties obtained were as follows:

Table XV

Saturant	Pickup	Tensile strength		Edge-tearing resistance		Elongation at failure—percent of original length		(Tensile strength \times elongation) product	
		MD	CD	MD	CD	MD	CD	MD	CD
A-----	Ca. 65%---	24	10	12	18	17	35	408	350
B-----	-----do-----	17	8	20	41	30	61	510	488

It is remarkable that with this particular synthetic fiber paper not only the product obtained by multiplying the tensile strength by the elongation but also the edge-tearing resistance is markedly increased.

We claim:

1. A method which comprises impregnating throughout its mass a porous fibrous saturating paper sheet of 5 to 250 mils thickness formed of cellulosic fibers having a Canadian freeness value of at least 450 with an aqueous dispersion containing 5 to 60% by weight of a water-insoluble polymer of an acrylic acid ester selected from the group consisting of polymers of methyl acrylate and ethyl acrylate, copolymers of acrylic acid esters of alcohols having 1 to 4 carbon atoms with each other and copolymers of an acrylic acid ester of an alcohol having from 1 to 4 carbon atoms with a compound selected from the group consisting of methyl, ethyl, propyl, and butyl methacrylates, styrene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, and vinylidene chloride, said polymer having a T_1 between -17°C . and $+17^{\circ}\text{C}$. and a molecular weight between about 20,000 and 950,000, and subsequently drying the impregnated sheet.

2. A method as defined in claim 1 in which the initial sheet is unmodified by wet-strength resins and the molecular weight of the polymer is between about 20,000 and 300,000.

3. A method as defined in claim 1 in which the initial sheet comprises cellulosic fibers modified by a thermosetting aminoplast resin imparting high wet-strength thereto and the molecular weight of the polymer is between about 20,000 and 300,000.

4. A method as defined in claim 1 in which the polymer contains 0.5 to 7% by weight of polymerized units of a monomer selected from the group consisting of acrylic acid and salts thereof, methacrylic acid and salts thereof, itaconic acid and salts thereof, aconitic acid and salts thereof, maleic acid and salts thereof, fumaric acid and salts thereof, methacrylic acid dimer and salts thereof, methacrylic acid trimer and salts thereof, acrylamide, methacrylamide, N-methyl-acrylamide, N-methylolacrylamide, and N-ethylacrylamide.

5. A method which comprises impregnating throughout its mass a porous fibrous saturating paper sheet of 5 to 250 mils thickness formed of cellulosic fibers having a Canadian freeness value of at least 450 with an aqueous dispersion containing 5 to 60% by weight of a water-insoluble polymer of an acrylic acid ester selected from the group consisting of polymers of methyl acrylate and ethyl acrylate, copolymers of acrylic acid esters of alcohols having 1 to 4 carbon atoms with each other and copolymers of an acrylic acid ester of an alcohol having from 1 to 4 carbon atoms with a compound selected from the group consisting of methyl, ethyl, propyl, and butyl methacrylates, styrene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, and vinylidene chloride, said

copolymer containing 0.5 to 7% by weight of polymerized units of a monomer selected from the group consisting of acrylic acid and salts thereof, methacrylic acid and salts thereof, itaconic acid and salts thereof, aconitic acid and salts thereof, maleic acid and salts thereof, fumaric acid and salts thereof, methacrylic acid dimer and salts thereof, methacrylic acid trimer and salts thereof, acrylamide, methacrylamide, N-methyl-acrylamide, N-methylolacrylamide, and N-ethylacrylamide, said polymer having a T_1 between -17°C . and $+17^{\circ}\text{C}$. and a molecular weight between about 20,000 and 950,000, the impregnation being controlled to deposit at least 10% by weight, based on dry fiber weight, of the polymer on the sheet, and subsequently drying the impregnated sheet and heating the impregnated sheet at a temperature between 210°F . and 400°F . for a period of time to set the polymer and render the dried product solvent-resistant.

6. A method which comprises impregnating throughout its mass a porous fibrous saturating paper sheet of 5 to 250 mils thickness formed of cellulosic fibers having a Canadian freeness value of 675 to 500 with an aqueous dispersion containing 15 to 60% by weight of a water-insoluble polymer of an acrylic acid ester selected from the group consisting of polymers of methyl acrylate and ethyl acrylate, copolymers of acrylic acid esters of alcohols having 1 to 4 carbon atoms with each other and copolymers of an acrylic acid ester of an alcohol having from 1 to 4 carbon atoms with a compound selected from the group consisting of methyl, ethyl, propyl, and butyl methacrylates, styrene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, and vinylidene chloride, said polymer having a T_1 between -17°C . and $+17^{\circ}\text{C}$. and a molecular weight between about 20,000 and 300,000, and subsequently drying the impregnated sheet.

7. A method which comprises impregnating throughout its mass a porous fibrous saturating paper sheet of 5 to 250 mils thickness formed of cellulosic fibers having a Canadian freeness value of 675 to 500 with an aqueous dispersion containing 15 to 60% by weight of a water-insoluble polymer of an acrylic acid ester selected from the group consisting of polymers of methyl acrylate and ethyl acrylate, copolymers of acrylic acid esters of alcohols having 1 to 4 carbon atoms with each other and copolymers of an acrylic acid ester of an alcohol having from 1 to 4 carbon atoms with a compound selected from the group consisting of methyl, ethyl, propyl, and butyl methacrylates, styrene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, and vinylidene chloride, said copolymer containing 0.5 to 7% by weight of polymerized units of a monomer selected from the group consisting of acrylic acid and salts thereof, methacrylic acid and salts thereof, itaconic acid and salts thereof, aconitic acid and salts thereof, maleic acid and salts thereof, fumaric acid and salts thereof, methacrylic acid dimer and salts thereof, methacrylic acid trimer and salts thereof, acrylamide, methacrylamide, N-methylacrylamide, N-methylolacrylamide, and N-ethylacrylamide, said polymer having a T_1 between -17°C . and $+17^{\circ}\text{C}$. and a molecular weight between about 20,000 and 300,000, the impregnation being controlled to deposit at least 10% by weight, based on dry fiber weight, of the polymer on the sheet, and subsequently drying the impregnated sheet and heating the impregnated sheet at a temperature between 210°F . and 400°F . for a period of time to set the polymer and render the dried product solvent-resistant.

8. A method which comprises impregnating throughout its mass a porous fibrous saturating paper sheet of 5 to 250 mils thickness formed of a mixture of cellulosic fibers with fibers selected from the group consisting of glass, nylon, polyethylene glycol terephthalate and copolymers containing 75 to 90% by weight of acrylonitrile, said mixture having a Canadian freeness value of 675 to 500 with an aqueous dispersion containing 15 to 60% by weight of a water-insoluble polymer of an acrylic acid ester selected from the group consisting of polymers of

methyl acrylate and ethyl acrylate, copolymers of acrylic acid esters of alcohols having 1 to 4 carbon atoms with each other and copolymers of an acrylic acid ester of an alcohol having from 1 to 4 carbon atoms with a compound selected from the group consisting of methyl, ethyl, propyl, and butyl methacrylates, styrene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, and vinylidene chloride, said polymer having a T_g between -17°C . and $+17^\circ\text{C}$. and a molecular weight between about 20,000 and 300,000, and subsequently drying the impregnated sheet.

9. A fibrous product comprising a sheet of wet-laid fibers formed of a mixture of cellulosic fibers with fibers selected from the group consisting of glass, nylon, polyethylene glycol terephthalate and copolymers containing 75 to 90% by weight of acrylonitrile, said mixture having a Canadian freeness value of 675 to 500, said product carrying distributed throughout the fibrous mass about 10 to 130% by weight, based on the dry fiber weight, of a water-insoluble polymer of an acrylic acid ester selected from the group consisting of polymers of methyl acrylate and ethyl acrylate, copolymers of acrylic acid esters of alcohols having 1 to 4 carbon atoms with each other and copolymers of an acrylic acid ester of an alcohol having from 1 to 4 carbon atoms with a compound selected from the group consisting of methyl, ethyl, propyl, and butyl methacrylates, styrene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, and vinylidene chloride, said polymer having a T_g between -17°C . and $+17^\circ\text{C}$. and a viscosity average molecular weight between about 20,000 and 300,000.

10. A fibrous product comprising a sheet of a wet-laid mixture of cellulose fibers and polyethylene glycol terephthalate fibers carrying distributed throughout the fibrous mass about 10 to 130% by weight, based on the dry fiber weight, of a water-insoluble copolymer of ethyl acrylate and 0.5 to 7% of itaconic acid, said polymer having a T_g between -17°C . and $+17^\circ\text{C}$. and a viscosity

average molecular weight between about 20,000 and 300,000.

11. A fibrous product comprising a sheet of a wet-laid mixture of cellulose fibers and fibers of an acrylonitrile polymer containing 75 to 90% of acrylonitrile carrying distributed throughout the fibrous mass about 10 to 130% by weight, based on the dry fiber weight, of a water-insoluble copolymer of ethyl acrylate and 0.5 to 7% of itaconic acid, said polymer having a T_g between -17°C . and $+17^\circ\text{C}$. and a viscosity average molecular weight between about 20,000 and 300,000.

12. A fibrous product comprising a sheet of a wet-laid mixture of cellulose fibers and nylon fibers carrying distributed throughout the fibrous mass about 10 to 130% by weight, based on the dry fiber weight, of a water-insoluble copolymer of ethyl acrylate and aconitic acid, said polymer having a T_g between -17°C . and $+17^\circ\text{C}$. and a viscosity average molecular weight between about 20,000 and 300,000.

13. A fibrous product comprising a sheet of a wet-laid mixture of cellulose fibers and nylon fibers carrying distributed throughout the fibrous mass about 10 to 130% by weight, based on the dry fiber weight, of a water-insoluble copolymer of ethyl acrylate, methyl methacrylate, and 0.5 to 7% of methacrylamide, said polymer having a T_g between -17°C . and $+17^\circ\text{C}$. and a viscosity average molecular weight between about 20,000 and 300,000.

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