

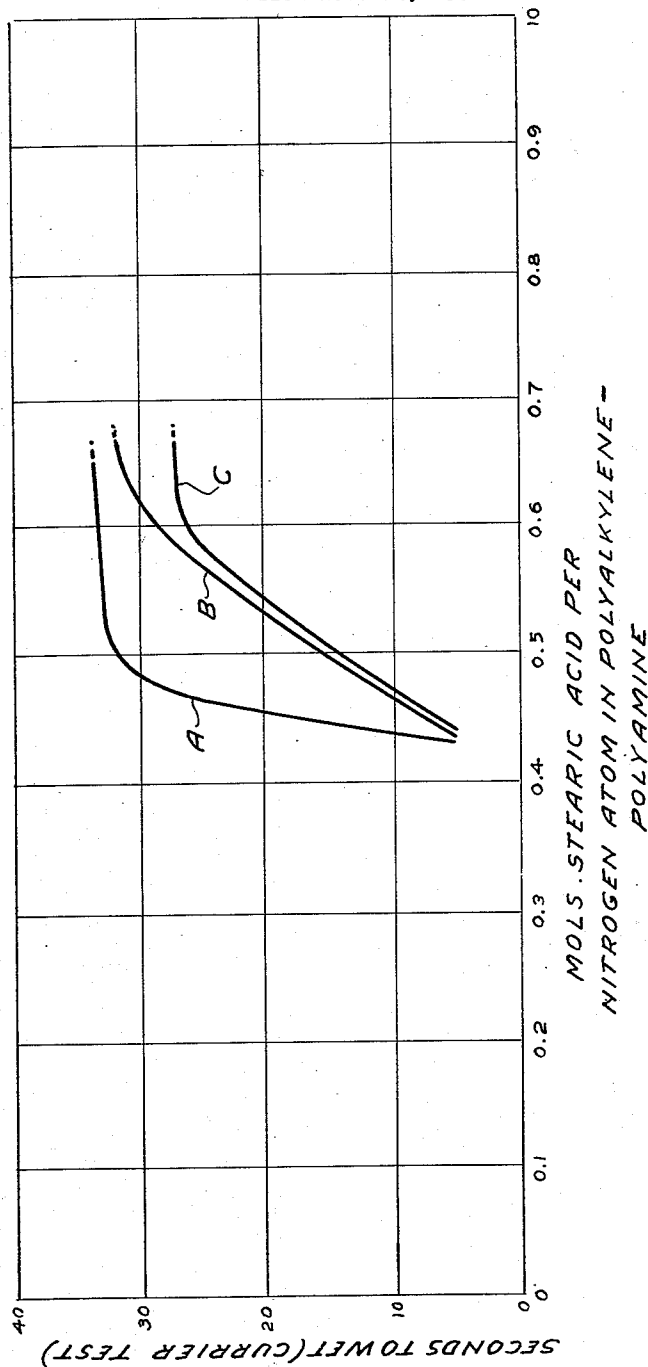
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SIZING OF PAPER WITH FATTY ACID POLYALKYLENEPOLYAMINE COMPOSITIONS

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SIZING OF PAPER WITH FATTY ACID POLY-ALKYLENEPOLYAMINE COMPOSITIONS

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8 Claims. (Cl. 92—21)

This application is a continuation-in-part of our co-pending applications Serial No. 221,725 and No. 221,726, filed on April 18, 1951 (now abandoned).

The invention relates to the production of sized paper by contacting cellulosic fibers with a novel class of hydrophilic, colloidal, cationic sizing agents characterized by their high sizing efficiency and their ability to make sized cellulosic fibers under neutral and alkaline conditions, as when calcium carbonate or other alkaline filler is used. The invention includes the step of forming the sized fibers into various types of dry paper and the thus sized paper themselves.

The manufacture of sized papers containing alkaline fillers has long presented a difficult problem to the art. The principal difficulty arises from the fact that the alkaline fillers commonly used, for example, calcium carbonate and Raffold (calcium carbonate-magnesium hydroxide) impart an excessively high pH to paper pulp suspensions on the order of 8.0–9.0, whereas ordinary sizes such as rosin size can be fixed on the fibers only under acid conditions, for example, at pH values between about 4 and 6. It is not practical first to apply the rosin size under acid conditions and in a subsequent step to incorporate the carbonate filler under alkaline conditions, as under alkaline conditions rosin size is rapidly desorbed by the fibers, resulting in the formation of paper of reduced water and ink resistance. The reverse procedure wherein the calcium carbonate is added under alkaline conditions, and the rosin size and alum are added in succession thereafter under acid conditions is equally impractical as the carbonate is highly acid-sensitive and is decomposed by the acidity imparted by the alum, developing foam and bubbles in the stock. Paper formed therefrom normally contains weak spots and may even contain holes.

Our copending applications Serial Nos. 221,725 and 221,726 disclose the production of sized paper by the use of certain fatty acid polyalkylenepolyamines combined with a water-soluble acid. The sizing agents are prepared by reacting a fatty acid with a polyalkylenepolyamine, and combining 1 to 2 mols of a water-soluble acid with the reaction product. The sizing agents thus obtained are dispersed in water, from which they are adsorbed by the cellulosic fibers. According to those applications, the reaction between the fatty acid and the polyalkylenepolyamine should be continued until acylation is substantially complete.

It has now been discovered that excellent sizing agents are obtained when the ratio of the number of mols of fatty acid to the number of nitrogen atoms in the polyalkylenepolyamine is between 3:7 and 2:3; that formation of an effective sizing agent begins when the acylation reaction is only about 50% complete; that an excellent size is obtained when the reaction is carried to about 90% completion; and that dispersion of the size in water is very greatly facilitated if the molten size, subsequent to addition of the water-soluble acid, is rapidly cooled through its solidification point.

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It has further been discovered that the sizes thus prepared are extensively adsorbed by cellulosic fibers at pH values as high as 11; that the sizes are very rapidly and substantially completely adsorbed with development of the greatest water repellence at pH values between about 3 and 9; and that the sizes are not desorbed or otherwise rendered ineffective when the pH of the stock is raised to 11 or higher or when its temperature is raised to 135° F.

It has still further been found that the sizes are powerful cationic dispersing agents, and that by their use a wide variety of waxes and oils may be applied to the fibers simultaneously with the sizing agent.

The sizing agents, when applied by the beater addition process, are added to dilute aqueous suspension of cellulosic fibers in amounts between 0.2%–0.5% and 5% based on the dry weight of the cellulosic fibers. The fibers are formed into paper in any ordinary manner and the paper is heated to between 105° C. and 150° C. for ½ to 3 minutes, depending on the thickness of the paper, to dry the paper and develop the water-repellent properties of the size. The sizes of the present invention do not polymerize during such brief heating, and therefore it is believed that the primary effect of the heating is to soften or melt the particles of adsorbed size and permit them to flow along the fibers, extending greatly the fiber area protected. The sizing effect obtained is due to the partially acylated polyalkylenepolyamine fatty acid salt adsorbed on the fibers, and not to any part of the acetic acid or other water-soluble acid which may be associated therewith.

It is an outstanding advantage of the sizes of the present invention that they permit the production of fully sized sheets containing large amounts of acid-sensitive alkaline fillers, particularly calcium carbonate. Since the sizes are rapidly adsorbed under alkaline conditions and are not desorbed at pH values up to 11, sized paper of excellent quality containing calcium carbonate filler is made by adsorbing the size on the fibers and then adding sufficient calcium carbonate, which causes the pH to rise to at most about 9.

Paper sized according to the present invention displays additional most advantageous properties. One important property imparted by the sizes of the present invention is that paper sized therewith displays a much reduced tendency to curl when wet on one side with water. As a result, improved types of wallpaper have been prepared which are considerably easier to hang. Moreover, gummed labels have been prepared which show a reduced tendency to curl away from the container while the adhesive is in the process of drying. Moreover, when the size is applied by the tub sizing or calender sizing methods, the paper obtained possesses a lower coefficient of friction and acquires a very uniform degree of "slip." As a result, filing cards, playing cards, and similar cards can be prepared which can be more easily manipulated and which, when "fanned," open out in a very uniform manner permitting them to be sorted more readily. Still further, paper sized according to the present invention and particularly by the beater addition method displays good resistance to penetration by alkaline liquids having pH values up to the point where the fibers themselves are attacked. The foregoing comparisons are made with respect to the best rosin sizes now commercially available.

In addition, the sizes of the present invention permit the production of sized papers which are completely free from formaldehyde or substances yielding formaldehyde, from abietic acid, and from alum. Since cellulosic fibers are known to deteriorate rapidly under acidic conditions usually ascribed to the presence of these materials or their oxidation products, the papers produced by the present process at a pH above 7 exhibit substantially increased dry strength and durability. The sizes of the

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present invention, while useful in the manufacture of all types of paper, will thus find particular use in the manufacture of wall paper, record paper, bond paper, paper for multiwall paper bags, and fiber boxes. In general the sizes will be used where maximum durability is desired, and particularly where the paper contains or is intended for use with an alkaline material. The dried unsheeted fibers themselves are of value as non-absorbent cotton.

A further advantage derived from the use of our sizes is that papers made therefrom can be bleached with alkaline bleaching agents such as alkaline hydrogen peroxide solution without detriment to the effectiveness of the size.

The sizes of the present invention, when applied by the beater addition method, have the extremely beneficial property of permitting a substantial increase in the rate of production of paper by utilization of high stock temperatures, without more than negligible foaming. It is known that when a stock of cellulosic fibers is heated, the freeness of the stock increases with the rise in temperature, permitting more rapid drainage of the water and therefore more rapid operation of the papermaking machine. With rosin size, the maximum economical temperature to which stocks can be heated to increase machine speed is about 100° F. When this temperature is materially exceeded, the effect of the size is seriously impaired and the advantage of increased machine speed is more than offset by the resulting deterioration in sizing obtained. It has been found, however that cellulosic fibers sized in accordance with the present invention do not deteriorate when the temperature of the stock is raised to as much as 135° F. and that in fact paper made therefrom is somewhat better sized than paper made from stock which has not been heated at all.

The present invention makes possible the incorporation in the paper of all commercially used neutral or alkaline fillers including barium sulfate, calcium silicate, Raffold (calcium carbonate-magnesium hydroxide), calcium sulfite, and titanium dioxide, without harm to the stock. These fillers are usually applied in quantities ranging from 5% to 50% up to 100% or more of the dry weight of the paper fibers in order to obtain paper containing from 2%–30% of its weight of filler.

A further important advantage of the novel sizing agents of the present invention resides in the improved results obtainable when they are applied along with starches, gums, glues, wax sizes and other organic sizing or filling agents. We have found that the addition of from 0.1% to 3% or more of these materials, along with from about 0.5% to 1.5% or more of the sizes of the present invention, based on the dry weight of the paper pulp, results in still further improvements both in water resistance and in ink resistance in the finished paper. Suitable starches are corn starch, potato starch, wheat starch and the like. Locust bean gum and other mannogalactans, casein and other proteins and similar gums may be employed, preferably after solubilization with borax or other alkali. Any of the commercially available wax size emulsions may also be employed. The use of sizes containing sizes of the rosin type should be avoided, as the sizes of the present invention yield low water penetration values when used in conjunction with rosin size.

It has been discovered that the sizing agents of the present invention are powerful dispersing and stabilizing agents of the cationic type. When the sizes are melted and mixed with as much as their own weight of hydrophobic waxes such as paraffin wax, carnauba, myrtle, candelilla wax, and beeswax, completely homogeneous solutions are obtained which can be dispersed in water as described below to yield colloidal dispersions which do not separate on standing. It has further been found that the wax-size dispersions thus formed are substantive to paper fibers when applied by the beater addition method and that paper made therefrom exhibits very nearly as much water-repellency as paper containing an equal

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amount of the corresponding size of the present invention and no wax at all. As a result, it is possible to replace as much as one-half of the sizes of the present invention with one or more of the aforementioned or similar waxes with only a negligible decrease in sizing results obtained.

The sizes referred to may be applied to any of the stocks commercially used for the manufacture of paper. Included among these are bleached and unbleached northern kraft pulps, sulfite pulps, sulfite-soda pulps and groundwood-sulfite pulps. They may also be used to advantage in the highly hydrated forms of pulp including those used for the manufacture of glassine paper. They are particularly useful in rag paper, which is notably difficult to size by means of rosin.

They may be applied by any of the commonly known methods. They are particularly adapted for application by the "beater" method, in which the size is added to dilute aqueous suspension of cellulosic fibers and deposited on the fibers before they are made into paper. Absorption of the size is rapid, and is often complete within 10 seconds, permitting the addition of the sizing agent at any desired point ahead of the wire, even in high speed papermaking machines. Where fillers are used, the fillers are more advantageously added after adsorption of the size than before.

The sizes may also be applied by the "tub" sizing or impregnation methods. In the tub method, and the paper web is passed into an aqueous dispersion containing from about 0.1% to 10% of the size, excess liquid squeezed off by rolls, and the paper dried. In the impregnation method the aqueous dispersion or solution of the amide is sprayed upon one or both sides of the paper, which is then squeezed and dried as in the case of tub sizing. In both instances rapid and uniform pickup of the size takes place even when very dilute solutions are used owing to the extremely cationic, cellulose-substantive nature of the size.

The process of our invention therefore in its broadest aspect consists in adsorbing the requisite quantities of the aforementioned sizing material upon cellulosic fibers and heating the fibers in order to develop the sizing properties of the material thereon.

The sizing agents referred to as well as their method of preparation are disclosed and claimed in copending application Serial Number 321,574, filed herewith by L. A. Lundberg (now abandoned), and are prepared by a procedure which comprises three principal steps. In the first step, a polyalkylenepolyamine is heated at an acylation temperature with between about $\frac{3}{4}$ mol and $\frac{5}{8}$ mol of a saturated higher fatty acid for each nitrogen atom in the polyalkylenepolyamine until 50% to 90% of the fatty acid has amidated, that is, until 50% to 90% of the fatty acid has reacted with the amine with evolution of water. In the second step, the product of the first step, at a temperature above its melting point, is made water-dispersible by combination with a water-soluble acid such as acetic acid. In the third step the product, which is a sizing agent according to the present invention, is cooled to room temperature and comminuted to a convenient particle size range. The materials obtained are prepared for use as sizing agents by agitation with hot water.

The sizing agents of the present invention are not pure compounds, but are mixtures which can be separated by crystallization into fractions which vary somewhat in effectiveness. In the specification and the claims, consequently, the sizing agents as well as the intermediates therefor can best be identified and described in terms of their average composition.

Very dilute, for example, 0.1% aqueous dispersions of these sizing agents when viewed by transmitted light appear milky, hazy, or opalescent. It is accordingly evident that when thus dispersed the sizing agents exist not as true solutions but as stable colloidal suspensions.

When the beater addition method is employed, the

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quantity of sizing agent to be added depends principally on the type and purity of fiber used, on the degree of sizing desired, and on the heating times and temperatures employed in drying the paper. In the case of most pulps, a perceptible sizing effect is noted when as little as 0.2%–0.5% of the size is added based on the dry weight of the fibers. A marked improvement takes place when the amount is increased to about 1.0%, while about 1.5%–3.0% of size produces close to the optimum effect in most instances and avoids the danger of adding too little. The addition of more produces an increase in water repellency which is usually less than proportional to the additional amount of size used and the maximum effective amount generally is about 5%.

In the preparation of sizes of the type described above, we have found empirically that the reaction mixture should contain at least 3 mols of fatty acid for each 7 nitrogen atoms of the polyalkylenepolyamine. When less than this proportion of fatty acid is used, the final agents are more water-soluble than colloidal or are hydrophilic and give only a negligible sizing effect. At the other extreme, not more than 2 mols of fatty acid should be added for every 3 nitrogen atoms present in the polyalkylenepolyamine, as when this ratio is materially exceeded the size thus produced is virtually impossible to disperse completely in water without the use of pressure. Thus in the case of diethylenetriamine, about 1.3 mols of fatty acid per mol of diethylenetriamine is the least which yields a perceptibly beneficial sizing agent, and 2.0 mols of the fatty acid per mol of the amine is about the most which can be used to form a size which can be dispersed in boiling water at atmospheric pressure.

The proportion of fatty acid which should be amidated, that is, converted into acyl groups during the reaction, is also of interest. When the degree of acylation is too low, that is, when less than 50% of the fatty acid has reacted by way of acylation, the sizing agents obtained on completion of the remaining steps cannot be dispersed completely, and the dispersions obtained yield sizes of negligible water-repellence, whereas the colloidal dispersions of the present invention are very effective for this purpose.

Any remaining fatty acid groups, that is, any fatty acid groups which do not amidate are associated as salts with the unacylated amino or imino nitrogen atoms of the partially acylated polyalkylenepolyamine.

At least 50% amidation takes place by the time the temperature of the reagents has reached 170° C. in a normal heating cycle, and a 75% amidation within about 15 minutes at that temperature. A 90% amidation takes place within about an hour at that temperature or immediately once the reagents have reached 200° C. On the other hand, 4 to 10 hours at 200° C. are necessary to amidate 97%–99% of the fatty acid. Since the sizing agents obtained from condensations in which only 75% to 90% of the fatty acid has amidated are substantially as effective as those made by condensation in which 97%–99% of the fatty acid has amidated, and since sizing agents which contain as little as 50% of the fatty acid in amidated form yield satisfactory results, it is evident that important economies in heat, labor, and utilization of equipment can be made by producing condensation products in which only 50% to 90% and preferably 75% to 90% of the fatty acid has amidated. In such condensates the ratio of the number of acyl groups attached to the polyalkylenepolyamine to the number of mols of fatty acid associated as salt groups with the unacylated amino or imino nitrogen atoms of the polyalkylenepolyamine will fall between 1:1 and 9:1 and preferably will fall between 3:1 and 9:1.

The acylation reaction described may cause dehydration of a small proportion of the acyl groups to form imidazoline rings. Such unavoidable dehydration is not unduly detrimental and is included within the present invention.

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The practical effect of varying the molar ratio of acid to polyalkylenepolyamine as set forth above is illustrated by the graphs shown in the drawing, which are based upon adjusted data obtained from a large number of experiments. In the drawing, the ordinate represents the wetting time in seconds of the paper samples thus prepared and tested, and the abscissa represents the number of mols of fatty acid used in the preparation of the sizes employed in each instance divided by the number of nitrogen atoms in the polyalkylenepolyamine.

Graph A indicates typical results obtained from stearic acid-tetraethylenepentamine sizes, graph B represents the results obtained from similar stearic acid-triethylenetetramine sizes, and graph C designates the results obtained from similar stearic acid-diethylenetriamine sizes.

The data were obtained by heating stearic acid with a designated polyalkylenepolyamine in the ratios indicated for about 4 hours at 170° C.–200° C., adding 1 mol of glacial acetic acid to the product per mol of polyalkylenepolyamine taken, dispersing the product in water at 95° C. and adding the dispersion thus obtained to a pulp of cellulosic fibers, the proportion of size added being 1% (non-acetate solids) on the dry weight of the fibers. Handsheets were formed from the stock, pressed between blotters, dried for 1 minute at 240° F., and tested for their resistance to penetration by water by the Currier method, in which water is applied to one side of a sheet and the effectiveness of the size is evaluated as the number of seconds required for the water to pass through the paper.

From the curves it will be noted that an appreciable sizing effect is obtained only when the number of mols of stearic acid divided by the number of nitrogen atoms in the polyalkylenepolyamine is more than about 0.43–0.45, i. e., when the ratio between the two is more than about 3:7. The agents obtained below this ratio are either extensively water-soluble, and do not form the necessary colloidal dispersions, or are hydrophilic yielding sizes of negligible water-repellence. The curves rise steeply, eventually reaching a plateau, and terminate at the values of about 0.64–0.70, that is, when the ratio of the number of mols of stearic acid divided by the number of nitrogen atoms in the polyalkylenepolyamine is about 2:3. Above this ratio the characteristics of the product are such that they cannot be dispersed in water by any practical means. It will be further seen that very good results are obtained in each instance at an intermediate point where the value is about 0.60, equivalent to the ratio of about 3:5.

The acylation, to which the first step is directed, may be carried out simply by heating the reagents together at temperatures of about 130° C. to 200° C. until between about 0.5 and 0.9 mol of water have been evolved per mol of fatty acid taken. An organic solvent, such as toluene, xylene and the like, may be employed to facilitate the reaction, and in this event lower temperatures are employed, the water evolving as an azeotrope. In addition, it is within the scope of the present invention to effect the acylation by the use of the appropriate acyl chlorides. When acyl chlorides are used, the products may contain sufficient hydrochloric acid to render them water-dispersible. Furthermore, esters of the acid may be used including glycerides, in which case the product may contain alcohol or glycerol which, however, may be removed by vacuum distillation if desired.

The partially acylated polyalkylenepolyamine fatty acid salts referred to are hard, insoluble waxes which are valueless for the sizing of cellulosic fibers by the beater addition method. It has been found that these materials can be made hydrophilic and water-dispersible so that they will form stable colloidal suspensions when agitated with water at 190° F. by combination with a water-soluble acid to form a salt. Only sufficient acid need be added to render the product water-dispersible.

The least amount which should be added in each instance varies principally with the type of acid selected, the type and amount of fatty acid used in the acylation, and the degree to which the polyalkylenepolyamine has been acylated. As a result, the exact amount cannot be specified numerically. Almost always, however, 1 mol of acid is sufficient per mol of polyalkylenepolyamine initially taken, this proportion insuring satisfactory dispersibility while avoiding the dangers of adding too little. A large proportion of acid does no harm. As acids, hydrochloric, formic, propionic, lactic, chloroacetic and glycolic have given good results. Acetic acid is preferred because it introduces no extraneous ions and because of the outstanding degree of water-dispersibility which this acid confers. In the case of this acid as little as 0.25 mol has proved satisfactory in numerous instances. Most advantageously the acids are added when the temperature of the material is just above its melting point, this temperature permitting rapid introduction of the acid while minimizing loss thereof by volatilization.

The sizes thus prepared may be cooled in trays forming hard brown waxy solids. The necessary dispersions may be prepared by grinding the dispersions to a convenient size, for example, about 14 mesh, soaking the particles in water for an hour or two and then agitating with sufficient water at 190° F. to form a dispersion containing about 5% by weight of the size. At least about two hours of agitation are required, after which the dispersion is passed through a cloth to remove undispersed particles. The discovery has been made, however, that the size is much more easily dispersed when it is rapidly chilled from a temperature above its melting point to a temperature below its solidification point. A cold revolving chilling drum provided with a scraper blade is suitable for this purpose. Such a procedure is described and claimed in the copending application of L. A. Lundberg referred to above.

The polyalkylenepolyamines referred to are well known compounds, the most widely used group corresponding to the formula $H_2N(C_nH_{2n}NH)_xH$, in which n and x are integers greater than 1 and preferably between 2 and 4 inclusive. Typical amines of this class are diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. The corresponding polypropylenepolyamines and polybutylenepolyamines are substantial equivalents. All these polyalkylenepolyamines are water-soluble and basic and are characterized by the property of condensing with higher fatty acids to yield partially acylated polyalkylenepolyamines. In addition, the higher molecular weight polyalkylenepolyamines formed by homopolymerizing the lower alkyleneimines including ethyleneimine are also useful permitting a reduction of more than one-half of the fatty acid required, as well as the amines derived by reaction of methylenebisacrylamide with a polyalkylenepolyamine. All these and similar polyalkylenepolyamines are suitable for the practice of the present invention.

As fatty acids it is preferred to use the saturated fatty acids of 14 to 22 carbon atoms, particularly the acids containing 16 to 18 carbon atoms such as palmitic and stearic since these are relatively low in cost and yield sizes having the best combination of ease of dispersion and water repellency. Unsaturated fatty acids are tolerated well in small amounts, usually up to about 10%, but confer no advantage to the product. Mixtures of acids may also be used, and because of their low price and ready availability hydrogenated cottonseed oil fatty acids, hydrogenated coconut oil fatty acids, hydrogenated fish oils, and the acids from hydrogenated tallow represent the type of mixed acids which are preferred.

The hydrochloric acid may be replaced in whole or part by epichlorohydrin or a similar material which releases hydrogen chloride on reaction with primary or secondary amines. When epichlorohydrin is used the amide may be melted and the epichlorohydrin is added dropwise or

in a slow stream with agitation. Under these conditions reaction times of about 1-3 hours are usually employed, these being sufficient to complete the epichlorohydrin condensation but not so long as to produce cross linkages with formation of water-insoluble products. The amide may be dissolved in a polar solvent such as ethanol, isopropanol, and tertiary butanol, and in this event the alkylation is preferably carried out under reflux conditions; i. e., at the boiling point of the solution at atmospheric pressure and for reaction times of about 1-5 hours, after which the solvent and any unreacted epichlorohydrin are stripped off. It is a particular advantage of epichlorohydrin that the hydrochlorides formed have substantially the same melting point and are substantially as easily dispersible in water as the products obtained by the hydrochloric acid alone is added. They are thus acylated polyalkylenepolyamines and are included in the scope of the present invention.

The invention has been fully set forth above. It is further described by the following specific examples. Although these examples describe certain features of the invention in detail, they are given solely for the purposes of illustration and the invention is in no way limited thereto.

Example 1

189 g. (1 mol) of tetraethylenepentamine was mixed with 804 g. (2.9 mol) of technical stearic acid containing about 10% palmitic acid. This mixture, containing 0.58 mol of fatty acid per nitrogen atom present in the amine, was charged into a reaction flask provided with an agitator, a side arm containing a tube extending below the surface of the mixture and connecting with the source of nitrogen gas, a second side arm venting to the atmosphere through a condenser and an electric heating mantle. The mixture was heated in this flask up to 200° C. under nitrogen gas and then flowed out into a cooling tray 3" deep as soon as this temperature was attained and then allowed to cool. The product was hard, brown wax having a melting point of about 110° C. (Dennis bar method). The wax was melted to 115° C. and 60 g. of glacial acetic acid (1 mol) were stirred in.

One portion of the sizing agent thus prepared was poured into a tray forming a layer about 2" thick, where it slowly cooled to room temperature. The solid material was broken up and ground in a hammer mill to 14 mesh and 50 parts were soaked in 950 parts of deionized water at 30° C. for 2 hours. The mixture was heated to 190° F. with steam and vigorously stirred by a Lightnin' stirrer. Two hours were required for an apparently homogeneous dispersion to form. Filtration of a sample diluted to 0.1% solids through filter cloth disclosed that an objectionable number of particles of size had failed to disperse, spots of size being observed on the filter cloth.

Another portion of the size was quickly cooled by flowing it out into a layer about 1/8" on a Pyrex glass plate. 50 parts of the size recovered from the plate was similarly ground and intensively agitated with 950 parts of deionized water at 190° F. A homogeneous dispersion formed within 15 minutes. 10 parts of the pasty dispersion were diluted with 500 cc. of hot water and filtered. No particles of size could be found on the filter cloth, showing that dispersion was substantially complete. When viewed by transmitting light, the diluted dispersion containing 0.1% of size exhibited the blue milky haze characteristic of colloidal cationic cellulose-substantive wet strength melamineformaldehyde acid resins.

The liquefaction point (Dennis bar method) of the slowly cooled material was 109.5° C., whereas the liquefaction point of the rapidly cooled material was 92° C.

Example 2

The procedure of Example 1 was repeated, the reaction mixture being heated to only 175° C. and maintained at that temperature for 15 minutes. The product was rapidly

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chilled on a glass plate, ground and dispersed in water by the method of Example 1.

Example 3

500 grams (1.8 mols) of hydrogenated tallow acids and 103 grams (1 mol) of diethylenetriamine were mixed and heated to 200° C. under nitrogen according to the procedure of Example 1. One-half of the reaction product was acidified with 36 g. of glacial acetic acid. The product was rapidly chilled on a glass plate and dispersed in water by the method of Example 1.

Example 4

The remainder of the reaction product of Example 3 was heated for 4 hours at 200° C. under nitrogen and was then acidified with 30 g. of glacial acetic acid. The product was rapidly chilled on a glass plate, ground, and then dispersed in water by the method of Example 1.

Example 5

A 2-liter flask was charged with 762 grams (2.75 mols) of stearic acid, 189 grams (1 mol) of tetraethylenepentamine, equivalent to 0.55 mol of acid per nitrogen atom in the amine and 250 cc. of xylene. The mixture was heated on a steam bath until fluid and then with agitation at its distillation temperature (150–165° C.) until 40 grams of water had evolved, equivalent to about 80% completion of the acylation reaction. Reduced pressure was then applied and the remaining xylene was stripped off. The product was a tan, hard, brittle wax.

A portion of this product was melted and 2 mols of concentrated aqueous hydrochloric acid per mol of tetraethylenepentamine equivalent present was added with stirring below the surface of the melt. The product was rapidly chilled and dispersed in water at 195° F. by the method of Example 1.

Example 6

Following the procedure of Example 5, a mixture of 3580 grams (12.6 mols) of stearic acid, 649 grams (6.3 mols) of diethylenetriamine and 100 cc. of xylene was reacted until 9 mols of water had evolved, equivalent to about 75% completion of the acylation reaction. The ratio of acid to amine was equivalent to 0.67 mol of acid per nitrogen atom in the amine. The remaining xylene was removed by heating under reduced pressure to 160° C. The product weighing 3891 grams was a light tan hard wax, samples of which were dispersible in hot dilute acetic and hydrochloric acids. The remainder of the product was made into a sizing agent and dispersed in water by the method of Example 5.

Example 7

Fatty acids containing from 14 to 22 carbon atoms can be used in preparing the polyalkylenepolyamine amides used in practicing the present invention since they impart the necessary hydrophobic properties to produce good water resistance and ink resistance. Mixtures of these fatty acids are particularly useful as they are available commercially in large quantities. Thus, for example, a commercial mixture of hydrogenated fish oil acids has the following approximate analysis:

C ₂₁ H ₄₃ COOH	percent	20
C ₁₉ H ₃₉ COOH	do	20
C ₁₇ H ₃₅ COOH	do	23
C ₁₅ H ₃₁ COOH	do	30
C ₁₃ H ₂₇ COOH	do	7
Average molecular weight		288

A polyethylenepolyamine was prepared by reacting 805 grams (2.8 mols) of this fatty acid mixture with 189 g.

of tetraethylenepentamine (1 mol) by the procedure described in Example 5, 40 grams of water being evolved, equivalent to 75% reaction. The ratio of reagents corresponded to 0.56 mol of acid per nitrogen atom in the amine. This amide was melted, mixed with 60 g. of glacial acetic acid, and quickly chilled and dispersed in water by the method of Example 1.

Example 8

A beaten stock composed of 60% sulfite and 40% soda pulp was diluted with demineralized water to 0.6% consistency, adjusted to pH 5.0, and separated into a number of portions. One portion was reserved as control. To each of the remaining portions was added 1% of the aqueous sizing dispersion (non-acetate solids on the dry weight of the fibers) of one of the foregoing examples, as shown in the table below. Before use, the sizes were diluted with water to 3% solids.

A quantity of finely divided calcium carbonate filler equal to the dry weight of the paper fibers was then added, causing the pH of the stock to rise to about 9.0, and the stock was made into paper on a Nash laboratory handsheet machine. The handsheets were couched on to blotting paper and dried at the temperatures and during the times shown in the table below. The dried sheets contained 10%–12% calcium carbonate and were tested for sizing (water resistance) by the Currier size tester (slack scale) and for ink resistance on the B. K. Y. tester. All of the condensation products produced handsheets having ink penetration times greater than 300 seconds. The calcium carbonate content and the size tests with different sizing agents are shown in the following table:

Size Added, Example	Size Test ² After Heating			
	1 min. at 115° C.	2 min. at 115° C.	1 min. at 130° C.	2 min. at 130° C.
Control ¹	0	0	0	0
1	25	28	35	34
2	24	29	28	31
3	26	31	25	32
4	25	32	26	27
5	24	30	31	32
6	27	25	36	38
7	26	27	28	32

¹ No size added.

² Time in seconds for water to penetrate the paper.

These results show that a high degree of sizing coupled with excellent ink resistance is obtainable in calcium carbonate-filled sheets by the sizing agents of the present invention.

Example 9

In order to determine the sizing action of the higher fatty acid-polyalkylenepolyamine condensation products separately from their action in the presence of alkaline fillers, a set of handsheets was prepared in which no filler was used. The beaten paper pulp was diluted to 0.6% consistency in the usual manner, adjusted to pH 5.0, and 1% of the dispersion of Example 2 was added, based on the dry weight (non-acetate solids) of the fibers. One portion of the stock was made into handsheets without further treatment; other portions were adjusted to the pH value indicated in the table below by adding sodium hydroxide solution and then made into paper on a laboratory handsheet machine. The paper was dried under the conditions indicated and tested for sizing and ink resistance. In all cases the B. K. Y. ink resistance was more than 300 seconds. The Currier size test (slack scale) gave the following penetration times in seconds. The corresponding figures for paper from the same stock treated with 1% of rosin size followed by 1.5% of alum,

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based on the weight of the paper fibers, and dried for 2 minutes at 130° C. are also given.

Drying		Final pH of Stock			
Minutes	Temp., °C.	5.0	7.0	9.0	11.0
1.....	115	33	31	33	21
2.....	115	38	37	35	25
1.....	130	37	38	39	26
2.....	130	38	35	45	27
(Rosin sized paper).....		70	12	0	0

Example 10

The new sizing agents of the present invention can be used advantageously along with starches, gums, rosin-free wax sizes and the like. This is illustrated by the following results, which were obtained by first applying 1% of the size dispersion of Example 6 to a beater stock by the procedure described in Example 8, the addition of calcium carbonate being omitted, and then adding a cooked starch to the fiber suspension in the amounts indicated below, followed by making the treated stock into paper. The Currier (slack scale) size tests, in seconds, for paper dried at varying temperatures and times are given in the following table; in all cases the B. K. Y. ink resistance was more than 300 seconds.

Percent Starch on Fiber ¹	Dried at 115° C.		Dried at 130° C.	
	1 min.	2 min.	1 min.	2 min.
None.....	23	23	35	41
1.....	37	39	46	53
2.....	31	37	41	37
5.....	27	35	37	41

¹ Based on the dry weight of the fibers.

Example 11

A beaten 100% unbleached kraft pulp was diluted to 0.8% consistency and portions treated with the sizing dispersions of Example 1 in amounts varying from 0.25% to 1.5% (non-acetate solids) based on dry fiber as shown in the table. In all cases the treated pulp was adjusted with NaOH to pH 9.0 and made into handsheets on a Nash laboratory handsheet machine. The handsheets were couched on blotting paper and pressed between wool felts in a laboratory rotary press. The handsheets were dried on a drum dryer for 1 minute at 115° C. Handsheets were tested for water resistance by the Currier size tester (hard scale) and for ink resistance by the B. K. Y. tester. The tests are shown in the following table.

Percent Size Added	Water Resistance, Seconds	Ink Resistance, Seconds
0.....	<2	<5
0.25.....	<2	10
0.50.....	17	over 300
0.75.....	21	over 300
1.00.....	24	over 300
1.50.....	27	over 300

Example 12

A beaten 100% unbleached sulfite pulp was diluted with demineralized water to 0.6% consistency and treated at pH 5.0 with 1.5% (non-acetate solids based on dry weight of fiber) of the sizing dispersion of Example 1. The stock so treated was adjusted to pH 9.0 with NaOH and made into paper on a Nash laboratory handsheet machine. The handsheets were couched on blotting paper, pressed between wool felts on a laboratory rotary press and dried on a heated drum for 4 minutes at 115° C.

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Portions of these handsheets were subjected to peroxide bleaching by impregnating the sheets with an alkaline aqueous peroxide bleaching solution containing 0.5% hydrogen peroxide and 0.75% trisodium phosphate. A 60% pickup of bleaching liquor was realized. The impregnated sheets were dried on a heated drum dryer at 105° C. for 2 minutes. The "brightness" (percent reflectance at 454 millimicrons) and water resistance were determined for the bleached and unbleached sheets. 10 The Currier size tester (hard scale) was employed for the water resistance size test. The tests are shown in the following table.

Treatment	Brightness	Currier Size Test, Seconds
Peroxide Bleached.....	58.0	52
No Bleaching.....	53.7	74

Under similar circumstances, a rosin sized sheet would lose practically all of its water resistance on bleaching.

As a result of the resistance of the size to penetration by the alkaline peroxide solution, only the surface of the sheet was bleached, minimizing consumption of the peroxide solution.

Example 13

4518 g. of technical stearic acid having an average molecular weight of 276 (16.5 mols) were raised to melting temperature in a flask provided with a nitrogen gas inlet tube, thermometer, dropping funnel, and water condenser. 1014 g. of triethylenetetramine (6.9 mols) were then run in causing an exothermic reaction. 35 The reaction mixture containing 0.60 mol of stearic acid per nitrogen atom in the polyalkylenepolyamine was heated to about 190° C., under nitrogen and at once cooled to 125° C. and 468 parts of glacial acetic acid (7.8 mols) added below the surface of the mixture with stirring. A sample of the size was poured into a 3" deep cooling tray and allowed to cool to room temperature. The remainder of the size was poured on a rotating chilling roll cooled with water at 18° C. Hard brown flakes were obtained from the scraper blade of the roll having a melting point (Dennis bar) of 93° C. 45 The flakes were rapidly agitated with deionized water at 180° F. at 5% solids and dispersion was complete within 15 minutes as evidenced by a filtration test.

The slowly cooled material had a melting point of 107° C. When broken up, ground, and rapidly agitated with water at 195° F. at 5% solids, dispersion was incomplete after 90 minutes as evidenced by the filtration test.

Example 14

In a round-bottomed flask equipped with stirrer, thermometer, reflux condenser, nitrogen gas inlet tube and electric heating mantle were placed 146 g. (1 mol) of tetraethylenepentamine and 650 g. (2.4 mols) of technical stearic acid. The reaction mixture was heated to 170°-175° C. and maintained at that temperature until evolution of water became very slow. During the reaction nitrogen gas was bubbled through the contents of the flask. Aliquots were withdrawn from time to time as shown in the table, and a part of each aliquot was analyzed for its free stearic acid content to determine the progress of the reaction. In making these analyses 1.0 g. of each aliquot was dissolved in 100 cc. of alcohol and titrated to a phenolphthalein endpoint with N/10 alcoholic KOH. The percent by weight of unreacted stearic acid in the sample was calculated from the titration values, and from this was calculated the percent of the stearic acid originally taken which had reacted by way of amidation.

The remainder of each aliquot was reacted with one

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mol of acetic acid per mol of combined tetraethylene-pentamine present in accordance with Example 1 and the size thus obtained was used in the preparation of sized paper by the method of Example 8, except that the weight of the size added was 1.5% of the dry weight of the fibers and no calcium carbonate was added. The final hand-sheets were tested for their water repellence by the Currier method (slack scale). Results are as follows including the results obtained on an untreated control sheet.

Sample	Reaction Time		Temp., °C.	Percent Unamidated Stearic Acid ¹	Percent Stearic Acid Amidated ²	Currier Test ³
	Hrs.	Min.				
(Control)-----	Start		28	100	0	0
1-----	1	55	151	41.2	50.6	4
2-----	1	59	155	36.9	56.2	5
3-----	2	03	162	32.3	61.5	9
4-----	2	10	171	25.1	71.0	23
5-----	2	14	170	20.9	75.5	32
6-----	3	15	169	10.6	88.0	36
7-----	3	50	175	7.17	91.5	38
8-----	6	25	169	5.43	93.7	43
9-----	7	45	170	4.39	95.0	45

¹ Based on total weight of the samples.

² Based on weight of stearic acid originally present.

³ Time in seconds for water to penetrate the paper.

When a graph is made showing the percent of fatty acid amidated in this and similar reactions as a function of time, the curves obtained demonstrate that the amidation reaction proceeds rapidly to the point at which the reaction is about 90% complete and that thereafter the reaction proceeds at a much slower rate. A plot of the sizing test results yields an essentially parallel curve, showing that the improvement in the size obtained as the reaction proceeds also levels off with attainment of 90% amidation of the stearic acid. As a consequence, by running the reaction to about 90% completion excellent sizes are obtained while minimizing the duration of the reaction.

Example 15

A glassine paper stock was prepared by beating bleached sulfite pulp for 15 minutes in a laboratory Valley beater and refining in a laboratory Morden refiner for 20 minutes to a Green freeness of 50 cc. A highly hydrated pulp resulted. The pulp was adjusted to a consistency of 0.6% and divided into two sets of aliquots. The pH of one set of aliquots was adjusted to 5.0 and the pH of the other set to 8.5-9.0. One sample of each set was reserved as control. The aliquots were then divided in half.

The temperature of one set of aliquots having pH values of 5.0 and 8.5-9.0 was adjusted to 75° F. and the temperature of the other set to 120° F., the Green freeness values of which became respectively 50 and 110. Certain of the samples in the high and low temperature sets having pH values of 5.0 and 8.5-9.0 were treated with the size of Example 13. In addition, samples of the high and low temperature sets having a pH of 5.0 with commercial rosin size followed by alum, and one untreated sample in each set was reserved as control. In each instance in the case of rosin, 2% of the rosin size was added first, based on the weight of the fibers, followed by 3% of alum. In the case of the size of Example 13 the amounts added in each instance are shown in the table, also based on the dry weight of the fibers. Five minutes after the solution of the respective sizes of the pH of the samples of stock were adjusted to the "final" values shown, maintained at that pH for 5 additional minutes, and then formed into handsheets on a Nash handsheet machine using deckle water of the temperature and pH shown. The handsheets were dried at 240° F. for 1 minute and tested for their water resistance

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(Currier, slack scale) and ink resistance (B. K. Y. method).

5	Run	Size	Stock pH		Basis Wt. ³	Resistance, Sec.	
			Initial ¹	Final ²		H ₂ O	Ink
Stock temperatures 75° F.							
10	Control---		5.0	9.0	50.0	<5	<5
	1-----	Ex. 13—2.0%---	5.0	9.0	51.0	29	>600
	2-----	do-----	8.5	8.5	50.7	33	>600
	3-----	do-----	5.0	5.0	50.5	30	>600
	4-----	Rosin+alum---	5.0	5.0	48.7	7	<10
	5-----	do-----	5.0	9.0	49.0	<5	<5
15	Stock temperatures 120° F.						
	Control---		5.0	9.0	51.6	<5	<5
20	6-----	Ex. 13—2.0%---	5.0	9.0	51.4	37	>600
	7-----	do-----	8.5	8.5	48.7	34	>600
	8-----	Ex. 13—1.5%---	5.0	9.0	49.7	29	>600
	9-----	do-----	8.5	8.5	48.3	27	>600
	10-----	Ex. 13—1.0%---	5.0	9.0	50.7	20	>600
	11-----	do-----	8.5	8.5	51.0	22	>600
	12-----	Ex. 13—0.75%---	5.0	9.0	51.6	7	300
	13-----	do-----	8.5	8.5	50.6	8	300
	14-----	Rosin+alum---	5.0	5.0	49.5	<5	<5

¹ During addition of size and 5 minutes thereafter.

² After addition of the size and during sheetmaking.

³ Basis 25 x 40-500.

This table shows that the sizes of the present invention are very effective on highly refined stocks both acid and alkaline and both at normal and at elevated temperatures, and demonstrates that rosin size cannot be used satisfactorily as an equivalent.

Example 16

Impregnating baths were prepared by adjusting the concentration and pH of the dispersion of Example 13 to the values shown. Sheets of a 50-lb. weight unsized bleached kraft paper, both unfilled and filled (20% CaCO₃ content), were drawn through the baths, passed through a clothes wringer to squeeze out excess water, dried for 1 minute at 240° F., and tested for their water and ink resistance by the Currier method (slack scale) and B. K. Y. method. Results are as follows:

UNFILLED PAPER

Bath		Water Resistance (Currier)	Ink Resistance (B. K. Y.)
Size	Concen., Percent		
0-----	5.0	0	0
0-----	8.0	0	0
0.11-----	5.0	5	0
0.275-----	5.0	9	35
0.55-----	5.0	30	>600
1.10-----	5.0	46	>600
1.10-----	8.0	43	>600

FILLED PAPER

Size	Concen., Percent	Water Resistance (Currier)	Ink Resistance (B. K. Y.)
0-----	5.0	0	0
0.275-----	5.0	>5	0
0.55-----	5.0	10	300
1.1-----	5.0	35	>600
1.1-----	8.0	30	>600

Example 17

100 parts of the flaked size prepared according to Example 13 was mixed with 100 parts of paraffin wax (M. P. ca. 135° F.) and the mixture heated. A homogeneous melt formed at 102° C. The product was chill-cooled, ground, and dispersed at 5% solids in water by the method of Example 1 and added to a paper stock in accordance with the method of Example 8, no calcium carbonate being present. The pH of the stock was maintained at 8.0 throughout. A control experiment was

performed utilizing the size dispersion of Example 13. Results are as follows:

Test	Composition of Size Added		Percent Size Added ¹	Basis Wt. ²	Currier Test (Sec.)
	Ex. 13, percent	Paraffin, percent			
1 (Control).....	100	-----	0.75	47.3	10
2 (Control).....	100	-----	1.50	46.5	48
3.....	50	50	1.50	48.4	43

¹ Non-acetate solids based on dry weight of paper fibers.

² 25 x 40-500.

Comparison of the results of test 3 with the results of tests 1 and 2 shows that only a slight loss in sizing occurs when one-half of the size is replaced by approximately an equal weight of paraffin wax.

We claim:

1. A method of producing sized paper which comprises: adsorbing on cellulosic fibers in the absence of rosin size between about 0.2% and 5%, based on the dry weight thereof, of a long chain fatty acid-polyalkylenepolyamine reaction product corresponding to that formed by heating a water-soluble polyalkylenepolyamine at an acylation temperature with between about $\frac{3}{4}$ and $\frac{2}{3}$ molecule of a higher saturated fatty acid for each nitrogen atom in the polyalkylenepolyamine, until between about 50% to about 99% of the fatty acid has reacted with the amine with evolution of water, thereby forming a water-insoluble higher fatty acid salt of a higher fatty acid acylated polyalkylenepolyamine, said polyalkylenepolyamine containing between 3 and 5 nitrogen atoms and said fatty acid containing 14 to 22 carbon atoms, and combining said water-insoluble acylated polyalkylenepolyamine salt with a water-soluble acid to render said acylated polyalkylenepolyamine salt water-dispersible; and heating said treated fibers at between about 105° C. and 150° C. for about $\frac{1}{2}$ to 3 minutes to dry the same and develop the water-repellent properties of the acylated polyalkylenepolyamine thereon.

2. A method of producing sized paper which comprises: adsorbing on cellulosic fibers between about 0.2% and 5%, based on the dry weight thereof, of a sizing agent consisting of a long chain fatty acid-polyalkylenepolyamine reaction product corresponding to that formed by heating a water-soluble polyalkylenepolyamine at an acylation temperature with between about $\frac{3}{4}$ and $\frac{2}{3}$ molecule of a higher saturated fatty acid for each nitrogen atom in the polyalkylenepolyamine, until between about 50% to about 99% of the fatty acid has reacted with the amine with evolution of water, thereby forming a water-insoluble higher fatty acid salt of a higher fatty acid acylated polyalkylenepolyamine, said polyalkylenepolyamine containing between 3 and 5 nitrogen atoms and said fatty acid containing 14 to 22 carbon atoms, and combining said water-insoluble acylated polyalkylenepolyamine salt with a water-soluble acid to render said acylated polyalkylenepolyamine salt water-dispersible; and heating said treated fibers at between about 105° C. and 150° C. for about $\frac{1}{2}$ to 3 minutes to dry the same and develop the water-repellent properties of the acylated polyalkylenepolyamine thereon.

3. A method of producing sized paper which comprises forming an aqueous suspension of cellulosic papermaking

fibers at a pH between 2 and 11; mixing with said suspension in the absence of rosin size an aqueous colloidal cationic dispersion containing between about 0.2% and 5%, based upon the dry weight of the fibers, of a long chain fatty acid-polyalkylenepolyamine reaction product corresponding to that formed by heating a water-soluble polyalkylenepolyamine at an acylation temperature with between about $\frac{3}{4}$ and $\frac{2}{3}$ molecule of a higher saturated fatty acid for each nitrogen atom in the polyalkylenepolyamine, until between about 50% to about 99% of the fatty acid has reacted with the amine with evolution of water, thereby forming a water-insoluble higher fatty acid salt of a higher fatty acid acylated polyalkylenepolyamine, said polyalkylenepolyamine containing between 3 and 5 nitrogen atoms and said fatty acid containing 14 to 22 carbon atoms, forming the suspension into a sheet, and heating said sheet at between about 105° C. and 150° C. for about $\frac{1}{2}$ to 3 minutes to dry the same and develop the water-repellent properties of the reaction product therein.

4. A method according to claim 3 wherein the cellulosic suspension has a pH between 7 and 9.

5. A method according to claim 3 wherein between 5% and 100%, based on the dry weight of the fibers, of an alkaline filler is added to the suspension subsequent to addition of the fatty acid-polyalkylenepolyamine reaction product.

6. A method of producing sized paper which comprises impregnating at least one surface of a cellulosic sheet free from rosin size with an aqueous colloidal cationic dispersion containing between about 0.1% and 10% by weight of a long chain fatty acid-polyalkylenepolyamine reaction product corresponding to that formed by heating a water-soluble polyalkylenepolyamine at an acylation temperature with between about $\frac{3}{4}$ and $\frac{2}{3}$ molecule of a higher saturated fatty acid for each nitrogen atom in the polyalkylenepolyamine, until between about 50% to about 99% of the fatty acid has reacted with the amine with evolution of water, thereby forming a water-insoluble higher fatty acid salt of a higher fatty acid acylated polyalkylenepolyamine, said polyalkylenepolyamine containing between 3 and 5 nitrogen atoms and said fatty acid containing 14 to 22 carbon atoms, said dispersion being free from rosin size, and heating said sheet between 105° C. and 150° C. for about $\frac{1}{2}$ to 3 minutes to dry the same and develop the water-repellent properties of the fatty acid-polyalkylenepolyamine reaction product thereon.

7. Paper produced according to the process of claim 1.

8. A method according to claim 1 wherein the water-dispersible acylated polyalkylenepolyamine salt is added as a homogeneous blend with about an equal weight of a hydrophobic wax.

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