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METHOD OF SIZING PAPER WITH THE CONDENSATION PRODUCT OF A LONG CHAIN ALKYLAMINE WITH METHYLENEBISACRYLAMIDE

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The present invention relates to cellulosic webs, including paper, sized by a content of a condensation product of about 1 mol of a long chain alkylamine with 1 mol of methylenebisacrylamide, and processes for the manufacture of such webs. The invention includes webs sized by a content of such material in at least partially polymerized form.

The present invention is chiefly based upon the discovery that the condensation product of about 1 mol of a long chain saturated fatty amine with methylenebisacrylamide, in the form of its water-soluble salts, are valuable sizing agents which are cationic and substantive to cellulosic fibers dispersed in aqueous medium, and that these materials act as sizing agents which greatly increase the water-resistance of fibers having a content of the same when formed into paper, etc. We have still further found that the condensation products referred to may be partially polymerized while in aqueous dispersion and that when so polymerized they yield superior results when employed in the manner described.

The papers of the present invention have the particular advantage that they retain their water-resistance although contacted with strongly alkaline materials such as cement and plaster. They are thus particularly suitable for use as containers for such materials, as well as for the wrapping of other alkaline materials such as soap.

The cellulosic webs of the present invention, broadly, are made by a process which includes the steps of contacting cellulosic fibers with an aqueous dispersion of the sizing materials referred to in either monomeric or partially prepolymerized form, depositing an effective amount on the fibers, and heating the fibers to dry the same and develop the sizing properties of the condensation products thereon. During this heating, further polymerization may take place and the condensation product may melt and flow along the fibers, greatly extending the area protected.

Sized webs of the present invention may be prepared by the tub sizing method in which a preformed cellulosic web is immersed or sprayed or padded with a dilute (1%–5%) aqueous dispersion of the sizing material, after which the web is dried by heating.

The webs may be more conveniently prepared by the beater addition method, this method taking advantage of the cationic, cellulose-substantive characteristics of the sizing material. According to this method, a dilute dispersion of the size is added to an aqueous cellulosic fiber dispersion at an alkaline pH, that is, a pH between about 7 and 9. Adsorption is rapid, a sufficiently effective amount usually being adsorbed within about 1 minute and often within a few seconds. The fibers are then sheeted to form paper or other web. Development of the water-repellence of the condensation product substantially takes place when the web is heated for about one-half minute at 160° F. or 3–10 minutes at 210° F.

Alkaline filled paper may be manufactured by adding sufficient calcium carbonate or other alkaline filler after addition of the resin to the aqueous fibrous suspension. Usually 5% to 100% of filler is added, thereby incorpor-

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ating 2% to 30% in the paper based on the dry weight thereof.

A peculiarity of the condensation products of the present invention is that their water-repellent properties are best developed when the fibers are sheeted on the alkaline side. We have found that the water-resistance of the condensation products of the fibers is far less when the fibers are sheeted at an acid pH, that is, at a pH below about 7. As a result, while the sizing dispersion itself may be added to the suspension while the suspension is at any normal pH, acid or alkaline, the suspension should have an alkaline pH and preferably a pH between about 7.5 and 9 while the fibers are being sheeted. In commercial operations it will be found most convenient to add the sizing dispersion to the cellulosic suspension at its normal pH and then raise the pH to within the range mentioned at a point well in advance of the headbox. Elevation of the pH may be performed by the addition of caustic solution, but where an alkaline filler is added in usual amounts, that is, in amount sufficient to deposit between about 2% and 30% of alkaline filler on the fibers, the addition of caustic solution becomes unnecessary. Calcium carbonate filler is fully suitable for this purpose.

Some sizing action may be expected when as little as 0.1%–0.5% of the sizing material is added, based on the dry weight of the fibers, and the addition of this amount is therefore within the scope of the present invention. Much better results are obtained when about 1%–3% is added, this amount being considered about the minimum needed for useful results in the absence of other sizing agents, and up to about 5% may be added with continued increase in water-resistance.

The sizing material is conveniently prepared by heating about 1 mol of a long chain saturated fatty amine with 1 mol of methylenebisacrylamide, a known material. The use of materially less than 1 mol of the amine causes some unreacted methylenebisacrylamide to remain in the product, and this material does not act significantly as a sizing agent. On the other hand, the use of materially more than about 1 mol of the fatty amine causes a part of the methylenebisacrylamide to be converted to a non-polymerizable form which form, we have found, is less advantageous as a sizing agent. We therefore prefer to react about 1 mol of the fatty amine with 1 mol of the methylenebisacrylamide.

The amines referred to are long chain saturated fatty amines, that is, alkylamines containing 16–22 carbon atoms, the water-repellence afforded decreasing rapidly when chains of shorter length are employed and the dispersibility of the addition products, even in the form of their salts, being unduly difficult in the case of chains of greater length. In practice, we prefer to use octadecylamine, this material being readily available while yielding a product which disperses readily and provides satisfactory water-resistance. Unsaturated fatty amines are tolerated well in small amounts and thus there may be used the commercial, not quite completely hydrogenated amines derived from naturally-occurring fatty acids containing up to about 10% of unsaturated material.

The condensation products, after removal of any solvent present, are normally waxy solids and are conveniently made into size by grinding to a powder and slowly pouring the powder into a volume of rapidly agitated hot water containing sufficient of a lower water-soluble acid to form a fluid suspension or dispersion containing up to about 15% of the addition product as an amine salt thereof, beyond which concentration the dispersion is very viscous. It is preferred that less of the condensation product be added so that the dispersion is quite fluid. Ordinarily, about 1 mol of acid is employed per mol of combined long chain fatty amine, but often a lesser amount has proved satisfactory while an excess does no-

harm. As acids, chloroacetic (mono-, di-, or tri-), formic, hydrochloric, glycolic, and propionic may be used. Acetic acid is preferred, this acid being non-toxic, readily available and appearing to yield salts of the lowest softening point. The dispersions thus formed, when diluted, exhibit the opalescent bluish haze indicative of the presence of colloidal matter therein, and may be employed without further treatment in the manufacture of paper.

More advantageously, however, the dispersions are subjected to a preliminary partial polymerization. This is most conveniently done by treating the dispersions, hot or cold, with a small amount of any of the organic catalysts heretofore known to promote vinyl polymerization. *t*-Butyl hydroperoxide, peracetic acid, methylethyl ketone peroxide, performic acid, and the like are suitable, but because of its ready availability, freedom from color, and lack of toxicity we prefer to use hydrogen peroxide which yields entirely satisfactory results. Catalysts of the inorganic salt type are less convenient since these act quite rapidly and tend to cause the dispersions to flocculate or gel in a comparatively short time. Completion of the action of the catalysts and therefore of the polymerization, occurs when the dispersions cease increasing in viscosity, this in the case of hydrogen peroxide usually requiring from about 30 minutes to 24 hours depending on the temperature, concentration of the dispersion, and the amount of catalyst added. It is unnecessary to wait for termination of the prepolymerization reaction, excellent results having been obtained when the material has reacted to a roughly estimated quarter of completion. The dispersions are best added to the cellulosic fiber suspension before they have entered the gel stage or have flocculated, depending upon the effect of the particular catalyst used.

The effect of this prepolymerization is to increase the sizes and cationic strength of the particles, as a result of which paper and other cellulosic products are obtained having better water-resistance without increase in the temperature or duration of the curing step.

A particular advantage associated with hydrogen peroxide as catalyst is that only a very small amount is effective and the use of a very large amount is not accompanied by any serious detriment. Moreover, it acts with sufficient rapidity at room temperature. The addition of 10% of hydrogen peroxide based on the weight of solids in the dispersion has given very satisfactory results, and from related experience it is known that as little as 5% or less can be used equally satisfactorily.

At room temperature polymerization is practically complete after 24 hours of standing, but the major part takes place during the first 1-3 hours.

The invention will be further illustrated by the examples which follow. These examples are preferred embodiments of the invention and are not to be construed in limitation thereof.

Example 1

A mixture of 39.8 g. (0.25 mol) of methylenebisacrylamide and 72.5 g. of octadecylamine (0.25 mol) was heated at 175° C. plus or minus 5° C. for 7 hours under a nitrogen gas blanket. A translucent, ivory, slightly fiber-forming wax was obtained. 51.3 g. (0.116 mol) of the product was heated to 163° C. and 2 cc. of glacial acetic acid stirred in. The product was cooled to 130° C. and 4.65 cc. of glacial acetic acid stirred in. The product was further cooled to 110° C. and slowly poured into sufficient rapidly agitated water at 95° C. to give a creamy emulsion containing 5% solids by weight. The emulsion was cooled and the resulting dispersion remained stable.

Example 2

The following illustrates the results obtained when the sizing dispersions of the present invention are employed in the manufacture of alkaline sized paper, with and without partial prepolymerization.

To a suspension of unbleached northern kraft pulp beaten to a Green freeness of 475 cc. at a consistency of 0.6% was added sufficient of the foregoing dispersion diluted with water to 1.5% solids, to provide 5% of sizing solids based on the dry weight of the fibers. The pH of the suspension was then adjusted to 9.0 by the addition of aqueous sodium hydroxide solution, after which the sample was sheeted on a Nash handsheet machine at a basis weight of 46 lbs. per 25" x 40"/500 ream. The sheets were dried for 1 minute at 240° F., conditioned for at least 24 hours at 73° F. and 50% relative humidity and their water and ink resistance determined by the Currier (slack scale) and BKY methods respectively.

A part of the diluted sizing dispersion was at least partially prepolymerized by adding thereto sufficient 30% H₂O₂ to provide 10% of H₂O₂ based on the weight of solids in the dispersion and allowing the mixture to stand for 3 hours at room temperature. Handsheets were made in the same manner containing the thus prepolymerized size.

Control handsheets were also made in similar manner which contained no sizing material. Results were as follows.

Size	Currier (sec.)	BKY (Sec.)
Nil (Control)	Instantaneous	Instantaneous
Not prepolymerized	39	<600
Prepolymerized	43	<600

The results show that a significant improvement was effected by the prepolymerization step.

Example 3

The following illustrates an alternative method for preparing a sizing dispersion corresponding to that of Example 1.

A mixture of 47.7 g. of methylenebisacrylamide (0.3 mol), 84.6 g. of octadecylamine (0.3 mol) and 159 cc. of ethanol as solvent was refluxed under a nitrogen blanket for 3 hours and the ethanol stripped off under vacuum. A white translucent brittle wax was obtained. 70.8 g. (0.16 mol) of the wax was melted and slowly poured into 1000 cc. of rapidly agitated water at 95° C. containing 9.15 ml. (0.16 mol) of glacial acetic acid. A creamy emulsion formed which was cooled and which remained stable.

Tests showed that this product was substantially the same as the product of Example 1, and can be prepolymerized in the same manner.

We claim:

1. A process for manufacturing sized paper which comprises contacting cellulosic fibers with a dilute aqueous dispersion of a salt of a condensation product of about 1 mol of a C₁₆-C₂₂ long chain alkylamine with 1 mol of methylenebisacrylamide, thereby uniformly depositing between about 0.1% and 5% of said product on said fibers based on the dry weight thereof, and heating the fibers at about 190°-260° F. for one-half to ten minutes to dry the same and to develop the sizing properties of the condensation product thereon.

2. A process for manufacturing sized paper which comprises forming an aqueous dispersion of cellulosic fibers, adding to said dispersion a dilute aqueous dispersion of a salt of a condensation product of about 1 mol of a C₁₆-C₂₂ long chain alkylamine with 1 mol of methylenebisacrylamide, thereby uniformly absorbing said condensation product on said fibers, sheeting the fibers at a pH between about 7 and 9 to form a cellulosic web, and heating the web at about 190°-260° F. for one-half to ten minutes to dry the same and to develop the sizing properties of the condensation product thereon.

3. A process according to claim 2 wherein the con-

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densation product is added in at least partially pre-polymerized form.

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