United States Patent Office 3,427,219
Patented Feb. 11, 1969

3,427,219

PAPER SIZING WITH A DIAMINE AMIDE DERIVATIVE

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No Drawing. Filed Sept. 17, 1965, Ser. No. 488,279
U.S. Cl. 162—168 8 Claims
Int. Cl. D21h 3/44, 3/38

ABSTRACT OF THE DISCLOSURE

The use of a diamine amide derivative of an interpolymer of a hydrophobic alkenyl ester of a fatty acid and an alpha, beta olefinically unsaturated polycarboxylic acid anhydride as a sizing agent in the preparation of sized paper having increased resistance to the penetration of aqueous liquids.

This invention relates to the sizing of paper, to a new method for accomplishing the sizing of paper, and to new sized paper products.

In the internal sizing of paper and cellulosic products, i.e., sizing by treating the aqueous slurry of cellulose pulp used to make the paper or cellulose products, rosin sizes are used extensively. Rosin sizes are economical sizes but the effectiveness of rosin sizes is usually limited to their use in conditions of pH ranging from about 3.9 to 5.0 or 5.2. The value of rosin sizing generally decreases as the pH of the papermaking conditions is raised. For some applications of paper it is desirable to make the paper under substantially neutral or more alkaline papermaking conditions. Those in the papermaking art are seeking sizing materials that will be effective over a broader range of papermaking pH conditions than are rosin sizes, and also that will be more effective sizing agents and more substantive to the paper product or pulp, whether alum or other ionic precipitating agent is used or not.

An object of this invention is to provide paper sized with hydrophobic polymers which are substantive to the paper pulp and paper product over a broader range of pH papermaking conditions than is economically permissible with rosin sizes.

Another object is to provide a method of sizing paper under substantially neutral or alkaline pH conditions with polymeric hydrophobic, substantive polymers.

Briefly, the above objects are accomplished according to this invention by providing paper sized with a polymeric amide which is a diamine amide derivative of an hydrophobic alkenyl fatty acid monoester/alpha, beta-olefinically unsaturated polycarboxylic acid anhydride interpolymer. Sizing of the paper with these polymeric hydrophobic amides is accomplished by either applying them in organic solvent solution or aqueous emulsion to the surfaces of a cellulose web, e.g., as by tub sizing or surface sizing techiques, or preferably by internal sizing of the aqueous pulp of fibers used to prepare the paper. When applied to or mixed with the pulp fibers by internal sizing it is not necessary to use additional precipitating or flocculating agents such as alum, sodium aluminate, ferric chloride, aluminum chloride, etc. but such materials may be used without deleterious effects with the polymeric amides described herein. In addition, the sized papers can be cured in relatively short periods of time to obtain very hard sized cellulosic webs therefrom.

The polymeric amides used to effect the sizing according to this invention are obtained by reacting a diamine having at least one primary amino group, the other amino group being a secondary, or preferably a tertiary amino group, with an alcohol containing solution of an alkenyl fatty acid ester alpha, beta-olefinically unsaturated polycarboxylic acid anhydride. The diamine may be aliphatic or aromatic and preferably has one of the amino nitrogens substituted with lower alkyl groups, i.e., this one nitrogen in the secondary or tertiary amino condition. Preferably, the diamine is an aliphatic primary-tertiary diamine having from 4 to about 30 carbon atoms. Simple aromatic amines such as dialkylamino-1,4-phenylenediamine, and alkyl substituted dialkylaminophenylene diamines such as dimethylaminophenylenediamine, diethylamino-3-ethyl-1,4-phenylenediamine may be used as the diamine. For reasons of availability and cost dialkylaminoalkylenediamines having from 1 to about 4 carbon atoms in each alkyl group and from 2 to about 20 carbon atoms in the alkylene group are preferred. However, dialkylaminoalkylenediamines having up to about 20 carbon atoms in the alkyl groups to provide additional hydrophobicity may also be used. Specific examples of useful diamines of this type include dimethylaminopropylenediamine, diethylaminopropylenediamine, dipropylaminoethylenediamine, dibutylaminopropylenediamine, dimethylaminohexylenediamine, diethylaminododecylenediamine, dimethylaminooctadecylenediamine, dimethylaminoeicosenylenediamine, as well as mixed alkylaminoalkylenediamines such as methyloctadecylaminopropylenediamine, ethyldodecylaminobutylenediamine, methylbutylaminooctadecylenediamine, and diamines having non-interfering substituents such as hydroxy, cyano, acetyl, aryl, benzoyl, tert-amino, ether groups, sulfonyl, arylthio, alkylthio and the like. Mixtures of diamines may also be used. For example a mixture of a dialkylaminoalkylenediamine and a N-(hydroxyalkyl)-alkylenediamines are especially useful. For example, a 50:50 mixture of dimethylaminopropylenediamine and N-(2-hydroxyethyl)ethylenediamine may readily be used. In conjunction with the diamines minor amounts (up to about 20 mole percent) of unsubstituted polyamines may be substituted in order to attain higher viscosity, if such is desired. Representative polyamines include ethylenediamine, propylenediamine, 1,6-hexanediamine, diethylenetriamine, iminobispropylamine, triethylenetetramine, and tetraethylenepentamine.

The alkenyl fatty acid ester/alpha, betaolefinically unsatuarted polycarboxylic acid anhydride interpolymer utilized as a starting material in the preparation of the sizing materials used in this invention must contain hydrophobic groups, that is chemical groups which permit the polymeric resin coated paper to repell water, at least for a desired period of time. The hydrophobicity of the polymer may be provided by polymerizing the alpha, beta-olefinically unsaturated polycarboxylic acid anhydride with polymerizable lower alkenyl esters of long chained alkanoic acids, that is C_2 to C_4 alkenyl esters of alkanoic acids having from about 9 to about 23 or more carbon atoms. Examples of such polymerizable alkenyl fatty acid esters are the vinyl, allyl, and 1-butenyl esters of nonanoic, decanoic, undecanoic, dodecanoic, tridecanoic, tetradecanoic, pentadecanoic, hexadecanoic, heptadecanoic, octadecanoic, nonadecanoic, eicosanoic, docosanoic, tricosanoic acids. These alkenyl alkanoates may be derived from straight or branched chained materials. Mixtures of alkenyl fatty acid esters may be used. Thus, this invention involves the use of lower alkenyl esters of acids derived from natural oils as linseed oil, cottonseed oil, castor oil, olive oil, safflower oil, palm oil, coconut oil, fish oils, chinawood oils, peanut oil, oiticica oil and soybean oil. The fatty acids contained in such oils, all of which are generally designated as glyceride oils, will usually contain from 12 to 18 or more carbon atoms and include caprylic acid, lauric acid, stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, ricenoleic acid, and the like. Fatty acids from non-glyceride sources such as tall oil and the like can also be used. The resulting polymer may thus be an interpolymer of two or more

alkenyl fatty acid esters and one or more alpha, beta-olefinically unsaturated polycarboxylic acid anhydride.

For reasons of availability and favorable cost maleic anhydride is preferred as the alpha, beta-olefinically unsaturated polycarboxylic acid anhydride comonomer in preparing the interpolymers which are used to make the sizing agents for this invention. However, unsatuarted polybasic carboxylic acid anhydrides, in general, having from 4 to about 10 carbon atoms could readily be used to prepare the copolymer starting materials. Examples are anhydrides such as itaconic acid anhydride, citraconic acid anhydride, and other copolymerizable related homologous unsatuarted polycarboxylic acid anhydrides.

The molecular weights of the alkenyl fatty acid/alpha, beta-olefinically unsaturated polycarboxylic acid interpolymers which are used for this invention generally have molecular weights of from about 1,000 to about 25,000. Interpolymers of lower molecular weight give poor sizing results whereas copolymers much above about 25,000 are difficult to prepare. The molecular weight of the polymer used can also depend upon the monomers used. For example, allyl stearate/maleic anhydride copolymers generally are lower in molecular weight than those of vinyl stearate/maleic anhydride, made by similar methods.

The diamine amide derivative of the hydrophobic alkenyl fatty acid ester/alpha, beta-olefinically unsaturated polycarboxylic anhydride interpolymer may be prepared by mixing the chosen diamine with an alcohol containing solution of the polymer. The alcohol may be the only solvent or may be mixed with other appropriate solvents or diluents but the amount of alcohol used is usually present in an amount equivalent to the anhydride content of the polymer being dissolved therein. The alcohol may be aromatic or aliphatic. It may be necesasry that the alcohol be capable of opening the anhydride rings and at least partially esterifying the polymer. Examples of effective alcohols include the lower alkanols such as methanol, ethanol, isopropanol, butanol-1, isobutanol, hexanol, alkoxyalkaols such as 2-butoxy-1-ethanol, 2-ethoxy-1-ethanol, and aromatic alocohols such as xylol, phenylmethanol, etc. The alcohol may be used alone or mixed with with common organic solvents such as hexane, benzene, acetone, etc. A small amount of amine such as a tertiary amine or an acid such as p-toluenesulfonic acid appears to aid the anhydride ring opening. Primary tertiary diamines added in small amount to the alcoholic solution of the polymer may be used as the catalyst, just prior to addition of the remaining diamine to the polymer solution. The chosen diamine is added rapidly to the alcohol containing solution of the polymer and stirred preferably at room temperature, or from about 0° C. to about 50° C. to replace ester groups and to form amide groups on the polymer. The diamine is generally added in an amount which is about stoichiometrically equivalent to the anhydride content of the polymer. However, it is not essential to amidate all of the anhydride or esterified groups. Good sizing can be accomplished if at least a majority of such groups are amidated. Best results are obtained when at least about 85% of the anhydride or esterified acid groups are amidated. Stirring of the diamine treated polymer solution for about 0.5 to 2.0 hours is generally sufficient to obtain a good size product. Some of the amidated interpolymer products are formed as precipitates and may be recovered as such and dispersed in water to any desired concentration with the aid of a small amount of amomnia or other base. Usually, not more than about 5 percent of ammonia based on the weight of the polymeric amide is necesasry.

The polymeric amide, may be dispersed in water, as above and applied to paper or pulp slurries in any desired concentration. Sizing effects may be observed on paper containing as little as about 0.1 percent based on weight of the dry pulp in the pulp slurry treated. It is not usually necessary or desirable, because of cost, to apply more than about 5 percent based on the weight of the pulp. It is usually preferred to provide from about 0.3 to about 2 percent of the polymeric amide size, based on the weight of the pulp or paper treated therewith. These materials may be used to size papers which are made from cellulosic pulps treated at pH conditions ranging from about 3.9 to about 8.5. They are most effective when used at pH's ranging from about 4.5 to about 7.5.

The treated pulps may be formed into cellulosic webs and dried in the usual manner to obtain sized paper. The amount of sizing may be controlled by the amount of the sizing agent and by the conditions of drying. These sizing agents when applied to cellulosic webs may be cured to make a hard sized web by use of high temperatures of drying for a short period of time, e.g., from about 225°–300° F. for from 1 to 5 minutes.

This invention is further exemplified by the following detailed examples.

Example 1

This example illustrates how the alkenyl fatty acid ester/alpha, beta-olefinically unsaturated polycarboxylic acid anhydride polymers, and the diamine derivatives used in this invention may be prepared.

A mixture of 162 g. (0.50 mole) of allyl stearate, 49 g. (0.50 mole) of maleic anhydride and 1.0 ml. of di-t-butyl peroxide was warmed in a 500 ml. round bottomed flask. The two phased system which resulted was diluted with 100 g. of toluene and heated to reflux (133° C.) under a condenser. Heating was continued 25 hours at 133–125° C. The resulting reaction mixture was stripped by heating on an oil bath at 220–225° C. and 0.6 torr. There remained as residue 180 g. of the allyl stearate/maleic anhydride copolymer. It was a soft, brittle solid. It was soluble in toluene and in hexane.

A 20 g. portion of an allyl stearate/maleic anhydride copolymer, prepared as described above, was dissolved in a mixture of 35 ml. of xylol and 250 ml. of acetone. To the resulting solution there was slowly added 6.37 g. of diethylaminopropanediamine (weight equivalent to the anhydride content of the polymer) with stirring at 25° C. A flocculant precipitate formed during stirring for five minutes. The mixture was filtered washed with acetone and air dried over night. There was obtained 22.9 g. the diethylaminepropanediamine amide of the allyl stearate/maleic copolymer.

Example 2

This example illustrates the exceptionally good sizing imparted to paper made from aqueous pulp slurries treated with the diamine derivatives of the alkenyl fatty acid ester alpha, beta-olefinically unsaturated polycarboxylic acid anhydride copolymers according to this invention.

To a 1500 g. aliquot (containing 30 g. of pulp) of an aqueous slurry of bleached sulfite pulp there was added 3 g. of the diethylaminopropanediamine amide of the allyl stearate/maleic anhydride copolymer dispersed in sufficient water to make a 1 percent concentration with the aid of 0.2 ml. of concentrated ammonia, which dispersion had been stirred cold for 30 minutes. The treated pulp slurry, thus obtained, was used to make paper therefrom and dried on a Noble and Wood paper making machine. Similar test sheets of paper were prepared from untreated pulp, and from pulp slurries treated with 3 percent of a commercially available dry, substantially completely neutralized rosin size, dispersed in water. Some samples were also treated with 5% of papermaker's alum. The pH of the aqueous pulp slurries were adjusted to either 4.5 or 6.5 before sheet formation.

The dried test sheets were tested for the amount of sizing by a standard ink test method in which test sheets were floated on an ink bath having a pH of 1.5 at 25° C. The time in seconds for an even blue coloration to appear on the upper observed surface of the test sheet was

noted and recorded. The results of this test are summarized in the following table:

TABLE I

Sizing agent	Percent size [1]	5% alum	pH of slurry	Ink penetration at 25° C., seconds
ASMA-NH_4 [2]	3	Yes	4.5	0
ASMA-DEAPA [3]	3	Yes	4.5	420
Dry rosin size [4]	1	Yes	4.5	240
ASMA-DEAPA	3	No	6.5	1,800+
ASMA-DEAPA	1	No	6.5	300
Dry rosin size	3	Yes	4.5	300

[1] Percent size means the weight percent based on the dry pulp used.
[2] ASMA-NH_4 means the allyl stearate/maleic anhydride copolymer ammonium salt.
[3] ASMA-DEAPA means the diethylaminopropanediamine amide of allyl stearate/maleic anhydride copolymer.
[4] Dry rosin size is the substantially completly saponified (neutralized) rosin size sold by Monsanto Company under its trademark "Mersize" RM dry.

The table shows that the ASMA-DEAPA gave exceptional sizing with and without the use of alum as a precipitating agent, at both 4.5 and 6.5 pH. The dry rosin size, used as a standard, gave less effective sizing. The ASMA.NH_4 salt example gave no sizing by the internal size method, indicating that for internal sizing, the DEAPA derivative is necessary to obtain substantivity, that is, adherence of the resin to the pulp and paper.

Example 3

Following the procedure described in Example 2 aqueous pulp slurries were treated with diethylaminopropylamine amide of vinyl stearate/maleic anhydride copolymer, dispersed in water with the aid of some ammonia, adjusted to pH 4.5 or 6.5 and formed into paper. At the lower pH alum was also added. The resulting test sheets gave 160 seconds of sizing at pH 4.5 using 5% alum, and 240 seconds of sizing at pH 6.5 using no alum.

Example 4

Samples of the dried papers sized with ASMA·DEAPA and with VSMA·DEAPA (VSMA means the vinyl stearate/maleic anhydride copolymer) were cured by heating at 105° C. for five minutes. Cured paper samples containing 1% of the resins showed no ink penetration after 30 minutes in the ink bath. Paper samples containing 3% of the resins showed no ink penetration. The side of the paper sheets of these samples in contact with the ink were not even stained with ink.

Example 5

In another test 0.5 g. of the N,N-diethylaminopropylamine amide of allyl stearate/maleic anhydride copolymer prepared as described in Example 1, was dissolved in 50 ml. of water and 0.15 ml. of ammonium hydroxide warmed to about 50° C. To a 1.5 liter portion of a 2% sulfite pulp aqueous slurry there was added 30 ml. of the above polymer solution and the pH was adjusted to 6.0 with formic acid. Handsheets were made from the thus treated pulp slurry and dried on a Noble and Wood Drier. The dried paper showed 1000 seconds of ink resistance sizing. Curing of the paper for 5 minutes at 105° C. resulted in increase of sizing efficiency to 1500 seconds by the same standard ink penetration resistance test. Samples cured for 1 hour at 105° C. gave 2400 seconds of sizing by the same test. Untreated samples of the same paper gave no sizing, i.e., 0 seconds by the ink penetration test.

What is claimed is:

1. Paper having increased resistance to penetration by aqueous liquids comprising a water laid web of cellulosic fibers treated with an amount of from about 0.1 to about 5.0 percent, based on the weight of the fibers, of a diamine amide derivative of an interpolymer having a molecular weight of from about 1,000 to about 25,000 of a hydrophobic alkenyl ester of a fatty acid wherein the alkenyl group has from 2 to 4 carbon atoms and the fatty acid group has from 9 to about 23 carbon atoms and an alpha, beta-olefinically unsaturated polycarboxylic acid anhydride having from 4 to about 10 carbon atoms, said diamine amide moiety being derived from a diamine having at least one primary amino group and from 2 to about 30 carbon atoms.

2. Sized paper as described in claim **1** wherein the diamine amide moiety is derived from a dialkylaminoalkylenediamine having from 1 to 4 carbon atoms in each alkyl group and from 2 to about 20 carbon atoms in the alkylene moiety.

3. Sized paper as described in claim **2** wherein the dialkylaminoalkylenediamine amide is derived from diethylaminopropylenediamine and the interpolymer is derived from an allyl stearate/maleic anhydride copolymer.

4. Sized paper as described in claim **2** wherein the dialkylaminoalkylenediamine amide moiety is derived from diethylaminopropylenediamine and the interpolymer is derived from a vinyl stearate/maleic anhydride copolymer.

5. A method of improving the properties of a water laid cellulosic web which comprises (a) adding to an aqueous slurry of papermaking cellulosic fibers, in an amount of from about 0.1 to about 5.0 percent, based on the weight of the fibers, a diamine amide derivative of an interpolymer having a molecular weight of from about 1,000 to about 25,000 of a hydrophobic alkenyl fatty acid ester wherein the alkenyl group has from 2 to 4 carbon atoms and the fatty acid group has from 9 to about 23 carbon atoms and an alpha-beta-olefinically unsaturated polycarboxylic acid anhydride having from 4 to about 10 carbon atoms, said diamine amide moiety being derived from a diamine having at least one primary amino group and from 2 to about 30 carbon atoms, (b) affixing the diamine amide derivative on the fibers, and (c) forming the treated fibers thus obtained into a web.

6. A method as described in claim **5** wherein the diamine amide moiety is derived from a dialkylaminoalkylenediamine having from 1 to about 4 carbon atoms in each allyl group and from 2 to about 20 carbon atoms in said alkylene group.

7. A method as described in claim **6** wherein the dialkylaminoalkylenediamine amide moiety is derived from diethylaminopropylenediamine and the interpolymer is derived from an allyl stearate/maleic anhydride copolymer.

8. A method as described in claim **6** wherein the dialkylaminoalkylenediamine amide moiety is derived from diethylaminopropylenediamine and the interpolymer is derived from a vinyl stearate/maleic anhydride copolymer.

References Cited

UNITED STATES PATENTS

2,582,235	1/1952	Cowan et al.	260—78
2,641,593	6/1953	Teeter et al.	260—18
2,767,089	10/1956	Renfrew et al.	162—179
2,772,967	12/1956	Padbury et al.	162—179

FOREIGN PATENTS

250,386	3/1964	Australia.

S. LEON BASHORE, *Primary Examiner.*

U.S. Cl. X.R.

162—179; 260—18, 78

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,427,219

February 11, 1969

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It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 45, "allyl" should read -- alkyl --.

Signed and sealed this 17th day of March 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents