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3,526,524

FORTIFIED PASTE ROSIN SIZE CONTAINING A DISSOLVED CONTENT OF A CATIONIC WATER-SOLUBLE POLYALKYLENEPOLYAMINE

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No Drawing. Continuation-in-part of applications Ser. No. 372,115, June 2, 1964, and Ser. No. 546,200, Apr. 29, 1966. This application July 14, 1967, Ser. No. 653,354 Int. Cl. C08h 11/04, 11/06; D21h 3/34 U.S. Cl. 106—238

6 Claims

ABSTRACT OF THE DISCLOSURE

The invention provides paste rosin size of superior sizing properties resulting from the presence in the size of a dissolved content of a water-soluble cationic polyalkylenepolyamine containing at least 10 amino nitrogen atoms, the size may contain a small amount of a highly ionized water-soluble salt as an agent which decreases the viscosity of the size.

This is a continuation-in-part of consecutively copending applications Ser. Nos. 372,115 and 546,200 filed on June 2, 1964, and Apr. 29, 1966, respectively. Both applications are now abandoned.

The present invention relates to paste rosin size of improved sizing properties, and to paper sized therewith.

Paste rosin size is the most widely used agent for the manufacture of sized paper and consists essentially of a rosin which has been saponified with an aqueous alkali metal alkali solution. The amounts of water and of alkali used are predetermined so that the product contains 60%—80% by weight of rosin size solids and 5%—25% of rosin acids based on the weight of the rosin solids (cf. U.S. Pat. No. 2,873,203) while having a viscosity at which it is pumpable, and small amounts of highly ionizing water soluble salts and lower alkanols may be present to decrease the viscosity of the size. Among the rosins used for the manufacture of this size are gum rosin, wood rosin, tall oil rosin, and mixtures thereof, as well as the "fortified" rosins prepared by reacting the aforementioned rosins with a small amount of formaldehyde, saligenin, maleic anhydride, fumaric acid, acetylenedicarboxylic acid, etc. The term "fortifying" means that the added component increases the effectiveness of the size as an agent which renders cellulose fibers water-resistant when applied thereto in aqueous suspension by the action of alum.

The discovery has now been made that paste rosin size is very appreciably increased in its effectiveness as a sizing agent for paper when it contains a small dissolved amount of a cationic polyalkylenepolyamine containing at least 10 amino nitrogen atoms per macromolecule. Since rosin size is anionic and since the polyalkylenepolyamines are cationic, the present invention results from the discovery that an agent previously deemed incompatible with rosin size is in fact compatible therewith, up to a limit, and that up to that limit the agent enhances the beneficial properties of the size. The invention possesses the following additional advantages:

(1) It is applicable to sizes made from ordinary rosin as well as to sizes made from previously-known fortified rosins.

(2) It does not require that the rosin size be subjected to any unusual or difficult processing step.

(3) It improves the resistance of cellulose fibers sized therewith to penetration not merely by water, but by hot aqueous lactic acid solutions as well.

The polyalkylenepolyamine fortifying agent produces

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the greatest percentage increase in the lactic acid resistance imparted by rosin size when the amount of the polyalkylenepolyamine fortifying agent which is added to the size and the amount of rosin size which is added to the fibrous suspension are both small.

In preferred instances the polyalkylenepolyamine more than doubles the lactic acid sizing efficiency of the rosin size.

The fortifying action of the polyalkylenepolyamine increases per increment of polyalkylenepolyamine added to the size but at a decreasing percentage rate per increment, up to the point where the polyalkylenepolyamine causes the size to flocculate or gel, and thus to pass from its paste state. Hence, there does not appear to be any critical amount of polyalkylenepolyamine fortifying agent below this limit which rosin size must contain to receive at least partial benefit of the present invention.

In general, the polyalkylenepolyamine fortifying agents present in the sizes of the present invention are normally water-soluble polyalkylenepolyamines of any configuration which contain more than (and preferably many more than) 10 basic amino nitrogen atoms per macromolecule and which do not decompose in paste rosin size, which is necessarily hot (50° C.—100° C.).

A variety of such polyalkylenepolyamine compounds are known which are suitable for use as fortifying agents in paste rosin size compositions of the present invention.

One type is the unmodified polyalkylenepolyamine type: for example, polyethylenimine itself; the substantially complete reaction product of one mol of ethylene dichloride and one mol of triethylenetetramine; and the substantially complete reaction product of one mol of ethylene dichloride with 3,3'-iminobispropylamine in the presence of an acid acceptor, so as to form a condensate having a molecular weight in excess of about 2,000.

The evidence is that the presence of amide groups in polyalkylenepolyamine fortifying agents is advantageous, and accordingly there may be used the linear polyamido-polyamines formed by reacting one mol of adipic acid (or similar acid) with one mol of a lower polyalkylenepolyamine, preferably tetraethylenepentamine until about two mols of water have evolved.

Another class of polyamine which can be used are those formed by condensation methylenabisacrylamide with ethylenediamine to form a substantially linear polymer having a molecular weight in excess of about 2,000.

The aforementioned polyalkylenepolyamines may be thermosetting or non-thermosetting, and each type is effective as fortifying agent.

Our evidence is that the higher the molecular weight of the polyalkylenepolyamine, the better is the fortifying action which it imparts.

The paste rosin sizes of the present invention are conveniently prepared by stirring a desired amount of a suitable water-soluble polyalkylenepolyamine fortifying agent directly into paste rosin size. The polyalkylenepolyamine is added in aqueous or solvent solution state; and the added solvent may be removed from the size by vacuum evaporation so as to return the size to its original solids content.

The fortifying agents of the present invention, being cationic, possess the property of flocculating paste rosin size when added in too large amount. Necessarily, then, the maximum amount of the cationic fortifying agent which is present in paste rosin size according to the present invention is the largest amount which permits the size to remain in unflocculated paste condition. This is usually less than 20% of the dry weight of the size.

This maximum amount depends both on the cationic strength of the fortifying agent and on the ionic strength of the size and consequently varies from instance to instance, and may be as much as 20% of the weight of size

solids in the size. The preferred amount in any instance is most easily determined by laboratory trial, as illustrated in the examples which follow. The presence of too much of the polyalkylenepolyamine fortifying agent in the size is evidenced by loss of paste consistency, so that the size is no longer of pumpable viscosity (less than 50 poises at 70° C.). Flocculation and precipitation of the size, when they occur, occur rapidly and are clearly visible to the eye.

In practice, we have found it preferable to use a strong polyalkylenepolyamine as fortifying agent and for the amount of polyalkylenepolyamine fortifying agent to be between about 0.5% and 3% of the dry weight of the sizing solids of the paste rosin size, as an amount of such fortifying agent within this range provides a significant improvement in sizing efficiency while usually avoiding the dangers of flocculation and precipitation of the size.

The size of the present invention is used in the manufacture of rosin sized paper in the same manner as paste rosin size has been used in the past, except that somewhat less is needed in any one instance to achieve a given level of sizing. The paper which is produced by the process is composed of paper sized by the rosin size and the polyalkylenepolyamine fortifying agent working in combination. The manner in which the cationic fortifying agent cooperates with the rosin size to produce this increase in sizing is not known, and applicant does not wish to be restricted to any theory.

The paste rosin size of the present invention may contain other materials such as are commercially present in paste rosin size, for example, isopropanol or other lower alkanols to decrease its viscosity, pentachlorophenol to prevent growth of microorganisms, and emulsified wax as supplementary sizing material. These materials are chemically inert and do not interfere with the action of the cationic fortifying agent. The size may also contain one or more highly ionizing water-soluble salts, for example sodium or potassium chloride or acetate or nitrate or preferably sodium or potassium sulfate or phosphate. These salts in small amount are fluidifying agents; i.e., they decrease the viscosity of the size.

The invention will be more particularly described by the examples which follow. These examples constitute specific embodiments of the invention, and are not to be construed as limitations thereof.

EXAMPLE 1

The following illustrates the preparation of paste rosin size compositions according to the present invention.

The rosin size used is a typical fortified rosin size of commercial grade prepared by reacting tall oil rosin with 2% by weight of paraformaldehyde at 150° C., heating the mixture at 270° C. for half an hour, cooling the mixture to 200° C., reacting the mixture with 5% of fumaric acid, and saponifying the resulting mixture with a solution of sodium hydroxide to form a paste rosin size containing 15% free rosin and 77% solids by weight.

Samples of the size are taken which are respectively treated at 70° C. (a typical temperature of paste rosin size) by incorporating therein the percentage of one of the polymers shown in the table below. The polymers are added as 10%–40% neutral aqueous solutions after which sufficient water is boiled off to return the solids content of the size to 77%.

One sample is reserved as control and to this nothing is added.

The sizes are stable against gelation and decomposition of the cationic agents when stored at 70° C. for seven days. The sizes are stable when diluted with water to 3% solids.

The comparative sizing efficiency of the sizes is determined by forming an aqueous suspension of a 70:30 bleached softwood: bleached hardwood pulp beaten to a Canadian standard freeness of 510 ml. and having a pH of 7. Aliquots are taken, and to these are added sufficient of the mixture to provide 1% of size based on the dry

weight of the fibers, followed by 1.5% of alum on the same basis. The pulp is sheeted to form handsheets having a basis weight of 200 lbs. per 25" x 40"/500 ream. The handsheets are pressed on a Noble & Wood press and are dried for 1.5 minutes on each side on a rotary laboratory drum drier having a drum temperature of 240° F.

The sheets are conditioned at 70° F. and 50% relative humidity to constant weight and their sizing is determined by ascertaining their resistance to penetration by 20% aqueous lactic acid solution at 100° F. applied to pene-scope under a 12" head.

Results are as follows:

Run No.	Desig.	Cationic fortifying agent		Sizing tests	
		Percent in size ¹	Name ²	Percent size added ³	Lactic acid resist ⁴
1	Control	None	Adipic acid-TEPA cond., low M.W.	1.0	435
2	A-1	4	Adipic acid-TEPA cond., low M.W.	1.0	566
3	A-2	4	Adipic acid-TEPA cond., high M.W.	1.0	685
4	B	0.5	Adipic acid-TEPA-epi condensate.	1.0	530
5	B	1.0	do	1.0	560
6	B	1.5	do	1.0	830
7	B	3.0	do	1.0	1,150
8	C	2.0	Bisphenol A-epi-ethylene dichloride-DETA	1.0	505
9	D	0.5	Polyethylenimine, M.W. 40,000.	1.0	475
10	E	0.5	Ethylenediamine-ethylene dichloride cond.	1.0	460
11			Cationic starch (Cato 8).	1.0	-----

¹ Based on weight of size solids in the size.

² For explanation of abbreviations, see text below. All fortifying agents are non-thermosetting.

³ Based on dry weight of the fibers.

⁴ Seconds.

Polymers A-1 and A-2

Prepared by mixing 1 mol of adipic acid and 1 mol of tetraethylenepentamine (TEPA) and heating at 150° C. A sample is removed after 1 hour when a low-molecular weight polymer forms (A-1) having a molecular weight of a few thousand, and when the reaction is substantially complete at the end of 2 hours (polymer A-2) with formation of polymer of considerably higher molecular weight.

Polymer B

Prepared by condensing 1 mol of adipic acid with 1 mol of TEPA at 150° C. to a viscosity of 1200 centipoises at that temperature, dissolving the condensate in 2 parts of water, heating the solution to 80° C., and slowly adding 0.3 mol of epichlorohydrin (epi) per mol of combined tetraethylenepentamine present. Reaction of the epichlorohydrin is complete in 90 minutes. The product is a non-thermosetting water-soluble resin having a molecular weight over 5,000.

Polymer C

Into 206 g. of vigorously stirred diethylenetriamine (DETA) at 90° C. is slowly dropped over 30 minutes 105 g. of the diepoxy derivative of 2 mols of epichlorohydrin and 1 mol of bisphenol A. The temperature is kept at 100° C. by cooling during the reaction and for 30 minutes thereafter. The mixture is diluted with 50 ml. of water and 160 g. of ethylenedichloride is added at such rate that the temperature of the liquid remains above 90° C., 50 ml. of water being added when the addition of the ethylene dichloride is 80% complete. The liquid is maintained at 90° C. after addition of all of the ethylene dichloride.

Polymer D

Polyethylenimine having a molecular weight of approximately 40,000.

Polymer E

Ethylene dichloride is added dropwise to hot ethylene-

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diamine containing sodium hydroxide as said acceptor until a viscous water-soluble condensate forms, which has a molecular weight in excess of three thousand.

EXAMPLE 2

The procedure of run 3 of Example 1 is repeated except that the pulp used is a 50:50 by weight bleached softwood:bleached hardwood pulp and the amount of size added is varied. Results with the size containing 0.5% of the polyalkylenepolyamine are illustrated by runs 1-5; control runs made in the same manner except that no cationic agent is present in the size are illustrated by runs 6-10. The comparative sizing of the handsheets was also determined by the total immersion test as percentage of water absorbed.

Run No.	Cat. agent in size, ¹ percent	Size added, ² percent	H ₂ O abs., percent	Lactic acid resist ³
1-----	0.5-----	0.50	46.0	289
2-----	0.5-----	0.75	40.0	583
3-----	0.5-----	1.0	38.4	867
4-----	0.5-----	1.5	38.1	1,524
5-----	0.5-----	2.0	36.4	-----
6-----	None-----	0.50	47.2	223
7-----	do-----	0.75	44.8	548
8-----	do-----	1.0	40.1	840
9-----	do-----	1.5	39.4	1,448
10-----	do-----	2.0	37.9	-----

¹ Based on weight of rosin in the size.

² Based on the dry weight of the fibers.

³ By method of Example 1.

EXAMPLE 3

The procedure of Example 2 is repeated except that the cationic compound which is added to the size is the thermosetting water-soluble polyalkylenepolyamine wet strength resin formed by condensing 1 mol of adipic acid with 1 mol of diethylenetriamine at 155° C. until about 2 mols of water have evolved, dissolving the resulting viscous condensate in water, and reacting the condensate with 1 mol of epichlorohydrin by the method shown for the preparation of the agent of resin B of Example 1. Results are as follows; the values for the control are those of the control of Example 2.

Run No.	Cat. agent in size ¹	Size added, ¹ percent	H ₂ O abs., percent	Lactic acid resist ¹
1-----	0.50	0.50	48.6	245
2-----	0.50	0.75	42.1	609
3-----	0.50	1.0	40.8	958
4-----	0.50	1.5	37.0	1,446

¹ For explanation see table of Example 2.

EXAMPLE 4

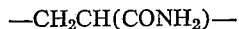
The procedure of run 5 of Example 1 is repeated, except that the rosin size to which the cationic agent is added is commercial gum rosin size containing no fortifying agent. The presence of the polyalkylenepolyamine fortifying agent approximately doubles the effectiveness of the size.

EXAMPLE 5

The procedure of Example 3 is repeated, except that the resin is the thermosetting water-soluble diethylenetriamine-epichlorohydrin (1:3 molar ratio) resin of Example 1 of Daniel et al., U.S. Pat. No. 2,595,935. The resin exerts a similar fortifying action as the resin of Example 3 herein.

EXAMPLE 6

The procedure of Example 3 is repeated, except that the resin is a thermosetting water-soluble resin prepared by subjecting polyacrylamide to the Hofmann degradation to form a polyvinylamine composed of



and $-\text{CH}_2\text{CH}(\text{NH}_2)-$ linkages in 3.7 ratio and then reacting with formaldehyde to form a thermosetting water-soluble resin. Similar results are obtained to those obtained in Example 3.

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EXAMPLE 7

The following illustrates the effect of highly ionizing salts and lower alkanols in decreasing the viscosity of compositions according to the present invention.

A fortified rosin size is prepared by reacting a tall oil rosin with 2% of paraformaldehyde at 150° C., heating the rosin at 270° C. for 30 minutes to remove foaming components, reacting the rosin at 200° C. with 4% of its weight of fumaric acid and saponifying the rosin to 75% solids and 15% free acid with aqueous sodium hydroxide. To the size is added 0.5% based on the weight of solids therein of polyethylenimine. Portions are taken. One is reserved as control and to this nothing is added. To the remaining portions are added aqueous solutions of the salts shown in the table below, after which all solutions are adjusted to 75% solids. The viscosities of the resulting paste sizes are then determined at 71° C. A similar preparation is made wherein the additive is isopropyl alcohol.

Results are as follows:

Run No.	Additive		Viscosity (cp.) at 71° C.	
	Name	Percent ¹	Percent PEI ¹	Percent decrease
1-----	None-----	-----	0.5	2,170 -----
2-----	KCl-----	1	0.5	2,075 4.4
3-----	K ₂ HPO ₄ -----	1	0.5	2,040 6.0
4-----	K ₂ SO ₄ -----	1	0.5	2,000 7.8
5-----	Isopropyl alcohol-----	1	0.5	1,850 14.8

¹ Based on weight of sizing solids in size.

The presence of the salt in the size does not interfere with the fortifying action of the polyalkylenepolyamine.

I claim:

1. Paste rosin size of pumpable viscosity of from about 5% to 25% free rosin acids content containing between about 60% to 80% of solids by weight, said size having a small but effective dissolved content of a cationic water-soluble polyalkylenepolyamine containing at least 10 amino nitrogen atoms per macromolecule as fortifying agent.

2. Paste rosin size according to claim 1 wherein the polyalkylenepolyamine is non-thermosetting.

3. Paste rosin size according to claim 1 wherein the polyalkylenepolyamine is a cationic 1:1 molar ratio adipic acid-tetraethylenepentamine condensate containing at least 10 amino nitrogen atoms per macromolecule.

4. Paste rosin size according to claim 1 wherein the polyalkylenepolyamine is the cationic reaction product of about 0.1 mol of epichlorohydrin with a 1:1 molar ratio adipic acid-tetraethylenepentamine condensate containing at least 10 amino nitrogen atoms per macromolecule.

5. Paste rosin size according to claim 1 wherein the polyalkylenepolyamine is a cationic 1:1 molar ratio diglycidyl ether-polyalkylenepolyamine condensate containing at least 10 amino nitrogen atoms per macromolecule.

6. Paste rosin size according to claim 1 wherein the polyalkylenepolyamine is a cationic normally thermosetting reaction product of about 1 mol of epichlorohydrin with a 1:1 molar ratio adipic acid-diethylenetriamine condensate in thermoset state, said reaction product containing at least 10 nitrogen atoms per macromolecule.

References Cited

UNITED STATES PATENTS

3,305,493 2/1967 Emmons ----- 162-164

ALLAN LIEBERMAN, Primary Examiner

U.S. Cl. X.R.

162-164, 180; 260-24

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,526,524 Dated September 1, 1970

Inventor(s) Russell Joseph Kulick

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

Column 5 line 23 "36.4" should be -- 36.5 --; Column 5 line 71 "3.7" should be -- 3:7 --.

ORIGINAL
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(SEAL)

Attest:

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Attesting Officer

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