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PROCESS FOR SIZING PAPER WITH POLYETHYLENE

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This invention relates to a novel process for sizing paper, and more particularly to a process for sizing paper by adding a sizing agent to the paper ingredients, e. g. in the beater stage of paper manufacture, or by means of a tub-sizing operation.

For about 150 years rosin has been employed as a paper sizing agent. During that period numerous attempts have been made to find a satisfactory substitute for rosin. Until recently, all such attempts have failed, since no agents were found which could produce the desired effect on paper at a relatively low cost as compared with the cost per ton of sizing paper with rosin. One of the few substances which can be used effectively as a rosin substitute in paper sizing is a polyamine derived from ethylene/carbon monoxide interpolymer, as disclosed in copending U. S. application S. N. 255,133, filed November 6, 1951. Among the chief disadvantages in employing rosin as a paper size is the fact that rosin must be applied in an acidic mixture, and this results in corrosion, as well as a lack of permanence in the end product, since paper which is made at a pH below 7, and particularly below 5, loses strength at an appreciable rate on storage. For certain purposes permanence is highly desirable and, while ordinary rosin-sized paper is serviceable over a period of many years, improvements in the ageing properties of paper, especially paper made under conditions heretofore requiring a low pH, is desirable. Moreover, it has been a common experience in paper manufacturing to observe that for reasons not fully understood inconsistent results are obtained from time to time in rosin-sizing operation, and therefore the trade has adopted the practice, during such periods of difficulty, of making unsized paper and returning to the production of sized paper only after the condition which affects the sizing operation adversely disappears.

In this country the average quantity of rosin employed in sizing paper varies from about 0.1 to about 5%. Paper which is to be employed in outside application, such as billboard paper and the like, is sized with a relatively high percentage of rosin, namely about 5%. In contrast with this, certain varieties of paper which are to be employed in connection with printing, twisting, etc. are either unsized or carry only a relatively small quantity of rosin, viz. 0.1%.

In view of the large quantities of rosin required in the paper industry, and also in view of the deficiencies which, as mentioned hereinabove, frequently occur in connection with the use of rosin as a paper size, a need has arisen for synthetic materials which can be employed effectively and economically as paper sizing agents.

The effectiveness of rosin as a paper size is believed to reside in part in its ability to form a monomolecular film over the individual fibers due in part to the fact that the rosin exists in the form of small particles having a magnitude of 1 to 2 microns. Synthetic resinous materials, in general, fail to do this, although they are frequently capable of imparting water repellence, e. g. by forming a more or less impermeable coating or layer.

To produce optimum sizing action without consuming excessive amounts of resin, it is considered that the resin must be capable of forming a monomolecular film over the fibers, for otherwise large amounts of resin would be needed, and therefore a relatively expensive synthetic resin could not compete with rosin. Thus it appears that a water-insoluble resin, to meet the requirements of a rosin substitute, would have to be capable of existing in the form of polarized, very small particles, such as those of submicroscopic magnitude, which are capable of coalescing on a fiber surface, such coalescing being caused by some ingredient within the fiber or by attractive forces of some other kind, causing the resin particles to be substantive to the fiber. Ordinary water repellents do not possess these desirable characteristics.

An object of this invention is to provide a paper sizing composition which can be employed satisfactorily as a substitute for rosin in paper sizing. A further object is to provide a rosin substitute which can be employed for this purpose without employing an acidic pH below 5 in the beater operation. A still further object is to provide a substitute for rosin which can be used in either clay or calcite filled paper (rosin being ineffective in carbonate-filled paper).

These objects are accomplished in accordance with the present invention by means of a sizing operation which comprises subjecting lignocellulosic fibers, in the beater stage of paper manufacture, or in a tub-sizing operation, to the action of an aqueous dispersion of submicroscopic particles of a normally solid ethylene homopolymer, the pH of the aqueous pulp after addition of the said dispersion being maintained at 5.0 to 8.5, preferably 5.5 to 6.0.

One of the outstanding advantages of the present invention is that it permits the use of a pH not lower than 5 in the beater operation. The sizing efficiency is excellent not only at pH ranges as low as 5.5 but also in substantially neutral mixtures and mildly alkaline mixtures in which the pH is not greater than about 8.5.

A critical feature of the sizing agent of this invention is the magnitude of the polymer particles in the dispersion. These particles, in the dispersions described herein, are of submicroscopic size, i. e. less than about .5 micron. In dilute mixtures (less than 1% concentration) the dispersions appear to be water clear; at a concentration of about 10% they have a slight but perceptible haze; at higher concentrations these dispersions are cloudy in appearance. When the particle size is larger, the low resin loadings employed in the process of this invention fail to give any sizing action. Concentrations as low as about 0.1% are effective, but of course much higher concentrations, up to about 5% or more, can be employed if desired. Use of these higher concentrations is of course less economical than the use of relatively lower concentrations.

It is important in practicing the present invention to use dispersions which are readily coagulable, in the sense that they are capable of depositing polymer particles on the pulp fibers under beater conditions. Control over coagulability can be exercised through the use of sizing aids, such as alum, or other agents known to have a coagulating effect. For example, it is possible to employ a sodium naphthalene sulfonate-formaldehyde condensation product, which can be added to the dispersion in controlled amounts up to the point at which there is incipient coagulation (pH=8.6). The ethylene polymer in such a dispersion is about 100% substantive to paper pulp (potassium laurate used as dispersing agent). In contrast with this, a sodium-alkyl-sulfate-containing dispersion of ethylene polymer failed to coagulate on paper pulp satisfactorily even when alum was present, without any other coagulating agent; thus it is essential to avoid the use of particular dispersing agents which make the dispersions un-

duly stable, unless provision is also made for enhancing coagulability by addition of effective coagulating agents.

Ethylene polymer in the form obtained by emulsion polymerization can be used in practicing the invention, and this form of polymer is relatively inexpensive, as compared with ethylene polymers in the form of dispersions obtained from isolated bulk polymer, and of course is considerably less expensive than animated ethylene/carbon monoxide interpolymer.

The dispersing agents which may be used in preparing the polyethylene dispersions employed herein include the alkali metal salts of long chain fatty acids (e. g. potassium laurate, sodium stearate, sodium palmitate, etc.) as well as any of the other anionic dispersing agents capable of use in emulsion polymerization systems. A representative list is as follows: sodium fatty alcohol sulfates, triethanolammonium stearate, sodium sulfosuccinate, octyl ester, alkylaryl sodium sulfates, ammonium perfluorocarboxylates, sodium salts of saturated hydrocarbon sulfonates, etc. Cationic dispersing agents may also be used. The peroxy compounds, or other free-radical generators include diacyl peroxides, such as diacetyl peroxide, dipropionyl peroxide, dibutyryl peroxide, dilauroyl peroxide, acetyl benzoyl peroxide, and dibenzoyl peroxide; dialkyl peroxides such as diethyl peroxide; dialkyl peroxides such as diethyl peroxide; other peroxides, such as acetal peroxides; alkali metal and ammonium persulfates, perborates and percarbonates. The so-called redox emulsion polymerization systems can be used very effectively.

Loadings of the paper with polymer to the extent of 0.1% to 5% are effective, but still higher loadings may be used. For low loadings, e. g. ca. 0.1 to 0.5%, it is practicable to employ polyethylene dispersions together with urea-formaldehyde resin ingredients, and it has been found surprisingly that the ethylene polymer dispersions are compatible with urea-formaldehyde resins in such applications. Moreover, the ethylene polymer dispersions have been found to be effective sizing agents for carbonate-filled papers.

The invention is illustrated further by means of the following examples.

Example 1.—A colloidal dispersion of polyethylene was prepared by emulsion polymerization of ethylene in the presence of a sodium persulfate catalyst and dipotassium hydrogen phosphate buffer at a pH 9.8–9.9 in an aqueous medium containing 1.4% potassium laurate, at 600 atmospheres pressure, and 140°–145° C. The polyethylene content of the dispersion was 28% by weight. This dispersion was diluted to 0.5% by weight (pH=7.7) and was added to a 2% slurry of unbleached kraft pulp beaten to a Canadian freeness of 600 cc., to give a theoretical loading of 1%. The mixing was continued for 5 minutes. A sufficient quantity (ca. 5% of the weight of the paper solids) of 5% aqueous solution of aluminum sulfate [$Al_2(SO_4)_3$, $18H_2O$] to flocculate the polyethylene on the pulp was added. The pH of the mixture was 5.5. The resulting slurry was beaten for another 5 minutes, and then diluted to 0.025% with water, the mixture having a final pH of 6.95. Paper sheet was made from this dilute suspension in the conventional way and dried at 220° F. for 2 minutes. The paper was then conditioned at 73° F., 50% R. H. for 12 hours. By using the TAPPI standard dry-indicator test for sizing a value of 30 seconds was obtained. (TAPPI Standards, T–433 M44.) The control paper had a dry tensile strength of 16.5 lbs. per inch and a wet tensile strength of 0.2 lb. per inch, while the polyethylene treated paper had a dry tensile of 18 lbs. per inch and a wet tensile of 1 lb. per inch. The same pulp was rosin sized to 1% loading at pH 4.5 in the beater and 5.5 in the head box (using 2% aqueous H_2SO_4 to adjust pH). After being conditioned in the same manner as above, the TAPPI size test gave a value of 25 seconds. In the absence of controlling pH to 5.5 in the head box the pH was 6.95, and virtually no sizing occurred.

Example 2.—Groundwood pulp of 400 cc. Canadian freeness was sized with polyethylene colloidal aqueous dispersion at pH 5.5 in the beater and 6.95 in the headbox at a loading of 0.5%, 1% and 3% respectively. In comparative tests, as shown in Example 1, rosin sizing of the same paper was carried out using the same degree of loading. The following results were obtained in the TAPPI tests: 36, 37, and 40 respectively for the polyethylene sizing and 36, 40, and 44 respectively for the rosin sizing.

Example 3.—A mixture of 80% groundwood and 20% bleached sulfite pulp (Canadian freeness 200 cc.) was sized with polyethylene colloidal dispersion at pH 5.5 in the beater and 6.95 in the headbox to a loading of 0.5% and 1% respectively. TAPPI sizing values of 31 and 37 seconds were thus obtained, while those of rosin in parallel tests (pH controlled to 4.5 in the beater and 5.5 in the headbox) were 31 and 35 seconds respectively.

Example 4.—A soda sulfite pulp (30% bleached sulfite and 70% bleached soda) of Canadian freeness 500 to 600 cc., was made into a 2% aqueous slurry. To this was added polyethylene colloidal aqueous dispersion (20 to 30% polythene) so as to produce loadings of 0.3, 0.6, 0.8, and 1.0%. Sufficient calcium carbonate was added to give 25% of $CaCO_3$ in the final sheet, and sufficient alum was added to give a pH of 7.5 in the beater. Sizing values were 1 sec., 2 sec., 4 sec., 10 sec., respectively. Since rosin was inoperative no comparison with rosin could be obtained in carbonate filled paper.

Example 5.—Example 1 was repeated except that a redox-persulfate polyethylene dispersion, obtained by polymerization in the presence of potassium laurate as dispersing agent, was used. The solids content of the dispersion was 5%, particle size being 1 millimicron. At 0.5% loading the TAPPI test gave a value of 55 sec.; 1% loading, 55 sec.; and 3% 60 seconds.

Example 6.—An unbleached kraft paper at 1% loading with polyethylene was prepared in the same manner as in Example 1, except that the pH in the beater was 3, and in the headbox 6.95. The resulting product gave a value of 12 in the TAPPI test. A similar run with the pH in the beater held at 7 gave a value of 30 in the TAPPI test.

The present invention does not include the treatment of fibrous materials with colloidal dispersions of paraffin or other thermoplastic materials admixed with rosin or similar resinoid substances derived from plants; such colloidal mixtures have been employed heretofore in sizing operations (cf. U. S. 2,356,882). Moreover, the present invention is not concerned with previously known processes wherein paper is merely coated with molten ethylene polymers or dispersions thereof. The discovery that colloidal particles of ethylene polymer are capable of producing an effect similar to that of rosin in the beater stage of paper manufacture, even in the absence of natural-occurring resinoid substances, thus provides a novel method which is entirely different from processes for impregnating or waterproofing paper with thermoplastic materials in the manner suggested in U. S. 2,153,553, 2,188,465, 2,219,700, 2,290,794, 2,298,846, 2,313,144, 2,369,741, 2,373,614, 2,373,615, 2,384,848, and 2,520,900.

We claim:

1. The method for sizing paper which comprises subjecting lignocellulosic fibers in the beater stage of paper manufacture to the action of ethylene homopolymer in the form of solid particles of submicroscopic size colloidally dispersed in an aqueous medium while coagulating the said dispersed homopolymer.

2. The method of claim 1 wherein the ethylene polymer is applied as a dispersion containing alum.

3. The method of claim 2 wherein the pH of the beater contents is 5 to 8.5.

4. The method of claim 2 wherein the dispersing agent is an alkali metal laurate.

5. In a process for manufacturing sized paper the steps which comprise introducing into the aqueous pulp in the

beater stage of paper manufacture and aqueous colloidal dispersion of submicroscopic solid particles of ethylene homopolymer, the pH of the aqueous pulp after addition of the said dispersion being maintained at 5.5 to 6.0, while coagulating the dispersed homopolymer and continuing the beater treatment until upon subsequent drying of the paper ingredients the paper is loaded with the said solid to the extent of 0.1% to 5.0%, whereby a sizing of the paper is effected.

6. The method for sizing calcite-filled paper which comprises subjecting lignocellulosic fibers in the beater stage of paper manufacture to the action of calcite and ethylene homopolymer in the form of solid particles of submicroscopic size colloidally dispersed in an aqueous medium while coagulating the said dispersed polymer.

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