

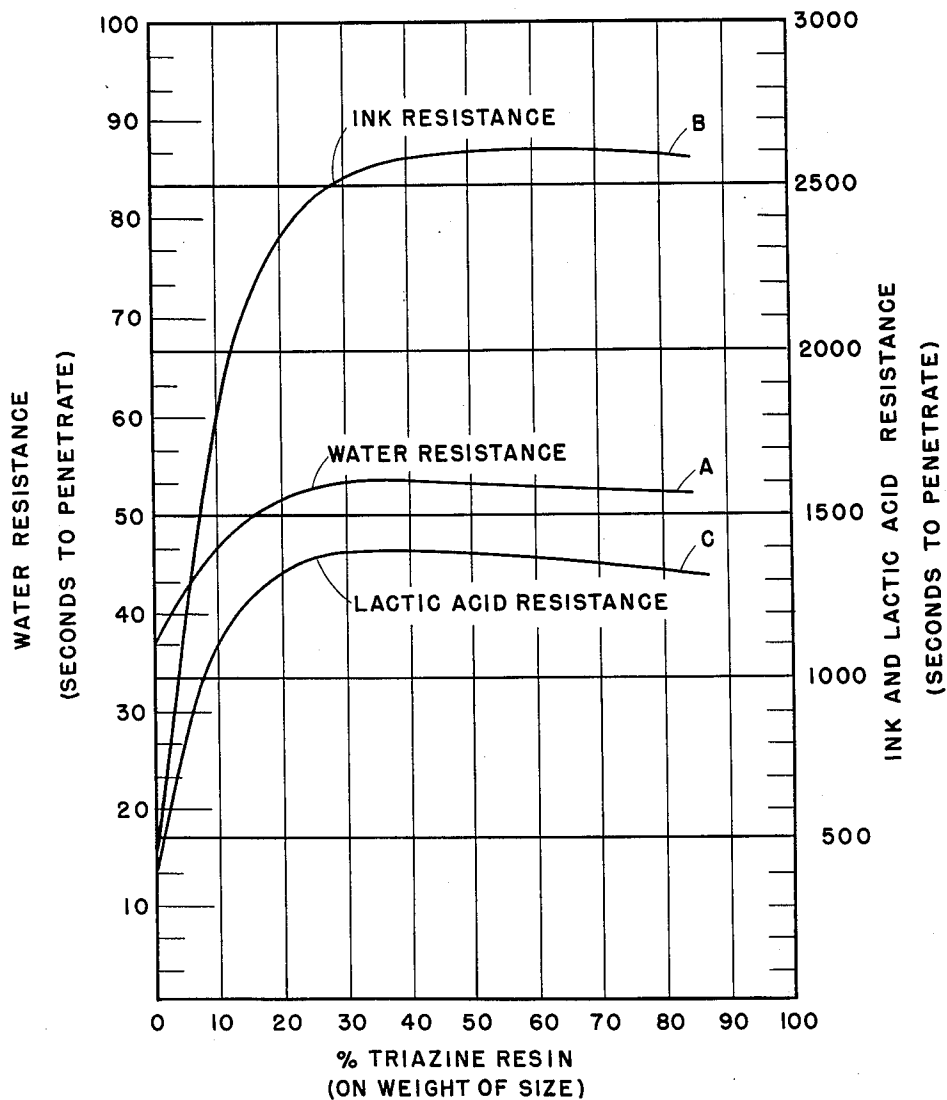
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S. T. MOORE ETAL

3,033,743

ROSIN SIZED PAPER CONTAINING SIZING PROMOTOR

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INVENTORS.
SEWELL T. MOORE
LEO A. LANDERS

BY

Evans Kahn

ATTORNEY

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3,033,743

ROSIN SIZED PAPER CONTAINING SIZING
PROMOTOR

Sewell T. Moore and Leo A. Landers, Stamford, Conn.,
assignors to American Cyanamid Company, New York,
N.Y., a corporation of Maine
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The invention relates to the manufacture of rosin sized paper. More particularly, the invention relates to the manufacture of rosin sized paper containing a small amount of a 2,4-diamino-s-triazine resin as agent promoting the action of the rosin sizing therein.

The largest part of paper intended for use in contact with aqueous materials (including writing inks and food) is manufactured today by a process which has as its principal steps the sizing of cellulose fibers in aqueous suspension by addition of a rosin size and alum thereto, sheeting the fibers to form a cellulosic web, and drying the web to form paper. The fibers carry an alum-rosin composition which renders the paper resistant to penetration by aqueous liquids.

The discovery has now been made that the sizing results afforded by the above process can be increased, and in preferred embodiments very greatly increased, by adding to the aqueous suspension of cellulose fibers (at some point prior to the sheeting step) a small amount of an aqueous acid solution of a cationic thermosetting hydrophilic 2,4-diamino-s-triazine-formaldehyde resin preferably at the "0° C. hydrophobe" or higher stage of condensation, after which manufacture of the paper is completed in customary manner.

By itself the resin effects substantially no sizing, and consequently its action may be regarded as a synergistic or fortifying one. The invention, however, does not depend on any particular explanation and we do not wish to be bound by any theory.

The type and extent of the improvement effected by addition of the 2,4-diamino-s-triazine resin is illustrated in the drawing, which is a plot of the sizing possessed by a series of rosin sized papers versus the amount of 2,4-diamino-s-triazine resin added during their manufacture.

The drawing represents the averaged results of a large number of laboratory experiments. Results are plotted in terms of the application of 2% of liquid gum rosin and 2% of alum to a well-beaten pulp without and with addition of 2,4-diamino-s-triazine-formaldehyde resin. The resin was added in increasing amounts up to 75% of the dry weight of the size, and was added after the rosin size has been added but before the alum. The pulp was treated and handsheets formed and tested by the general method set forth in Example 1 below.

In the drawing, graph A shows the water-resistance developed by the sheets (left-hand scale) and graphs B and C respectively show their ink and lactic acid resistance (right-hand scale).

Comparison of graphs A, B, and C shows that a distinct synergistic or other fortifying action occurs when the weight of the added resin is as little as 10% of the dry weight of the size. The curves rise sharply from the left hand ordinate scale, so that evidently there is no amount of resin, however small, which will not produce some benefit. The graphs further show that in all three cases most

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efficient fortifying action (in terms of the dry weight of resin added based on the dry weight of the size) occurs when the weight of the triazine resin is between 5% and 15%-25% of the weight of the size. The graphs finally show that very little, if any, further fortifying action takes place when the weight of triazine resin added is in excess of 33%-50% of the dry weight of the rosin size.

As the maximum amount of rosin size generally employed in paper manufacture is rarely in excess of 3% (sizing solids based on the dry weight of the fibers), the maximum amount of triazine resin in paper produced according to the present invention will preferably be about 0.45% or 0.75%. On the other hand, at least about 0.1% or 0.2% of the resin will preferably be present calculated on the same basis.

The added triazine resin, so far as has been observed, does not harm the paper in any way, and the dry strength of the paper is ordinarily slightly better. It is particularly important that the resin, though thermosetting, imparts practically no wet strength. Hence paper produced according to the present invention (including broke) can be repulped substantially as readily as ordinary rosin sized paper.

The present invention does not foreclose use of cationic wet-strength resins and such resins may be added in customary manner with normal effect as shown in U.S. Patent No. 2,559,220. The triazine resin solution may be added at any point in the papermaking machine, prior to web formation. Adsorption of the resin occurs rapidly within a minute or so and no separate aging period is therefore required. We have found, however, that best fortifying action takes place, all other conditions remaining the same, when the resin is added to the fibrous suspension at a point subsequent to addition of the rosin size and prior to addition of the alum. It is advantageous to dilute the triazine solution to 1% solids with water to facilitate uniform mixing.

The present invention does not require any change in the sheeting or drying procedure. Best sizing is usually developed when the web is maintained at a temperature in the range of 225° F. to 250° F. until thermosetting of the resin is substantially complete as judged by levelling off of sizing values. This generally occurs in about one minute at 250° F.

The manner in which the rosin sizing and triazine resin are present on the fibers and the manner in which they cooperate to effect improved sizing are not known. The paper of the invention is therefore most conveniently described in terms of the process used for its preparation.

The aqueous acid solutions referred to are preferably prepared by dissolving a hydrophilic "0° C. hydrophobe" resin (in dry or syrup form) in aqueous acid (preferably hydrochloric acid) containing about one mol of acid for every mol of combined triazine therein, adjusting the water content so that the solution contains about 10%-15% resin solids by weight, and aging the solution at room temperature for several hours or more to allow partial pre-polymerization to occur; cf. Wohnsiedler et al. U.S. Patent No. 2,356,718. The solution should be used before gelation has started.

The resins themselves may be prepared by refluxing one mol of the appropriate triazine with two or more mols of formaldehyde at about 60% calculated initial methylol-triazine content. The mixture is refluxed at an acid pH at least until it reaches the "0° C. hydrophobe" point, that

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is, the point at which a drop of the syrup forms a milky streak when allowed to fall into ice water. At this point the syrup is hydrophilic but is rapidly developing hydrophobic properties.

Better sizing is often obtained by use of syrups which have been condensed to the "20° C. 50% solids hydrophobe" point, that is, the point where a sample of the syrup hydrophobes when mixed with an equal volume of water at room temperature. The syrup is then converted to acid solution form with or without spray-drying.

The invention will be more particularly described in the examples which represent specific embodiments of the invention. These embodiments are illustrations of the invention and are not to be construed as limitation thereof.

Example 1

The following illustrates the improved sizing resulting from use of a cationic 2,4-diamino-s-triazine resin in conjunction with rosin size according to the present invention.

The triazine resin was made by refluxing one mol of 2,4-diamino-6- α -hydroxyethyl-s-triazine (lactoguanamine) with 2.0 mols of 37% formalin at pH 6.2 and at 60% resin solids by weight (calculated as the dimethyloltriazine) until a sample of the syrup hydrophobed when diluted to 50% solids with water and mixed with an equal volume of water at room temperature. The syrup was then dissolved in aqueous hydrochloric acid containing 1.0 mol of HCl per mol of the original triazine to form a solution containing 12% solids by weight, which was aged at room temperature over night.

Handsheets were prepared and tested in uniform manner according to standard laboratory procedure using well-beaten 60% sulfite-40% soda pulp at 0.6% consistency. The size was commercial liquid gum rosin size. The reagents were added in the order and amounts shown in the table below, five minutes of gentle stirring following each addition. The pH of the pulps were adjusted to 4.5 with hydrochloric acid before sheeting and sheets were made on a Nash handsheet machine at 50 lb. (25" x 40"/500 ream) basis weight. The sheets were dried for 1 minute at 240° F. on a laboratory drum drier and conditioned 16 hours at 73° F. and 50% relative humidity and tested. Results are as follows:

Run No.	Percent added ¹			Tensile lb./inch		Sizing results		
	Size	Resin	Alum	Dry	Wet	Water sec. ²	Ink sec. ³	Lactic Acid sec. ⁴
Control A	3.0	-----	3.0	15.0	1.0	77	425	365
Control B	-----	1.0	3.0	16.8	1.2	9	5	5
1	3.0	1.0	3.0	13.2	1.6	>600	>600	>600

¹ Based on dry weight of pulp.

² Seconds for water to penetrate, as determined by Wooding electric tester (U.S. Patent No. 2,691,135 using porous stainless steel head of U.S. Patent No. 2,691,136).

³ Seconds for reflectance of one surface of paper to fall by 20% when opposite size is wet with fountain pen ink (B.K.Y. test).

⁴ Seconds for 20% lactic acid solution at 100° F. under hydrostatic head of 10 inches to penetrate. Endpoint determined colorimetrically by penescope.

The results show that the water, ink and lactic acid resistance values obtained from the paper of run 1 were in excess of the sum of the values obtained from the papers of controls A and B.

From subsequent work it is known that similar results are obtained when the rosin size is prepared from wood

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rosin, tall oil rosin, or the reaction product of one of the foregoing rosins with $\frac{1}{10}$ - $\frac{1}{4}$ mol of maleic anhydride, citric acid, saligenin, or formaldehyde as fortifying agent.

Example 2

The following illustrates the effect the proportion of the triazine resin on the sizing obtained.

The method of Example 1 was repeated except for the amounts of resin, rosin size and alum added.

Run No.	Reagents added, ¹ percent			Percent on size ²	Sizing results		
	Resin	Size	Alum		Water sec. ¹	Ink sec. ¹	Lactic acid sec. ¹
Control	-----	2.0	2.0	-----	39	405	455
1	0.10	2.0	2.0	5.0	39	755	550
2	0.25	2.0	2.0	12.5	47	3,155	1,295
3	0.50	2.0	2.0	25.0	53	1,671	1,150
4	1.00	2.0	2.0	50.0	51	>2,000	1,400
5	1.50	2.0	2.0	75.0	53	>2,000	1,510

¹ See table of Example 1.

² Dry weight of 2,4-diamino-s-triazine resin over dry weight of size.

Example 3

The following illustrates the effect of the sequence of addition of the reagents. The general method of Example 1 was repeated, except that the resin was prepared from 2,4-diamino-6-methoxymethyl-s-triazine (which had barely passed the 0° C. hydrophobe point) as the raw material, and the rosin size was prepared from a maleated rosin containing $\frac{1}{10}$ mol of combined maleic anhydride equivalent as fortifying agent, as shown in U.S. Patent No. 2,684,300. In each run there was added 0.5% of triazine resin as the acid solution, 1.0% rosin size, and 1.0% alum (solids based on the dry weight of the paper). Results are as follows:

Run No.	Sequence of addition	Sizing results		
		Water sec. ¹	Ink sec. ¹	Lactic acid sec. ¹
1	Size—alum	44	285	250
2	Size—resin—alum	52	350	285
3	Size—alum—resin	49	305	255

¹ See table, Example 1.

The results show that best sizing was obtained (run No. 2) when the rosin size was added first, then the triazine resin, and finally the alum.

Example 4

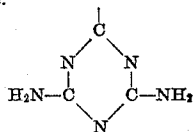
The following illustrates the results obtained with a number of 2,4-diamino-s-triazine resins according to the present invention. In each instance the general procedure of Example 1 was repeated except that the parent triazines, proportions of materials, and test pulps were varied as shown in the table.

Monotriazines

Run	Parent 2,4-diamino-s-triazine	Percent added ¹			Sizing			Pulp
		Resin	Size	Alum	Water sec. ²	Ink sec. ¹	Lactic Acid sec. ¹	
Control	-----	-----	1.0	1.0	30	280	230	Sulfite-soda
1	6-ethyl-----	0.3	1.0	1.0	45	780	591	
Control	-----	-----	1.0	1.0	41	60	60	
2	6-Allyloxymethyl-----	0.2	1.0	1.0	51	130	125	Bleached sulfite.
3	6- α -hydroxyisopropyl-----	0.2	1.0	1.0	47	150	175	
Control	-----	-----	1.0	1.0	44	59	95	Bleached sulfite.
4	6-Chloro-----	0.5	1.0	1.0	48	91	120	
5	6-Chloromethyl-----	0.5	1.0	1.0	50	85	105	

Bis-triazines

Control	-----	-----	³ 2.0	2.0	52	472	910	Bleached sulfite.
6	R-CH ₂ CH ₂ -N(C ₆ H ₅)-CH ₂ CH ₂ -R ⁴ -----	0.5	³ 2.0	2.0	54	1,356	2,305	
7	R-CH ₂ CH ₂ -N(CH ₃)-CH ₂ CH ₂ -R ⁴ -----	0.5	³ 2.0	2.0	54	702	1,270	

¹ See footnotes to table of Example 1.² By Currier test (slack scale).³ Fortified rosin size prepared by reacting gum rosin with 1/5 mol of maleic anhydride prior to saponification.⁴ Formula of bis-triazine; R's designate.

We claim:

1. In the manufacture of paper wherein cellulose paper-making fibers are sized in dilute aqueous suspension by addition of a rosin size and alum, said fibers are sheeted to form a cellulosic web, and said web is dried to form paper, the step of adding to said suspension a cationic "0° C. hydrophobe" thermosetting hydrophilic 2,4-diamino-s-triazine-formaldehyde resin in aqueous acid solution form in effective amount, not in excess of 50% of the weight of said size, as agent increasing the resistance imparted to said paper by said size to penetration by aqueous liquids.

2. A method according to claim 1 wherein the rosin size is added first, the triazine resin is added secondly, and the alum is added thirdly.

3. A method according to claim 1 wherein the dry weight of said triazine-formaldehyde resin is between 5% and 25% of the dry weight of the size.

4. A process according to claim 1 wherein the paper is maintained at a temperature of 225° F.-250° F. until said resin is substantially completely thermoset.

5. A method according to claim 1 wherein the rosin size is a fortified rosin size containing 1/10 to 1/4 mol of combined maleic anhydride.

6. In the manufacture of paper wherein cellulose paper-

making fibers are sized in dilute aqueous suspension by addition of rosin size and alum, said fibers are sheeted to form a cellulosic web, and said web is dried to form paper, the step of adding to said aqueous suspension an aqueous acid solution of a cationic "0° C. hydrophobe" hydrophilic thermosetting 2,4-diamino- α -hydroxyethyl-s-triazine resin in effective amount up to 33% of the weight of said size, as agent increasing the resistance imparted to said paper by said size to penetration by aqueous liquids.

7. Paper produced by a process according to claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

2,301,509	Bock et al. -----	Nov. 10, 1942
2,356,718	Wohnsiedler et al. -----	Aug. 22, 1944
2,559,220	Maxwell et al. -----	July 3, 1951
2,632,700	Niles -----	Mar. 24, 1953
2,684,300	Wilson et al. -----	July 20, 1954
2,785,149	Wohnsiedler -----	Mar. 12, 1957

FOREIGN PATENTS

654,305	Great Britain -----	June 13, 1951
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,033,743

May 8, 1963

Sewell T. Moore et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 21, for "alum-rosin" read -- aluminum-rosin --; line 42, for "2,4-8" read -- 2,4- --; line 51, for "has" read -- had --; column 2, line 51, for "hydrophode" read -- hydrophobe --; columns 5 and 6, in the table, "Monotriazines" should be centered underneath the columns "Resin", "Size" and "Alum" as follows:

Resin Size Alum

Monotriazines

Signed and sealed this 10th day of September 1963.

SEAL)

test:

ERNEST W. SWIDER
Testing Officer

DAVID L. LADD
Commissioner of Patents