United States Patent Office 2,964,445
Patented Dec. 13, 1960

2,964,445

METHOD OF SIZING PAPER AND RESULTING PRODUCT

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No Drawing. Filed Nov. 23, 1955, Ser. No. 548,773

14 Claims. (Cl. 162—168)

This invention relates to the sizing of paper, paper board and other products composed of or containing waterlaid cellulose fibers to impart thereto water-resistance, ink-resistance and other properties commonly found in well sized paper. The invention includes methods for the sizing of paper by applying to the cellulosic fibers thereof novel sizing agents by the sizing procedures hereinafter described as well as the novel paper products obtained thereby.

The most widely used sizing agent for paper and other water-laid cellulosic products is ordinary rosin size, which is precipitated on the fibers by the addition of aluminum sulfate or other mordant. Laboratory handsheets made from a pulp of bleached sulfite and bleached soda fibers on a Nash handsheet machine and sized by the addition of from 1% to about 3% of such rosin size, based on the dry weight of the cellulosic fibers, will have a Currier water resistance of about 45–55 seconds and a BKY ink resistance of about 200–250 seconds when measured on sheets having a basis weight of about 50 lbs. This degree of sizing is found in paper that is neutral or slightly acid, but if the paper becomes alkaline the sizing is almost completely destroyed. It is a principal object of the present invention to provide a class of organic sizing agents capable of producing paper having good water-repellency and ink-repellency under alkaline conditions as well as when the paper is neutral or acid.

The tensile strength and bursting strength of paper and other cellulosic products are materially reduced by the incorporation of the presently known sizing agents therein. For example, the rosin sized paper described above has a tensile strength that is about 10% less than that of a corresponding unsized paper prepared from the same stock. Another important object of the present invention is the provision of the particular class of styrene copolymers hereinafter described which actually increase the dry tensile strength and bursting strength of paper and which, in many cases, also impart a measurable increase in the wet strength thereof.

The invention is based on the discovery that a high degree of water-repellency and ink-repellency is imparted to paper and other similar products containing waterlaid cellulosic fibers by applying to the paper, or to the fibers from which it is made, one or more linear chain copolymer resins containing hydrophobic substituents imparting water-repellency thereto and also containing interspersed chain units having substituents containing basic nitrogen salt groups imparting hydrophilic properties to the polymer, followed by developing the sizing properties of the copolymer on the fibers by heating or other after-treatment. These copolymers are applied to the cellulosic fibers in a hydrophilic condition which permits their uniform distribution over the fibers in quantities of about 0.2% to 5%, based on the dry weight of the fibers, usually from a solution in water or a water-containing solvent such as a water-alcohol mixture. When the treated fibers are subsequently dried by heating at temperatures of about 100° C. or higher the copolymer

resin becomes hydrophobic in character and its sizing properties are developed on the fibers. The process of the invention therefore consists, in its broadest aspects, in first applying the hydrophilic linear chain copolymers to the fibers in the quantities indicated and then developing the sizing properties of the copolymers on the fibers either by a heat treatment or by treatment with an organic solvent as will hereinafter be more fully described.

The linear chain copolymers used in practicing the invention are thermoplastic resinous polymerization products of at least two essentially different types of monomers. The first type, which are usually employed in predominant amounts, are monoethylenically unsaturated monomers containing a $CH_2=C<$ or vinyl group having attached thereto hydrophobic substituents capable of imparting water-repellency to the cellulosic fibers; these hydrophobic substituents usually contain hydrocarbon radicals of 6 or more carbon atoms. The monomers of the second type are also monoethylenically unsaturated olefin compounds capable of copolymerizing with those of the first type through a $CH_2=C<$ group but contain either a basic amine substituent or a group capable of being replaced by a basic amine substituent after the copolymer has been formed. These are the essential ingredients of the copolymers used in practicing the invention but it will be understood that other copolymerizable compounds may also be present in minor amounts up to 15–20% of the weight of the copolymer in some cases.

A wide variety of organic monomers containing one or more hydrophobic groups may be used. Typical among these are compounds represented by the formula



wherein R is a hydrophobic group which contains a hydrocarbon radical of 6–18 or more carbon atoms and R′ is hydrogen or an alkyl radical of 1–2 carbon atoms. Examples of this type of compound are the aromatic hydrocarbons containing an olefinic substituent such as vinyl benzene, vinyl toluenes, vinyl naphthalenes and the like. The styrenes including styrene itself and nuclear-substituted styrenes such as ortho-, meta- and para-methylstyrene and mixtures thereof are particularly important and constitute a preferred class of monomers for use in preparing sizes because their copolymers have no adverse effect on the tensile and bursting strength of paper. Halogenated styrenes such as meta- and para-chlorstyrene can likewise be used.

Another important class of hydrophobic monomers are the esters of lower alpha-beta unsaturated aliphatic monocarboxylic acids of 3–6 carbon atoms such as acrylic acid, alpha-methyl acrylic acid, alpha-ethyl acrylic acid and the like with monohydric alcohols containing hydrophobic groups or with higher fatty acid partial esters of polyhydric alcohols such as stearic acid monoglyceride, stearic acid monoester of ethylene glycol and the like. Suitable monohydric alcohols are the aliphatic alcohols containing 6–18 or more carbon atoms in their aliphatic chains and aromatic alcohols such as benzyl alcohol and the like. Another important class consists of esters of the corresponding alpha-beta unsaturated aliphatic alcohols of 2–4 carbon atoms such as esters of vinyl alcohol with monocarboxylic acids containing aliphatic or aromatic hydrocarbon radicals of 6 or more carbon atoms. Typical carboxylic acids of this type are caproic acid, caprylic acid, capric acid, lauric acid, palmitic acid, stearic acid, benzoic acid, ortho-, meta- and para-toluic acids and other alkylbenzoic acids, cycloaliphatic acids such as naphthenic acids, naphthoic acids

and phenylacetic acid and similar aromatic-substituted aliphatic acids.

Typical of the monomers of the second class, which are employed for the purpose of imparting hydrophilic properties to the copolymers, are the olefin-substituted heterocyclic compounds containing a basic ring nitrogen such as the vinyl pyridines, vinyl quinolines and the basic nitrogen-containing esters of alpha-beta monoethylenically unsaturated acids. Esters of the lower alpha-beta unsaturated monocarboxylic acids with tertiary alkamines such as dimethylaminoethyl acrylate or methacrylate and 2-dimethylamino-1-methyl-ethyl acrylate or methacrylate may be used. Dialkylaminoalkylamides such as dimethylaminoethyl acrylamide may likewise be used.

Monomers containing a group that is reactive with or replaceable by a basic nitrogen substituent after the copolymer has been formed are typified by the esters of olefin alcohols described above with halogen-substituted carboxylic acids of the aliphatic series such as monochloracetic acid, monochloropropionic acid and the like.

Copolymers of compounds selected from the above two classes should contain from 1 to about 15 molar proportions of the hydrophobic monomer for each mol of the hydrophilic or potentially hydrophilic ingredient, the optimum proportions depending on the particular hydrophobic radicals present and on the degree of solubilizing power of the hydrophilic radicals employed. When the copolymer is made hydrophilic by conversion of part or all of its basic nitrogen groups into quaternary ammonium salt groups, which is the preferred solubilizing procedure, the optimum molar proportions will depend on the degree of quaternization. Thus when styrene is used as the hydrophilic monomer and at least 25% of the basic nitrogen groups are converted into quaternary ammonium salt groups by after-treatment of the copolymer with an alkyl halide the preferred ratio is from about 1 to 10 mols of styrene for each mol of basic monomer. When lauryl or stearyl acrylates or methacrylates are substituted for part or all of the styrene the same molar proportions (i.e., 1–10 mols of acrylate for each mol of basic monomer) may be used, but with molar ratios of more than 5:1 the degree of quaternization should preferably be at least 50%. In general, the necessary proportions of monomers of the two classes are those which will impart satisfactory water-repellency or sizing to the paper while obtaining a copolymer that can be rendered water-soluble or water-dispersible by the formation of basic nitrogen salt groups therein.

The copolymerization reaction can be carried out by any of the procedures known to be effective in polymerizing vinyl compounds. Preferably a small quantity on the order of 0.1–2% on the weight of the monomers of a polymerization initiator such as azobisisobutyronitrile, benzoyl peroxide, cumene hydroperoxide, pinane hydroperoxide and the like is added after which the reaction mixture is heated at temperatures of about 50°–150° C. until the copolymerization has been carried to the desired extent. Bulk polymerization procedures may be used in which the reagents are simply heated together in a closed vessel or the polymerization can be carried out in an organic solvent such as dioxane, toluene or other aromatic hydrocarbon solvent and the like. Emulsion polymerization procedures may also be used if desired; for example, by emulsifying a mixture of the monomers and polymerization inhibitor in water containing a suitable emulsifying agent such as the sodium soaps of completely disproportionated rosin, followed by heating the emulsion in an autoclave at temperatures of 80°–140° C. for the time necessary to carry out the polymerization.

The copolymers used in practicing the invention are thermoplastic resins which are insoluble in water and therefore must be solubilized so that they can be applied uniformly to the cellulosic fibers in the amounts of about

0.2–5% and preferably 0.5–3% with which optimum sizing properties are developed. In practicing the invention they are therefore solubilized by converting part or all of their basic nitrogen groups into the corresponding salt groups. This can be done by reaction with water-soluble acids such as acetic acid or hydrochloric acid but is preferably accomplished by quaternization with alkyl halides such as benzyl chloride, butyl bromide or other well-known quaternizing agents. As will be shown in the following examples, copolymers in which as little as about 25% of the basic nitrogen groups are quaternized may possess the requisite hydrophilic properties necessary for application to the cellulosic fibers of paper by beater sizing or tub sizing processes; from this minimum the degree of quaternization can be increased to as much as 90–100%. When the salt formation is accomplished by reaction with a water-soluble acid, usually all of the basic nitrogen of the copolymer is converted into the corresponding salt groups.

The molecular weights of the copolymers are not particularly important provided the degree of polymerization is such that water-insoluble thermoplastic resins are obtained. This occurs when the copolymers have attained molecular weights of at least 10,000, although it will be understood that the resins produced by the above-described processes ordinarily have molecular weights substantially higher than this minimum and usually within the range of about 50,000 to 500,000 or higher.

It will be seen, therefore, that the linear carbon chain polymers used in practicing the invention are copolymers of (*a*) polymerizable monomers containing hydrophobic substituents capable of imparting water-repellent properties to the fibers to which the copolymer is attached, which substituents are preferably hydrocarbon radicals of at least 6 carbon atoms such as phenyl and alkylphenyl radicals or aliphatic hydrocarbon radicals of 6–18 or more carbon atoms and (*b*) monomers copolymerizable with (*a*) and having substituents containing basic nitrogen groups, all or part of which have been converted into basic nitrogen salt groups either by forming simple salts of the copolymers with acids or by conversion of the copolymers into quaternary ammonium salts. In all of these copolymers the molar ratio of (*a*) to (*b*) is within the range of from 1:1 to about 15:1 and preferably between 1:1 and 10:1. In the quaternary ammonium salts the ratio of quaternized basic nitrogen groups to unquaternized or free basic nitrogen groups is most frequently within the range of from about 3:7 to 9:1 whereas in the salts with water-soluble acids such as acetic acid or hydrochloric acid the salt formation is substantially complete.

Although satisfactory water-repellency and ink-repellency can be developed in paper by the application thereto of the indicated quantities of copolymers prepared from any of the hydrophobic monomers outlined above, an unusual and extremely valuable combination of properties is obtained when a styrene is used as the principal hydrophobic monomer. I have found that the copolymers of styrenes with basic monomers of the types described above, when converted into the corresponding hydrophilic quaternary ammonium salts or water-soluble acid salts and applied to paper, do not decrease the dry tensile strength or bursting strength of the paper. Instead, they actually increase the dry strength of the paper materially and also increase the wet tensile strength thereof in addition to imparting good water-repellency and ink-repellency thereto. No other sizing composition of which I am aware is capable of increasing the dry strength of paper while imparting the requisite degree of sizing thereto.

The hydrophilic or water-solubilized copolymer resins may be applied to cellulosic paper fibers by soaking formed paper in an aqueous solution thereof or by brushing or spraying a solution of the resin in water or an organic solvent onto the paper. These and similar procedure in which

a size is applied to preformed paper are known collectively as tub sizing methods, and may be used in practicing the present invention if desired. Ordinarily quantities of about 0.2% to 5% of the solublized copolymer resin, based on the dry weight of the paper, are applied when tub sizing procedures are used and the paper is subsequently dried by heating at temperatures of at least 100° C. and preferably about 110°–140° C. for about 1–5 minutes. The sizing properties of the copolymer resin are developed on the paper by this procedure and paper having good water-repellency and ink-repellency is obtained.

The preferred method of practicing the process of the invention is, however, by applying the hydrophilic or solubilized copolymer resin to cellulosic papermaking fibers in aqueous suspension before they have been formed into paper; i.e., by the so-called beater sizing procedure. In this process the paper pulp is suspended in water and beaten to the desired degree of freeness and the requisite quantities of solubilized copolymer are added to and dissolved in the resulting paper stock suspension. Because of the substantive properties imparted by their basic nitrogen salt groups, the copolymer resins are adsorbed or exhausted substantially completely and uniformly on the paper fibers, even in dilute stock suspensions containing 0.5% to 6% solids, and therefore the particles of copolymer resin are attached uniformly to the cellulosic fibers. Fillers such as china clay and pigments such as titanium dioxide, calcium carbonate and the like may then be added if desired and the stock is formed into paper or board by any suitable forming procedure as on a Fourdrinier or cylinder papermaking machine. The paper is dried by the customary procedures, such as by passing it in contact with steam heated rolls, and by this means is heated to temperatures of 100° C. or higher with the result that the sizing properties of the copolymer resin are developed and water-repellent and ink-repellent paper is obtained. The optimum quantities of copolymer resin applied by beater sizing procedures are from about 0.2% to 5% based on the dry weight of the cellulosic papermaking fibers; usually quantities on the order of about 0.5% to 3% on the dry weight of the fibers are preferred.

Only a comparatively slight degree of sizing is imparted to paper by the linear carbon chain copolymer resin salts of the invention in the condition in which they are originally adsorbed on the paper fibers. Thus, paper formed from cellulosic fibers pretreated with 1% by weight of a 5:1 styrene-2-methyl-5-vinyl pyridine quaternary ammonium salt and air-dried without heating is only slightly more water-repellent and ink-repellent than a corresponding paper containing no sizing agent at all. However, when the paper is heated to temperatures of about 100° C. or higher the sizing properties of the copolymer resin are developed and the paper has good water-repellency and ink-repellency. The sizing properties of the copolymer can also be developed on paper to a corresponding degree by impregnating the paper with a solvent for the resin such as benzene, toluene, solvent naphtha and the like. Apparently the heating or solvent treatment brings about an orientation of the linear chain copolymer molecules on the cellulosic fibers of the paper such that good water-repellency is developed thereon. It will be understood, therefore, that as used in the present specification and claims the term "developing" the sizing properties of the copolymer of cellulosic fibers is intended to designate a suitable after-treatment of the paper, such as by heating or solvent treatment, which will bring out the latent water-repellency of the treated fibers.

The invention will be further described and illustrated by the following specific examples which show the preparation of typical linear carbon chain copolymers of the type described above and the application thereof to paper. In order to demonstrate the sizing obtained by these procedures the results of extensive laboratory tests of the paper are given and the particular testing procedures employed are designated in the headings of the tables in the examples. These tests are as follows:

The Currier test is a method of determining the rate of penetration of paper by water. It is based on the principle that as moisture gradually penetrates the paper, the latter becomes a better conductor of electricity. The apparatus consists of a means for wetting the paper in a uniform and reproducible way, and for measuring its conductivity over a suitable interval of time. The results are reported as the number of seconds necessary for the water to penetrate the paper until a predetermined degree of electrical conductivity has been obtained.

The Cobb test is a measure of the weight of water or other test liquid that will be absorbed by the paper in a given period of time. The test is conducted by first weighing a sample 12.5 cm. square, covering its central portion with a metal cylinder 10 cm. in diameter and pouring 25 cc. of water or other test liquid into the cylinder. After 15 minutes (or other predetermined test time) the excess water is poured off, surface moisture is removed from the paper, and the sample is again weighed. The weight of the adsorbed water is multiplied by 8 and the test results are reported as grams of moisture adsorbed by a sheet 100 cm. square.

The BKY tester measures the resistance of paper to ink by wetting the lower side of a sample with ink and measuring the time required for the reflectance to fall to a predetermined value.

The Cobb test and the Currier test are described in "A Laboratory Handbook of Pulp and Paper Manufacture," by Julius Grant, Longmans Green & Company, New York (1942), pages 218–220.

The Mullen test measures the bursting strength of a sample of paper and is reported as the number of pounds per square inch necessary to rupture a sample secured over a circular orifice having an effective diameter of 1.2 inches.

The tensile strength test measures the breaking strength of a strip of the paper and is reported as the number of pounds necessary to break a ribbon of paper 1 inch wide.

The basis weight of the paper is expressed as the weight in pounds of 500 sheets 25 inches by 40 inches in size.

Example 1

A styrene-dimethylaminoethyl methacrylate copolymer was prepared by heating a mixture of 52.05 grams (0.5 mol) of styrene, 15.7 grams (0.1 mol) of dimethylaminoethyl methacrylate and 0.068 gram of azobisiobutyronitrile as polymerization initiator. The mixture was heated at 60° C. for 16 hours and then polymerized at 105° C. for three days and then for one day at 150° C.

A portion of the resulting polymer was quaternized by refluxing it in dioxane with 28% of its weight of benzyl chloride for 30 minutes. The quaternary salt was dissolved by adding sufficient 50% aqueous isopropanol to give a 5% solution followed by dilution with water to 2% solids.

The product was evaluated as a sizing agent in paper prepared from a 60–40 sulfite-soda pulp. The stock was prepared by beating the sulfide pulp for 15 minutes in a laboratory beater, adding the soda pulp and beating for 5 minutes more. The Green freeness was then about 330 ml.

Samples of the beaten fiber suspension were treated with 1% of the resin (resin solids based on the dry weight of the pulp) after which the pH was adjusted by adding sodium hydroxide or hydrochloric acid where necessary to the values indicated in the following table. The stock was then made into 4.8 gram sheets of paper on a laboratory sheetmaking machine and the sheets were dried for 1 minute at 240° F. These sheets were tested for mechanical strength, wax pick and water and

ink resistance. Heavier sheets, weighing 20 grams and having a basis weight of about 200 lbs., were also made and dried at 240° F. for three minutes; these were used in the Cobb and lactic acid tests. The test results were as follows:

CONTROL

pH of Stock	8	4	7	9	10	11
Basis wt., lbs.	47.3	48.1	47.6	47.3	46.2	49.2
Mullen, lbs., dry	24.0	29	27.5	27.0	27.5	28.5
Mullen, lbs., wet	5.0	6.5	6.0	6.5	6.0	5.5
Tensile, lbs. per in., dry	15.6	16.8	17.0	17.2	16.7	17.7
Tensile, lbs. per in., wet	0.4	2.2	2.2	1.7	1.7	1.5
Fold, M.I.T.	21	34	40	36	38	38
Tear (Elmendorf), grams	45	44.5	43.0	42	40	44.5
Wax rick (Dennison)	8.5	9.5	8.5	8.0	8.0	8.0
Currier (water), sec.	Inst.	54	54	45	35	11
BKY (ink), sec.	Inst.	1,200	1,300	495	440	75
Cobb (15 min.—5% Na_2CO_3 at 73° F.), grams		0.83	0.80	0.85	0.77	1.01
Lactic acid, 20% at 100° F., sec.		155	110	95	65	20

These results show that paper sized with linear styrene copolymers possess a very unusual combination of properties. In addition to water and ink repellency under acid, neutral and alkaline conditions comparable to that obtained with rosin size under neutral and acid conditions only, the copolymers substantially improve the dry strength of the paper and also impart an appreciable degree of wet strength whereas the conventional sizes for acidic papers, such as wax and rosin size, either have no effect or a deleterious effect on dry strength.

Example 2

Copolymers of styrene with 2-methyl-5-vinyl pyridine were prepared in varying molecular ratios of 2:1, 5:1 and 10:1 by heating mixtures of the two materials in sealed tubes with 0.1% of azoisobutyronitrile under a nitrogen atmosphere. The polymerization was carried out at 60° C. for 17 hours followed by a final 24 hour heating at 150° C. The polymers were then crushed, dissolved in methyl ethyl ketone and precipitated by pouring into large volumes of n-hexane. By this procedure it was determined that the conversion into a polymer was close to 100% in all cases.

Portions of each of the copolymers were quaternized by heating with benzyl chloride and portions of some were quaternized with butyl bromide. In both cases the reagents were mixed together in nitromethane as the solvent and heated at 80° C. for 41 hours followed by evaporation to dryness at 60° C. and drying at 40° C. under a vacuum.

Several of the products were analyzed to determine their content of combined halogen. The 2:1 and 5:1 copolymers quaternized with benzyl chloride contained 5.7% and 3.5% total chloride, respectively, theory for 100% quaternization being 7.8% and 4.0%. The 2:1 copolymer quaternized with butyl bromide contained 13.3% Br, theory being 17.2%.

The products were designated as follows:

Sample No.	Styrene:MVP Ratio	Salt Former
1	2:1	Butyl bromide.
2	2:1	Benzyl chloride.
3	5:1	Butyl bromide.
4	5:1	Benzyl chloride.
5	10:1	Do.

Each of these materials was incorporated into paper pulp in the quantities indicated below and the stock was made into paper and tested for strength and degree of sizing by the procedures described in Example 1. In all cases the pH of the stock suspension was 8.0. The test results were as follows:

Sample No.	Percent Added	Tensile, lbs./in.		Size Tests	
		Dry	Wet	P.S.S.	BKY
1	0.5	17.1	1.6	30	655
2	0.33	17.1	1.4	10	>580
3	0.5	17.7	1.8	32	1,390
4	0.5	17.5	1.3	27	770
5	1.0	17.2	1.2	34	1,191
Control		15.4	<0.4	Inst.	Inst.

These results indicate that the solubilized styrene-methyl vinyl pyridine copolymers increase both the dry and wet tensile strength of paper while imparting good water and ink repellency thereto.

Example 3

A tripolymer was prepared by heating a mixture of 3 mols of styrene, 0.3 mol of lauryl methacrylate and 1 mol of 2-methyl-5-vinyl pyridine by the procedure of Example 2. The nitrogen content of the copolymer was 2.76%. One portion was quaternized by heating with 8 equivalents of benzyl chloride for 4 hours at 80° C. using dioxane as the solvent. The chloride content was found to be 5.15%, indicating that more than 90% of the basic nitrogen groups of the copolymer had been quaternized.

The product was tested as a cationic sizing agent for paper by the procedure described in Example 1, the pH of the stock suspension being 8.0. The following results were obtained:

Conc. in Pulp, Percent	Dry Strength (Mullen)	Water Repellency (Currier)
0.5	25	26
1.0	23.5	44
2.0	26	57
3.0	24.5	54
Control	23	Inst.

Example 4

A styrene-stearyl methacrylate-methyl vinyl pyridine having the same molar ratios of ingredients as the product of Example 3 was prepared by the process of that example. It contained 2.72% of nitrogen. The polymer was quaternized by heating with 8 equivalents of benzyl chloride in dioxane for 2 hours at 80° C. and was added to paper pulp suspensions which were made into paper at a pH of 8.0 and tested as previously described. The test results are shown in the following table:

Conc. in Pulp, percent	Basis Wt.	Dry Tensile, lbs./in.	Water Repellency, Currier	Ink Repellency, BKY
0.25	43.8	13.1	10	184.
0.5	46.0	12.9	35	442.
1.0	44.6	13.3	40	629.
2.0	46.5	13.4	39	1,115.
3.0	45.4	12.9	43	642.
Control	44.1	13.2	Instant	Instant.

Example 5

In order to investigate the effect of varying degrees of quaternization a series of styrene-methyl vinyl pyridine copolymers were prepared and reacted with varying proportions of benzyl chloride for varying times.

Mixtures of styrene and methyl vinyl pyridine were heated in toluene with 0.1% of benzoyl peroxide as the

catalyst and the conversions were stopped at a relatively low degree of polymerization to ensure homogeneity of composition in the copolymer. Four products were made by this procedure having molecluar ratios of styrene to MVP of 2:1, 4:1, 7:1 and 10:1. These were quaternized with benzyl chloride at 80° C. using dioxane (25 cc. for each 5 grams of copolymer) as the solvent. The quantities of benzyl chloride used and the degree of quaternization of the products obtained are shown in the following table:

Prod. No.	Styrene: MVP Ratio	Quaternary No.	Equivalents of BzCl Used	Hrs. at 80° C.	Degree of Quaternization, Percent
1	2:1	I	0.5	2	27
2	2:1	II	1.0	2	37
3	4:1	I	0.5	2	26
4	4:1	IV	10.0	2	60
5	4:1	VI	10.0	21	75
6	7:1	II	10.0	6	65
7	10:1	I	10.0	16	26
8	10:1	II	20.0	16	85

The products were dissolved in water by first swelling them in dioxane and then diluting with water to a 1% solution. In most cases the resulting solutions were clear, but in product No. 7 a milky white dispersion was obtained due to the combined effects of the low pyridine content and the low degree to which it was quaternized.

Representative products of this series were incorporated into aqueous paper pulp suspensions which were made into handsheets at a stock pH of 8.0. The paper was then tested with the following results.

PRODUCT NO. 1

Conc. in Pulp	Basis Wt.	Dry Tensile, lbs./in.	Water Resistance, Currier	Ink Resistance, BKY
0.75	46.0	15.0	28	135
1.0	46.0	15.4	41	145
2.0	46.5	16.6	49	200

PRODUCT NO. 2

0.75	46.5	15.4	35	130
1.0	46.2	16.3	43	128

PRODUCT NO. 3

1.0	46.0	15.4	40	590
2.0	47.4	16.6	50	>600
3.0	48.7	17.2	55	>600
5.0	46.4	16.4	50	>600

PRODUCT NO. 4

0.75	48.0	15.8	38	555
1.0	48.8	15.9	44	755
2.0	47.7	15.7	32	520
3.0	45.5	15.1	22	310

PRODUCT NO. 5

1.0		14.2	39	
2.0		15.5	55	
3.0		14.7	62	
5.0		14.3	53	
Control	46.9	14.2	Instant	Instant

PRODUCT NO. 6

0.5	48.0	15.8	3	60
0.75	46.5	15.0	35	335
1.0	48.2	16.7	44	835
2.0	49.5	18.3	59	>600
3.0	48.9	18.6	66	>600
4.0	47.8	18.4	67	>600

PRODUCT NO. 7

Conc. in Pulp	Basis Wt.	Dry Tensile, lbs./in.	Water Resistance, Currier	Ink Resistance, BKY
0.5	48.1	15.1	21	295
0.75	48.3	15.7	43	730
1.0	48.3	16.2	47	>600
1.5	48.9	17.0	57	>600
2.0	49.3	16.9	64	>600
3.0	48.3	15.6	58	>600
4.0	47.8	15.6	48	>600
5.0	48.7	15.2	49	>600
Control	48.7	15.1	Inst.	>600

PRODUCT NO. 8

1.5	48.5	16.3	52	>600
2.0	48.0	17.3	57	>600
3.0	48.7	17.4	67	>600
4.0	48.1	17.8	68	>600
5.0	47.9	16.8	63	>600

Example 6

Copolymers of stearyl methacrylate (SMA) and dimethylaminoethyl methacrylate (DMAEMA) were prepared at molar ratios of 1.2:1 (resin A) and 1.8:1 (resin B). The preparation of resin A is typical and was carried out by heating to reflux in a flask equipped with a stirrer and reflux condenser a mixture of 34 grams (1 mol) of SMA, 13 grams (0.083 mol) of DMAEMA and 50 cc. of dioxane and adding a total of 0.94 gram of cumene hydroperoxide (2% of the monomers) in one-quarter portions at the start of refluxing and at 30-minute intervals thereafter. After refluxing for 3 hours no further increase in viscosity was noted and the solvent was therefore removed by distillation and stripping under a vacuum. The distillate titrated 0.52% alkalinity as DMAEMA, indicating little residual basic monomer.

Part of the polymer solids was dissolved in two molar equivalents of acetic acid and sufficient water to form a 2.5% solution. Hydrochloric acid was used to dissolve another part and a third part was quaternized with benzyl chloride. Portions of the resin solutions were added to aqueous paper pulp suspensions which were made into paper at a pH of 5.0. Handsheets were also made from the same stock to which sufficient NaOH was added to raise the pH to 8.0. The paper was dried for 1 minute at 265° F. except where otherwise noted. The papermaking conditions and test results are shown in the following table:

Resin	Percent in Paper	pH	Basis Wt.	Tensile lbs./in.	Water Resistance, Currier	Ink Resistance, BKY
A (acetic acid)	5	5	43.8	4.6	24	[1] >600
	5	5	45.5		28	[2] >600
	2.5	5	46.1	4.2	32	>600
	1.25	5	46.9	6.2	30	175
	5	5	47.6	5.1	33	>600
	2.5	5	47.1	5.5	35	>600
	1.25	5	48.7	6.2	50	>600
	1.00	5	46.5	6.6	51	>600
B (acetic acid)	0.5	5	45.2	8.3	43	>600
	[3] 1.25	5	45.2	7.6	52	>600
	1.25	8	47.0	8.1	41	>600
	1.0	8	45.2	7.7	45	>600
	0.5	8	44.6	7.9	41	>600
A (HCl)	1.25	8	47.0	9.8	49	>600
A (benzyl chloride)	1.25	8	44.9	9.6	36	>600

Note [1]—Paper dried 2 minutes at 240° F.
Note [2]—Paper dried 2 minutes at 265° F.
Note [3]—3% alum added.

Example 7

A mixture of 15.6 grams (0.102 mol) of commercial vinyl naphthalene, consisting of approximately equal pro-

portions of alpha-vinyl and beta-vinyl naphthalenes, and 3.46 grams (0.3 mol) of 2-methyl-5-vinyl pyridine was copolymerized by heating with 0.019 gram of azobisisobutyronitrile at 70° C. for 3 hours. The polymer was dissolved in toluene and precipitated by pouring into a large volume of hexane and the precipitate was vacuum dried at 50° C. The purified polymer was a white powder weighing 10.2 grams.

A solution of 4 grams of the copolymer and 1.76 grams (2 molar equivalents) of benzyl chloride were suspended in 20 grams of dioxane and heated with stirring at 80° C. for 2 hours. The solvent was then distilled off and the quaternized salt (resin A) was vacuum dried at 60° C. to yield 5 grams of product.

This material was dissolved in dioxane, diluted with water and added to paper pulp suspensions which were made into paper at a pH of 8.0 and tested for tensile strength and sizing.

A copolymer of vinylnaphthalene with dimethylaminoethyl methacrylate was also prepared by the same procedure using 9.4 grams of vinyl naphthalene, 2.82 grams of DMAEMA and 0.12 gram of azobisisobutyronitrile. The quaternary compound (resin B) was made by reacting 4 grams of the copolymer with 0.456 gram of benzyl chloride in 20 cc. of dioxane. After drying a portion was dissolved in dioxane and the solution was diluted with water to 5% solids and added to paper pulp suspensions which were made into paper at a pH of 8.0. The test results are shown in the following table:

Resin	Percent in Paper	Basis Wt.	Tensile		Currier	BKY
			Dry	Wet		
A	1.0	46.8	14.8	0.5	4	110
A	1.5	48.0	16.3	0.9	38	360
B	1.0	45.5	15.4	0.7	26	525
B	1.5	46.3	15.4	1.0	37	485
Control		45.3	13.7	0.5		

Example 8

A copolymer was prepared by charging 26 grams of styrene, 5.96 grams of 2-methyl-5-vinyl pyridine (5:1 ratio) and 0.32 gram of azobisisobutyronitrile into sealed tubes under a nitrogen atmosphere and heating at 70° C. for 40 hours and then overnight at 100° C. A portion of the product weighing 4 grams was dissolved in 20 cc. of monobutyl ether of ethylene glycol along with 1.6 grams of benzyl chloride and heated with stirring at 160° C. for one-half hour. The solution was then diluted to 100 grams with 50% aqueous dioxane and further diluted with water to 400 grams (resin A).

Another 4-gram portion was quaternized with the same quantity of benzyl chloride in the same solvent by heating for 3 hours with stirring at 80° C. and then diluted by the same procedure (resin B).

Another copolymer was prepared at a styrene-MVP ratio of 7:1 and samples were quaternized with the same proportions of benzyl chloride in the same solvent at 160° C. (resin C) and at 80° C. (resin D) and dissolved in water by the same procedure.

The resins were added to aqueous paper pulp suspensions which were made into paper at a pH of 8.0 and tested as previously described. The test results were as follows:

Resin	Percent in Paper[1]	Basis Wt.	Tensile lbs./in.	Currier	BKY	Cobb	Lactic Acid
A	0.5		15.1	42	370		
	0.75		16.9	49	890		
	1.0		16.4	49	1,275		
	3.0		15.2	48	2,390		
	5.0		14.2	51	2,545		
B	0.5		16.4	35	310		
	0.75		16.4	44	560		
	1.0		16.8	45	975		
	3.0		16.0	54	>1,000		
	5.0		15.2	52	>1,000		
C	0.5	47.4	15.3	38	405	1.15	<10
	0.75	47.7	15.8	48	800	0.96	55
	1.0	47.6	16.4	52	>1,050	0.88	120
	1.5	47.2	16.6	61	>600	0.72	280
	2.0	47.7	16.7	66	>1,100	0.67	490
	3.0	47.7	16.6	75	>600	0.77	425
D	0.5	46.3	14.9	4	50	1.46	Inst.
	0.75	47.5	15.5	37	330	0.99	35
	1.0	49.0	16.8	50	500	0.99	125
	1.5	49.1	17.7	51	1,215	0.88	700
	2.0	48.0	17.4	56	1,865	0.72	1,940
	3.0	48.8	18.6	72	>1,100	0.72	2,715
Control		46.3	13.8	Inst.	<5	7.57	Inst.

[1] Percent added, based on paper.

Example 9

A vinyl stearate-vinyl chloroacetate copolymer was prepared by reacting together a solution of 31 grams (0.1 mol) of vinyl stearate and 12 grams (0.1 mol) of vinyl chloroacetate in 36 grams of benzene containing 0.26 grams (0.001 mol) of benzoyl peroxide. This reaction was carried out by boiling the solution under a reflux condenser for 6½ hours after which the copolymer was isolated by pouring the charge into a larger quantity of methanol. The weight of the recovered product was 43 grams, or about 87% of the monomers charged.

The pyridine quaternary was prepared by heating the polymer with 2 equivalents of pyridine in dioxane at 80° C. for 3 hours followed by evaporation to dryness. Portions of the product were dissolved in water and added to aqueous suspensions of sulfite-soda paper pulp having a pH of 8 and the stock was made into paper by the procedure described in Example 1. The paper was tested with the following results:

Sheet No.	Percent Resin Added	Basis Wt.	Currier	BKY	Cobb Test		20% Lactic Acid
					30 Min., Water	15 Min., 5% Na_2CO_3	
1	0.25	47.6	43	>1,800	0.85	1.33	260 Sec.
2	0.5	46.3	54	>1,800	0.83	0.61	>1 Hr.
3	1	46.5	58	>1,800	0.69	0.53	>1 Hr.
4	3	46.8	88	>1,800	0.75	0.45	>3 Hrs.
5	None	45.0	Instant				

Handsheets were also made from the same stock containing the same quantities of the resin but having pH values of 5 and 9.2. Similar test results were obtained, showing that the copolymer is effective both under acid conditions and under more strongly alkaline conditions.

Example 10

Copolymerization products of styrenes with vinyl pyridines were prepared as shown in the following table and quaternized with benzyl chloride to the extent indicated.

Resin No.	Monomers	Molar Ratio	Percent Quaternization
1	Styrene:4-vinyl pyridine	9:1	85
2	Methylstyrene:2-methyl-5-vinyl pyridine.	4:1	76.6
3	Styrene:2-methyl-5-vinyl pyridine	2:1	36.5
4	Styrene:2-methyl-5-vinyl pyridine	7:1	65

The procedure used in making these products is typified

by the preparation of resin No. 1. A reaction flask was charged with 93.8 grams of styrene, 10.5 grams of 4-vinyl pyridine and 417.2 grams of toluene, the mixture was heated and 1.04 grams of benzoyl peroxide were added. The charge was then refluxed with stirring for 5¼ hours, poured into hexane and the gummy solid that precipitated was vacuum dried at 55° C. for 8 hours. The dried product weighed 38 grams.

A portion of the product weighing 9 grams were suspended in 90 cc. of nitromethane, 20 cc. of benzyl chloride were added and the mixture was heated at 80° C. for 40 hours. The nitromethane solvent was evaporated on a steam bath and the product was vacuum dried at 45° C. The yield was 10.7 grams.

A portion of each resin weighing 2 grams was dissolved in a mixture of 20 cc. of dioxane and 10 cc. of water and the solutions were further diluted with water to 200 cc. Sheets of bond paper were saturated with these solutions, passed through squeeze rolls and dried by heating for 1 minute at 240° F. The paper used contained rosin size and had a BKY ink penetration time of 376 seconds. The corresponding values of the resin-impregnated sheets were as follows:

Resin No.	Percent in Paper	Ink Penetration time, Seconds
1	0.30	628
2	0.27	753
3	0.26	538
4	0.24	589

What I claim is:

1. A method of sizing paper containing cellulosic fibers which comprises applying to said fibers about 0.2% to 5%, based on the dry weight of the fibers, of a linear carbon chain copolymer salt obtained by copolymerizing at least one monomer containing a $CH_2=C<$ group having an attached substituent containing a hydrocarbon radical of at least 6 carbon atoms and a monoethylenically unsaturated monomer copolymerizable therewith having a substituent containing a basic nitrogen group followed by converting the resulting copolymer into a hydrophilic salt, the molar ratio of said hydrocarbon-substituted monomer to said basic nitrogen-containing monomer being from 1:1 to 15:1, and then developing the sizing properties of said copolymer on said fibers by heating the paper at a temperature of at least 100° C., thereby producing paper having good water-repellency and ink-repellency under both acid and alkaline conditions.

2. Sized paper composed of cellulosic fibers and having good water-repellency and ink repellency under both acid and alkaline conditions, said paper being the product produced by the process of claim 1.

3. A method according to claim 1 wherein the copolymer salt is applied by adding it to and dissolving it in a water suspension of cellulosic papermaking fibers, thereby adsorbing the copolymer uniformly on the fibers, and then forming the fibers so pretreated into paper.

4. A method of sizing paper containing cellulosic fibers which comprises applying to said fibers about 0.2% to 5%, based on the dry weight of the fibers, of a linear chain copolymer salt obtained by copolymerizing at least one monomer containing a $CH_2=C<$ group having an attached substituent containing a hydrocarbon radical of at least 6 carbon atoms and a monoethylenically unsaturated monomer having a substituent containing a basic nitrogen group followed by quaternizing at least 25% of the basic nitrogen groups of the copolymer to quaternary ammonium salt groups, the molar ratio of said hydrocarbon-substituted monomer to said basic nitrogen-containing monomer being from 1:1 to 15:1, and then developing the sizing properties of said copolymer on said fibers by heating the paper at a temperature of at least 100° C., thereby producing paper having good water-repellency and ink-repellency under both acid and alkaline conditions.

5. A method of sizing paper containing cellulosic fibers to impart both water-repellency and increased dry tensile strength thereto which comprises applying to said fibers about 0.2% to 5%, based on the dry weight of said fibers, of a linear chain copolymer salt obtained by copolymerizing a styrene and a vinyl-substituted organic nitrogen base in a molar ratio between about 1:1 and 15:1 and converting the resulting copolymer into a hydrophilic salt and then developing the sizing properties of said copolymer on said fibers.

6. Sized paper composed of cellulosic fibers and having both good water-repellency and increased dry tensile strength, said paper being the product produced by the process of claim 5.

7. A method according to claim 5 wherein the copolymer salt is applied by adding it to and dissolving it in a water suspension of cellulosic papermaking fibers, thereby adsorbing the copolymer uniformly on the fibers, and then forming the fibers so pretreated into paper.

8. A method of sizing paper containing cellulosic fibers to impart both water-repellency and increased dry tensile strength thereto which comprises applying to said fibers about 0.2% to 5%, based on the dry weight of said fibers, of a linear chain copolymer salt obtained by copolymerizing a styrene and a vinyl-substituted organic nitrogen base in a molar ratio between 1:1 and 10:1 and converting the resulting copolymer into a hydrophilic quaternary ammonium salt and then dveloping the sizing properties of said copolymer on said fibers by heating the paper at a temperature of at least 100° C.

9. A method of sizing paper containing cellulosic fibers which comprises applying to said fibers about 0.2% to 5%, based on the dry weight of said fibers, of a linear chain copolymer resin salt obtained by copolymerizing an ester of an alpha-beta unsaturated aliphatic monocarboxylic acid of 3–6 carbon atoms with an alcohol containing at least 6 carbon atoms and a vinyl-substituted organic nitrogen base in a molar ratio between about 1:1 and 15:1 and converting the resulting copolymer into a hydrophilic salt and then developing the sizing properties of said copolymer on said fibers.

10. A method of sizing paper containing cellulosic fibers which comprises applying to said fibers about 0.2% to 5%, based on the dry weight of said fibers, of a linear chain copolymer resin salt obtained by copolymerizing an ester of an acrylic acid with an alcohol containing at least 6 carbon atoms and a vinyl-substituted organic nitrogen base in a molar ratio between about 1:1 and 10:1 and converting the resulting copolymer into a hydrophilic quaternary ammonium salt and then developing the sizing properties of said copolymer on said fibers by heating the paper at a temperature of at least 100° C.

11. A method of sizing paper containing cellulosic fibers which comprises applying to said fibers about 0.2% to 5%, based on the dry weight of said fibers, of a linear chain copolymer resin salt obtained by copolymerizing an ester of an alpha-beta unsaturated alcohol of 2–4 carbon atoms with a monocarboxylic acid containing at least 6 carbon atoms and a vinyl-substituted organic nitrogen base in a molar ratio between about 1:1 and 15:1 and converting the resulting copolymer into a hydrophilic salt and then developing the sizing properties of said copolymer on said fibers.

12. A method of sizing paper containing cellulosic fibers which comprises applying to said fibers about 0.2% to 5%, based on the dry weight of said fibers, of a linear chain copolymer resin salt obtained by copolymerizing a vinyl ester of a monocarboxylic acid containing at least 6 carbon atoms and a vinyl-substituted organic nitrogen base in a molar ratio between about 1:1 and 10:1 and converting the resulting copolymer into a hydrophilic quaternary ammonium salt and then developing the sizing properties of said copolymer on said

fibers by heating the paper at a temperature of at lease 100° C.

13. A method of sizing paper containing cellulosic fibers which comprises applying to said fibers about 0.2% to 5%, based on the dry weight of said fibers, of a linear chain copolymer resin salt obtained by copolymerizing at least one monomer containing a $CH_2=C<$ group having an attached hydrocarbon radical of at least 6 carbon atoms and an ester of a halogen-substituted aliphatic monocarboxylic acid with an alcohol containing a $CH_2=C<$ group in a molar ratio between about 1:1 and 15:1 converting the resulting copolymer into a hydrophilic quaternary ammonium salt by reacting it with a tertiary organic nitrogen base and then developing the sizing properties of said copolymer resin on said fibers by heating the paper at a temperature of at least 100° C.

14. A method according to claim 12 wherein the resin is the copolymerization product of equimolecular amounts of vinyl stearate and vinyl chloroacetate.

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