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2,934,468

FORTIFIED ROSIN SIZE AND PAPER SIZED THEREWITH

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This invention relates to a novel fortified rosin size, i.e. rosin size which when applied in paper-making manufacture yields paper and other water-laid cellulose webs of improved resistance to penetration by aqueous fluids such as water, ink, and particularly lactic acid. The invention includes the size itself, water-laid cellulosic webs sized by a content thereof, and methods for making the size and the webs. Cellulose webs having high resistance to penetration by aqueous lactic acid solutions (representative of food acids in general) are required in the manufacture of milk containers, ice cream containers, paper cups, food wrap paper, etc.

It is known that rosin can be improved (in terms of the water, etc. resistance it imparts to cellulose fibers sized therewith) by pre-reacting the rosin with an alpha,beta unsaturated dicarboxylic anhydride containing not more than 6 carbon atoms such as maleic anhydride, maleic anhydride-dehydrated citric acid mixtures, etc. (cf. U.S. Patent Nos. 2,383,933, 2,628,918, and 2,684,300; also application Serial No. 359,445 filed on June 3, 1953, now U.S. Patent No. 2,771,464). The improvement effected by such prereaction is generally termed "fortification," and the size prepared from the treated rosin is generally termed "fortified rosin size." The anhydride is reacted in small but effective amounts, generally between $\frac{1}{12}$ to $\frac{1}{4}$ mol of anhydride per mol of rosin.

The discovery has now been made that formaldehyde, when irreversibly reacted with rosin, also acts as fortifying agent, greatly improving the effectiveness of size prepared therefrom. We have found that when formaldehyde is prereacted with the rosin and the rosin converted to size, the lactic acid resistance imparted by the size is often about doubled. In addition, the water resistance and ink resistance imparted are usually substantially improved. The amount of formaldehyde required for this effect is small, generally $\frac{1}{4}$ % to 7 % of the weight of the rosin, equivalent to about $\frac{1}{40}$ to $\frac{1}{2}$ mol.

This discovery was unexpected as the normal action of formaldehyde is to make compounds into which it is introduced more hydrophilic. The reacted formaldehyde present in liquid sizes prepared according to the present invention imparts the advantage of decreasing and often preventing the tendency of the size to crystallize. As a result, liquid sizes of the present invention can be held in storage longer than would otherwise be the case, thus permitting more flexible papermill operations.

The sizes of the present invention are prepared by irreversibly reacting a rosin with a small but effective amount of formaldehyde for the purpose described followed by saponifying the treated rosin in normal manner with aqueous alkali metal alkali solution to form liquid size which may be dried. According to present day commercial practice, the amount and strength of aqueous alkali solution employed is predetermined so that the saponification product contains from about 60% to 80% sizing solids by weight, and up to about 30% of free rosin acids, based on the weight of rosin acids originally present in the rosin. The rosin acids are thus at least 70% saponified and are usually substantially completely or 100% saponified when intended for conversion into dry size form. The particular manner in which the rosin is con-

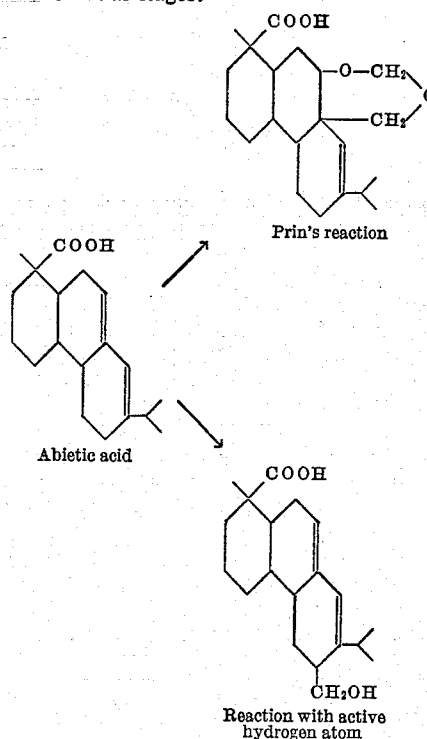
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verted into size, however, is not a primary feature of the invention.

The size is used in the same manner as ordinary rosin size by forming a dilute aqueous suspension of paper-making cellulose fibers, adding a dilute aqueous solution of the size, precipitating the size on the fibers by alum, sheeting the fibers to form a web, and drying the web to form paper. The size on addition to the pulp may contain other materials such as starch, locust bean gum, alkali-stable wax size, pitch dispersants of the naphthalene-sulfonic acid type known as Tanak A, casein, clay, etc.

A perceptible improvement resulting from the presence of irreversibly reacted formaldehyde has been noticed when as little as $\frac{1}{40}$ mol of formaldehyde is reacted per mol of rosin, so that evidently there is no amount of formaldehyde, however small, which will not produce some benefit. At the other extreme, the amount of formaldehyde added need not be materially in excess of $\frac{2}{3}$ mol calculated on the same basis, as in this upper range the benefit imparted by each increment of formaldehyde becomes less significant. In practice, we have found it preferable to react the rosin with between about $\frac{1}{10}$ to $\frac{1}{3}$ molar equivalents of formaldehyde (1% to 3.3% by weight) as in this range the benefits associated with the presence of the formaldehyde are most apparent, and waste of the formaldehyde is minimized. It will be understood, however, that it is within the scope of the invention to prepare the size by reacting the rosin with a larger amount of formaldehyde and blending the reaction product with untreated rosin to decrease the formaldehyde content of the blend within the range stated.

The mechanism by which the formaldehyde reacts is not known and I do not wish to be limited to any theory. Theoretical chemistry indicates, however, that the formaldehyde may react simultaneously according to several reactions, of which the following equations indicate two of the possible initial stages:



Theory further indicates that continued heating converts any such compounds present into complex polymer form.

The foregoing equations have not been proved and are presented for whatever value they may have in assisting an understanding of the invention. It is evident, how-

ever, that the formaldehyde reaction product is a complex mixture in which the formaldehyde is substantially irreversibly combined and that the sizes obtained therefrom are most conveniently described in terms of its preparation.

The irreversible reaction of rosin with formaldehyde begins at a temperature of approximately 135° C., below which only a loose association complex forms which is of no substantial value in the present invention, the presence of which may be determined by the phenylhydrazine test for free formaldehyde. Good results are obtained up to about 250° C., and even higher temperatures may be used with however, some decomposition resulting in decreased effectiveness. In plant practice, we prefer to carry out the reaction at a temperature between about 190° C. and 230° C., the reaction taking place rapidly while darkening of the rosin and formation of decomposition products are minimized. The reaction should be continued until the amount of formaldehyde which has irreversibly reacted is within the range indicated. Unreacted formaldehyde is tolerated and is lost with the white water during the sheeting step.

The formaldehyde may be added to the rosin in any convenient form. Formalin (37% aqueous formaldehyde solution), gaseous formaldehyde or trioxane are suitable when a closed reaction vessel is available. The reaction may be performed in an open vessel at atmospheric pressure when the formaldehyde is paraformaldehyde (added either as such or dissolved in the alcohol mixture known as Formcel), and for this reason paraformaldehyde is preferred.

The rosins used in the preparation of sizing agents, according to the present invention include gum rosin, wood rosin, and the newly developed rosin known as tall oil rosin (i.e., the rosin remaining after removal of the fatty acids from tall oil by fractional distillation), for

haps as the result of the reaction of rosin carboxyl groups with methylol groups introduced by the paraformaldehyde. The rosin was then cooled to 140° C. and saponified by adding thereto with stirring 190 gm. of 13% aqueous sodium hydroxide solution. A liquid rosin size of 70% solids and 19% free rosin acid content was obtained.

The foregoing procedure was repeated for purposes of control using the same rosin and the same volume of caustic solution except that the step of adding formaldehyde was omitted and a slightly stronger (14.5%) sodium hydroxide solution was used. The increase in strength of the caustic solution was required by the higher acid number of the rosin so as to obtain a size of the same free acid content.

The two sizes were tested according to standard laboratory procedure by preparing an aqueous slurry of bleached 60%:40% sulfite:soda pulp at 0.6% consistency and adding thereto 2% of the size diluted to about 5% solids with water, followed by the addition of 2% of alum. All weights represent solids based on the dry weight of the fibers.

The sized fibers were sheeted on a British handsheet machine at 200 lb. basis weight (lb. per 25" x 40"/500 ream) and dried on a laboratory drum drier at 240° F. for four minutes. The sheets were conditioned at 73° F. and 50% humidity for 24 hours and tested to determine their resistance to penetration by 20% aqueous lactic acid solution at 100° F., fountain pen ink, and water. The lactic acid values were obtained by penescope, the ink values by automatic reflectometer using the under side of the sheet as the base and the water adsorption values by the total immersion method, the time of immersion being 15 minutes at 73° F. Handsheets were similarly made at a basis weight of 50 lb. for determination of ink resistance values.

CH ₂ O React.		Lactic Acid Resistance		Water Absorption			Ink	
Mols	Percent	Secs.	Percent Incr.	Weight, Gm.			Secs.	Percent Incr.
				Init.	Final	Gain		
None		135		1.76	2.45	0.69	205	
1/2	2	265	96.4	1.72	2.31	0.59	290	41.5

which standards have been established by the U.S. Department of Agriculture. Additional rosins include the rosins prepared by condensing a natural rosin of an alpha, beta unsaturated dicarboxylic anhydride, etc., as described above, and pure abietic acid itself.

The invention will be more particularly illustrated by the examples. These examples represent specific embodiments of the invention and are not to be construed as limitations thereon.

Example 1

The following illustrates the increase in resistance to aqueous fluids imparted by rosin size containing a preferred amount of combined formaldehyde according to the present invention.

To 302 gm. (1 mol) of S grade tall oil rosin at 140° C. in an open glass vessel heated by an electric mantle and provided with slow agitation was added 6.0 gm. (1/2 mol) of paraformaldehyde coarse powder. The paraformaldehyde dissolved in about one hour with slow stirring. The temperature of the reaction mixture was then raised over a period of one hour to 220° C. and maintained at that temperature for another hour, at the end of which time the paraformaldehyde had irreversibly reacted. Analysis of the mixture by the phenylhydrazine method showed 0.004% free formaldehyde. The acid number of the rosin (corrected for addition of the formaldehyde) was found to have decreased slightly, per-

The table shows the presence of only 2% or 1/2 mol of reacted rosin nearly doubled the resistance of the paper to penetration by lactic acid solution and produced a substantial increase in the resistance of the sheets to absorption of water and penetration by ink.

The foregoing tests were essentially repeated, the significant change being the addition of 0.2% of petroleum wax emulsion size along with the rosin size (wax solids based on the dry weight of the fibers). The presence of combined formaldehyde in the rosin component did not adversely affect the lactic acid, water and ink values.

Samples of the two sizes as prepared (i.e., at 70% solids and 19% free acid content) were placed in an incubating oven at 80° C. and observed for crystallization. The control size started to develop crystals in five days and turned into a substantially solid mass of crystals in 20 days, but the test sample (which contained the 2% of reacted formaldehyde) remained entirely free from crystals for 25 days.

Example 2

The following illustrates the preparation of an improved fortified rosin size according to the present invention by simultaneously reacting formaldehyde and a minor amount of an alpha, beta unsaturated dicarboxylic anhydride with rosin followed by saponification. A mixture was prepared in the apparatus of Example 1 from 302 gm. (1 mol) of S-grade tall oil rosin at 150° C.,

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15.1 gm. of maleic anhydride (0.15 mol) and 11 gm. of 55% methyl Formcel (a 55% by weight solution of paraformaldehyde in methanol-water), the amount of the formaldehyde thus being equivalent to 0.2 mol based on the rosin. The methanol and water flashed off. The temperature was slowly raised to 220° C. and maintained at that point for one hour. At the end of this time, reaction of the maleic anhydride and the formaldehyde was substantially complete.

The molten fortified formaldehyde-containing rosin was saponified to form a 70% solids liquid size containing 19% free rosin acid as described in Example 1.

A control size was prepared by repeating the above procedure except that no formaldehyde was added and the amount of caustic used for saponification was adjusted so as to produce a liquid size of a same free acid content.

The lactic acid resistance imparted by the sizes was determined by the general method of Example 1 except that the pulp was bleached northern kraft, and the sheets were formed on a Nash handsheet machine. Results are as follows:

CH ₂ O Reacted		Maleic Anhydride Reacted		Lactic Acid Resistance	
Mols	Percent	Mols	Percent	Secs.	Percent Incr.
None	-----	None	-----	205	-----
None	-----	0.15	5	530	-----
1/2	2	0.15	5	1,005	89.5

The results show that adding formaldehyde along with the maleic anhydride very materially increased the fortifying effect. Other laboratory data show that similar results are obtained when the rosin and maleic anhydride are reacted separately in either sequence.

Example 3

The following tests were made to illustrate the comparative effectiveness of formaldehyde as fortifying agent on tall oil rosin using gum rosin as the standard. Tall oil rosin is the rosin which of all the commercial rosins usually imparts lowest water-resistance and so is the most important rosin to improve.

A series of liquid sizes was made according to the general method of Example 1 employing rosin, S-grade tall oil rosin as representative of commercial tall oil rosin and WG gum rosin as representative of commercial gum rosin. The formaldehyde was added in the form of paraformaldehyde in amounts shown in the table below and in each instance the sizes were prepared at 70% solids and 19% free acid content by the general method of Example 1, the sizes were tested by the method of Example 1, except that the amount of size added was 2.5% of the dry weight of the fibers and the size was precipitated by 3% of alum.

The efficiency of each size was determined on a 60%:40% bleached sulfite:bleached hardwood pulp, the hardwood component of which had been bleached with chlorine dioxide. It is well known that this pulp is unusually difficult to size.

The sheets were prepared on a British hand sheet machine (basis weight 200 lb. per 40" x 25"/500 ream) and were dried for four minutes at 240° F. and conditioned as described above. Results are as follows.

No.	Rosin	CH ₂ O Reacted		Lactic Acid Resistance		Water Absorption	
		Mols	Percent	Secs.	Percent Incr.	Gain, Percent	Percent Decr.
1	Gum	None	-----	55	-----	47.2	-----
2	do	1/2	2	100	82.0	41.2	12.7
3	Tall Oil	None	-----	35	-----	58.0	-----
4	do	1/2	2	80	128.0	40.6	30.0

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The table shows (Nos. 1 and 3) that while untreated gum rosin size is markedly superior to untreated tall oil rosin size, fortification of the tall oil rosin with formaldehyde (No. 4) increased the effectiveness of the size so that it surpassed untreated gum rosin (No. 1) in lactic acid resistance imparted and even became the equal of formaldehyde-reacted gum rosin in the water absorption test.

Example 4

The following illustrates the use of aqueous formalin as the fortifying agent.

302 gm. (1 mol) of N-grade wood rosin was placed in a laboratory autoclave and 16.3 gm. (0.2 mol) of 37% aqueous formalin added thereto. The autoclave was sealed, brought to a temperature of 220° C., allowed to remain at that temperature for one hour, and then allowed to cool. Analysis of the rosin by the phenylhydrazine method showed a content of 0.0003% by weight.

The treated rosin was formed into a liquid size at 70% sizing solids and 19% free acid content and tested by the method of Example 1 in comparison with corresponding wood rosin liquid size which, however, contained no combined formaldehyde. The sheets containing the size prepared from the treated rosin were markedly superior to the control sheets in their lactic acid resistance values.

Example 5

The following illustrates the effect on the lactic acid resistance imparted by variations in the proportion of formaldehyde reacted.

The general procedure of Example 1 was followed using S grade tall oil rosin, and the amount of caustic used for saponification was adjusted so as to obtain in each instance a 70% solids size containing 19% free rosin acids.

The resistance of the sheets to penetration by lactic acid was determined by the method of Example 1, except that 60/40 bleached sulfite and chlorine dioxide bleached hard wood pulp and 2 1/2 % sizes and 3% alum were used based on the dry fibers. Results are as follows:

CH ₂ O React.		Lactic Acid Resist.		Water Absorption	
Mols	Percent	Secs.	Percent Incr.	Percent Gain	Percent Decr.
None	-----	30	-----	54.4	-----
1/10	1.0	45	50	46.0	15.4
1/5	2.0	70	133	42.2	22.4
1/2	3.3	110	260	41.2	24.3
2/3	5.0	100	230	40.7	25.2
1	6.7	90	210	-----	-----

The results indicate that most efficient utilization of the formaldehyde occurs within the range 1/10-1/3 mol of formaldehyde per mol of rosin.

Example 6

The effect of the fortifying pretreatment of the present invention upon the tendency of the liquid rosin sizes to crystallize was determined as follows. Tall oil rosin was employed for this test because this yields liquid sizes which normally display greatest tendency to crystallize.

A series of sizes was prepared by fortifying S-grade tall oil rosin according to the method of Example 1 in the presence or absence of maleic anhydride as supplementary fortifying agent as shown in the table below. The rosins were converted into liquid size at 79% solids and 24% free acid content, experience having shown that liquid sizes having this total solids and free acid content display most pronounced tendency towards crystallization on storage.

The liquid sizes were tested by taking 2 ounce samples of each size, tightly stoppering the bottles, and incubating the bottles in an oven maintained at 70° C. The samples

were observed every day for evidence of crystallization, and the observations were discontinued when crystallization reached 50%.

The percent of crystallization was determined in each instance by viewing a sample of the size through a microscope and estimating the proportion of the field occupied by crystals. A crystallization value of 10% is about the most that can be tolerated in a paper size. Results are as follows:

No.	CH ₂ O React.		Maleic Anh. Reacted		Percent Crystallization				
	Mols ¹	Percent ²	Mols ¹	Percent ²	One Day	Two Days	Three Days	Seven Days	Forty Days
1-----	None	-----	None	-----	0	2	10	50	-----
2-----	None	-----	0.15	5.0	0	0	2	10	50
3-----	0.1	1	None	-----	0	0	2	10	50
4-----	0.2	2	None	-----	0	0	0	2	40
5-----	0.33	3.3	None	-----	0	0	0	0	0
6-----	0.5	5	None	-----	0	0	0	0	0
7-----	0.2	2	0.15	5.0	0	0	0	0	0

¹ Per mol of rosin.

² Based on weight of rosin.

Comparison of tests Nos. 1 and 3 shows that even 0.1 mol of formaldehyde had a clear effect in inhibiting crystallization and that 0.33 mol of formaldehyde (No. 5) entirely prevented crystallization. The table further shows (No. 7) that 1/2 of a mol of formaldehyde was sufficient to prevent crystallization of the size prepared from fortified rosin.

Example 7

A dry size was prepared according to the present invention by reacting 302 gm. of wood rosin (N grade) with .6 gm. of paraformaldehyde at 250° C. for 30 minutes, after which the reaction product was saponified with 38 gm. of sodium hydroxide in 175 gm. of boiling water.

The resulting liquid size was cooled and dried on a steam-heated laboratory drum drier provided with scraper knife. Flakes of excellent quality dry size were obtained.

I claim:

1. A liquid rosin size containing at least 60% of size solids by weight and up to 30% of free rosin acids based on the weight of rosin acids originally present in the rosin, and being the alkali metal alkali-saponification product of the material resulting from the irreversible reaction of a rosin with a small but effective amount of formaldehyde as fortifying agent.

2. A size according to claim 1 wherein the amount of formaldehyde is in the range of one-tenth to one-third molar equivalents.

3. A size according to claim 1 wherein the reacted formaldehyde is paraformaldehyde.

4. A size according to claim 1 wherein the rosin is tall oil rosin.

5. A size according to claim 1 wherein the formaldehyde is reacted at a temperature between 190° C. and 230° C.

6. A method of manufacturing a sized water-laid cellulosic web of improved resistance to penetration by aqueous fluids which comprises forming a dilute aqueous suspension of paper-making cellulose fibers, adding thereto liquid size according to claim 1 as sizing agent for the fibers, precipitating said size on said fibers by the action of alum, sheeting said fibers to form a web, and drying said web.

7. A liquid rosin size containing at least 60% of size solids by weight and up to 30% of free rosin acids based on the weight of rosin acids originally present in the rosin, and being the alkali metal alkali-saponification product of the material resulting from the irreversible reaction of a rosin with small but effective amounts of an alpha-beta unsaturated dicarboxylic anhydride containing not more than six carbon atoms and formaldehyde as fortifying agents.

8. A method of manufacturing a sized water-laid cellu-

losic web of improved resistance to penetration by aqueous fluids which comprises forming a dilute aqueous suspension of paper-making cellulose fibers, adding thereto liquid size according to claim 7 as sizing agent for the fibers, precipitating said size on said fibers by the action of alum, sheeting said fibers to form a web, and drying said web.

9. A liquid rosin size containing at least 60% of size solids by weight and up to 30% of free rosin acids based

on the weight of rosin acids originally present in the rosin, and being the alkali metal alkali-saponification product of the material resulting from the irreversible reaction of tall oil rosin and small but effective amounts of maleic anhydride and formaldehyde as fortifying agents.

10. A dry rosin size of increased sizing efficiency consisting essentially of the material produced by irreversibly reacting a rosin with a small but effective amount of formaldehyde as fortifying agent, substantially completely saponifying it with an aqueous alkali metal alkali, and drying the resulting liquid size.

11. A dry rosin size of increased sizing efficiency consisting essentially of the material produced by irreversibly reacting a rosin with small but effective amounts of an alpha-beta unsaturated dicarboxylic anhydride containing not more than six carbon atoms and formaldehyde as fortifying agents, substantially completely saponifying it with an aqueous alkali metal alkali, and drying the resulting liquid size.

12. Paper of improved resistance to penetration by aqueous fluids comprising a water-laid web of cellulosic fibers uniformly carrying sizing amounts of an alum-precipitated fortified rosin size, said size being the alkali metal alkali-saponification product of the material resulting from the irreversible reaction of a rosin with a small but effective amount of formaldehyde as fortifying agent.

13. Paper of improved resistance to penetration by aqueous fluids comprising a water-laid web of cellulosic fibers uniformly carrying sizing amounts of an alum-precipitated fortified rosin size, said size being the alkali metal alkali-saponification product of the material resulting from the irreversible reaction of a rosin with small but effective amounts of an alpha-beta unsaturated dicarboxylic anhydride containing not more than six carbon atoms and formaldehyde as fortifying agents.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,934,468

April 26, 1960

Edward Strazdins

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

Column 5, line 74, Example 3, in the table, third column thereof, under the heading "CH₂O Reacted" and subheading "Mols", last line, for "1/3" read -- 1/5 --.

Signed and sealed this 20th day of September 1960.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

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Commissioner of Patents