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2,764,483

PROCESS FOR SIZING PAPER

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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. In general, 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 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 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 applications, 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

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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 in the beater operation. A still further object is to provide a substitute for rosin in clay or carbonate filled paper. Other objects of the invention will appear hereinafter.

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 to the action of an aqueous dispersion of submicroscopic particles of an ethylene-carbon monoxide interpolymer polyamine carboxylate salt, as hereinafter defined, said polyamine salt being unmodified by formaldehyde, the carboxylic acid radical of the salt being that of a member of the class consisting of alkanolic and hydroxyalkanoic acids, e. g. acetic, hydroxyacetic, propionic, and lactic acids and mixtures thereof, the pH of the aqueous pulp after addition of the said dispersion being maintained at 5.5 to 8.5, preferably 7 to 7.5, the mol ratio of ethylene/carbon monoxide in the said carboxylate being 3:1 to 15:1, and the nitrogen content of the said carboxylate bring from about 1.0 to 6.0%, preferably 1.5 to 3.0%, until upon subsequent drying of the paper ingredients the paper is loaded with the said salt to the extent of 0.1 to 0.5%, whereby a sizing of the paper is effected. The ethylene-carbon monoxide interpolymer polyamines which are employed in the practice of the present invention are hereinafter referred to by the designation E/CO polyamines. These E/CO polyamines are the products which are obtained by hydrogenation of ethylene-carbon monoxide interpolymers in the presence of ammonia. The E/CO polyamines are disclosed in the Hoehn Patent U. S. 2,495,255 (cf. also British 652,566, French 975,461, Belgian 486,101). Salts of the said polyamines are disclosed in the Cupery application S. N. 48,161 now U. S. Patent 2,579,033, issued December 18, 1951. According to the Cupery application, these salts may be employed as agents for imparting water repellence to textiles. It is to be understood, however, that water repellents for textiles (e. g. paraffin wax, etc.) are generally of no value as rosin substitutes in paper sizing.

In general, the reductive amination of the ethylene/carbon monoxide polymers produces polyamines in which the number of amino groups is either equivalent to the number of carbonyl groups initially present in the interpolymer or is somewhat less than the number of carbonyl groups. The preferred polyamines employed in the practice of this invention have nitrogen contents corresponding to amino substitution somewhat less than the number of carbonyl groups initially present in the polymer. Some of the carbonyl groups which are not aminated may be reduced to hydroxyl groups, but this evidently does not seriously affect the sizing ability of the polymer. E/CO polyamines which have been modified with formaldehyde have been disclosed heretofore. Such formaldehyde-modified E/CO polyamines are not employed in the practice of the present invention.

It is essential, in the process of this invention, that the E/CO polyamine salt be employed in an aqueous

medium, which may be an aqueous acid medium containing a sufficient amount of organic carboxylic acid to produce the desired pH, as hereinabove disclosed. Excellent results are obtained with aqueous acetic acid as the medium. Aqueous hydroxyacetic acid or lactic acid may be employed for this purpose, if desired. The same acid which is employed in the aqueous medium may also be used as the source of the carboxylic acid radical of the polyamine salt, but this is not at all essential. Sources of the acid radical in the salt which are highly effective include acetic, hydroxyacetic, propionic, diglycollic, and lactic acids. Certain mixtures of these acids are outstandingly effective, as disclosed in further detail herein-after. The amount of acid introduced need not exceed the amount required for salt formation.

One of the outstanding advantages of the present invention is that it permits the use of a non-acidic pH 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 in 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 microns. 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, as it is in formaldehyde-modified E/CO polyamines, the low resin loadings employed in the process of this invention fail to give any sizing action.

The polyamine carboxylate salts which are highly substantive to the paper pulp include those in which the ratio of ethylene/carbon monoxide in the interpolymer is from 3:1 to 15:1 (mol proportions), (outstanding results being obtained at about 10:1 to 11:1), provided the nitrogen content of the polyamine carboxylate salt is from about 1.0 to 6.0%, optimum nitrogen content being about 2.4%. Under these circumstances the loading of the paper with the polymer takes place to the extent of about 0.1% to 0.5% based on the dry weight of the sized paper.

The concentration of E/CO polyamine carboxylate salt employed in the beater operation can be varied very widely, and, in view of the substantive nature of the poly-

these higher concentrations is of course less economical than the use of relatively lower concentrations.

Sizing aids such as alum, etc. which are required in the treatment of pulp with rosin are not necessarily employed in the process of the present invention.

The nature of the pulp which may be employed is not particularly critical, and good results are obtained with unbleached kraft, bleached sulfite, groundwood and other pulp.

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

Example 1.—A dispersion is prepared by mixing 20 grams of E/CO polyamine (ethylene:carbon monoxide ratio=11, N₂=2.38%, 2 grams hydroxyacetic acid, and 178 grams of water. This was accomplished by adding the polyamine very slowly to the hydroxyacetic acid, and later dissolving the resulting mixture in water, and maintaining the composition thus produced at a temperature of 70° C. with constant agitation. Finally the mixture was heated for five minutes at refluxing temperature and then cooled to room temperature. To 20 grams of the 100 cc. of water. Mixing of the pulp during addition of diglycollic acid. The resulting mixture was heated under boiling conditions for about 20 minutes. The relatively stable dispersion was thus obtained, which after two months' storage did not change in appearance and continued to have unchanged sizing properties. The particles in the dispersion were of sufficiently small size that they could not be discerned under the microscope. The sizing operation was carried out by diluting the dispersion to 0.5% concentration by addition of water, and introducing the resulting diluted dispersion into a mechanical slurry containing 2.5 grams of beaten, bone dry pulp in 100 cc. of water. Mixing of the pulp during addition of the dispersion was continuous, and the mixing was continued for about ten minutes following the addition of the polyamine composition. The pH of the mixture was 7.5. The slurry was placed on a sheet mold, and a wet web of paper was formed. The wet web was squeezed between felt pads to give a wet paper sheet having a consistency of 32.5%. This web was dried on a drum drier for two minutes at a surface temperature of 220° F. The sized paper of high quality was thus obtained.

Example 2.—Under conditions similar to those described in Example 1, a series of sizing operations was conducted with results as shown in the following table.

TABLE I
Sizing effect of E/CO Polyamines in the absence of formaldehyde

E/CO Polyamine ¹ Dispersion			pH		Drying Conditions		TAPPI Size Dry- Indicator Test, Sec.— Average for a series of tests
Acid		Resin Added, percent	Beater	Head- Box	Time, Min.	Temper- ature, ° F.	
Type	Conc., percent						
Acetic.....	10	0.3	7.4	7.5	2	220	25
Do.....	10	0.4	7.5	7.5	2	220	31
Do.....	10	0.5	7.5	7.5	2	220	32
Do.....	10	0.6	7.5	7.5	2	220	34
Lactic.....	10	0.5	7.5	7.5	2	220	34
Hydroxy-acetic.....	10	0.3	7.4	7.5	2	220	27
Do.....	10	0.4	7.4	7.5	2	220	30
Do.....	10	0.5	7.4	7.5	2	220	33
Do.....	10	0.6	7.4	7.5	2	220	34
Do.....	10	1.0	7.4	7.5	2	220	38
Do.....	10	1.5	7.3	7.5	2	220	36
Do.....	10	2.0	7.0	7.5	2	220	35
Do.....	10	3.0	6.8	7.5	2	220	40
Do.....	5	0.5	7.5	7.5	2	220	32
Do.....	20	0.3	7.5	7.5	2	220	27
Do.....	20	0.5	7.5	7.5	2	220	33

¹ E/CO polyamine analyzed. E/CO Ratio 11/1. Used as 10% aqueous dispersions. Pulp used was unbleached kraft.

mer, it is not critical to employ a relatively high concentration. 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

For comparison with the results given in the above examples it was found that 3% rosin size gave a size test (TAPPI) of 31; in other words, the data prove that the compositions of this invention produce an equal amount

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of sizing at loadings which are only one-tenth as great as the rosin loading.

It will be understood, of course, that the foregoing examples are illustrative only, and that numerous methods for carrying out the process of the invention will occur to those who are skilled in the art. For example, numerous ingredients in addition to the polyamines may be employed if desired. The introduction of paraffin wax, for example, is permissible in the process of the present invention. Dispersing agents, in general, are not required, although they are sometimes of value, especially when waxes, etc. are also present in the dispersion. All such modifications to the extent that they are within the terms of the appended claims are regarded as being within the scope of the present invention.

We claim:

1. In a process for manufacturing sized paper the steps which comprise introducing into the aqueous pulp in the beater stage of paper manufacture an aqueous dispersion of submicroscopic particles of an ethylene-carbon monoxide interpolymers polyamine carboxylate salt, said polyamine salt being unmodified by formaldehyde, the carboxylic acid radical of the said salt being that of a member of the class consisting of acetic, hydroxyacetic, propionic, diglycollic, and lactic acid, and mixtures

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thereof, the pH of the aqueous pulp after addition of the said dispersion being maintained at 5.5 to 8.5, the mol ratio of ethylene/CO in the said carboxylate being 3:1 to 15:1, the nitrogen content of the said carboxylate being from about 1.0 to 6.0%, until upon subsequent drying of the paper ingredients the paper is loaded with the said salt to the extent of 0.1% to 0.5%, whereby a sizing of the paper is effected.

2. Process of claim 1 wherein the pH of the beater contents is 7 to 8.5.

3. Process of claim 2 wherein the carboxylic acid includes both hydroxyacetic and diglycollic acid.

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