Patented Feb. 17, 1953

2,628,918

UNITED STATES PATENT OFFICE

2,628,918

SIZING AGENTS

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No Drawing. Application May 6, 1952, Serial No. 286,261

9 Claims. (Cl. 106—238)

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This invention relates to improved sizing agents and methods, and particularly to the use of aqueous dispersions capable of markedly increasing the efficiency of ordinary rosin dispersions in the engine sizing of paper pulp.

It is customary at the present time to engine size paper pulp by mixing with a suspension of the pulp a dilute aqueous dispersion of rosin. The rosin is then precipitated, coagulated and fixed on the pulp by adding to the suspension a small quantity of aluminum sulfate (known as "alum" in the papermaker's art), usually about 1% by weight of the dry pulp. The dispersed rosin may be added in varying amounts, depending upon the results desired, but is usually added in amounts between ¼ and 4% based on the weight of the dry pulp being treated.

One of the objects of this invention is to provide a method of improving the sizing efficiency of ordinary rosin size dispersions such as those described above.

A further object of the invention is to provide a sizing adjunct which, when employed in combination with rosin or other sizing agents in the engine sizing of pulp suspension, not only provides a considerably higher degree of sizing than an equivalent amount of rosin alone, but also permits equivalent sizing with much lower rosin dosages.

Still further objects and advantages of the invention will appear from the following description and appended claims.

The methods of the invention are carried out in general by first adding to the beater a predetermined amount of pulp in the form of a dilute aqueous suspension, after which a dilute aqueous dispersion of rosin which has been at least partially neutralized with caustic alkali, soda ash or the like, is added in an amount sufficient to supply from ¼ to 4% of rosin based on the weight of the dry pulp used. A dilute aqueous dispersion of the reaction product of rosin with an acidic compound containing the —CO—C=C group, which product has also been partially neutralized with alkali, is then added, preferably in an amount sufficient to supply between 5 and 40% of the reaction product based on the weight of the rosin employed. The dispersed mixture of rosin and resinous reaction product contained in the pulp is then fixed to the pulp fibres by adding a small amount of aluminum sulfate to the beater and thoroughly mixing the same with the treated pulp suspension.

Although the rosin, resinous reaction product and aluminum sulfate are preferably added to the pulp in the order described above, it is also possible to add the resinous reaction product

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first, and then the rosin. Moreover, the aluminum sulfate may be added at any stage, and if desired all of the above sizing materials may be added to the pulp at one time.

Suitable acidic compounds containing the —CO—C=C group include alpha-beta unsaturated polybasic organic acids or acid anhydrides, such as maleic, fumaric, itaconic and citraconic acids and their anhydrides. Thus, broadly the materials which are adapted to improve the sizing efficiency of rosin according to this invention include the reaction products of rosin with a compound of acidic character containing the —CO—C=C group, such as those referred to above. The most suitable resinous reaction product for the purposes of this invention, however, is the resin prepared from rosin and maleic anhydride. For the sake of simplicity, therefore, reference will be made primarily to the above resin in further describing the details and variables of the invention.

The resin, per se, is generally prepared by heating maleic anhydride with rosin, at 160 to 170° C. for about four hours. The amount of maleic anhydride employed may be varied from about one-quarter to one mol for each mol of rosin, and in many instances somewhat lower or higher temperatures than the above may be used. If lower temperatures are used a longer period of heating than four hours may be required, while if higher temperatures are used, the heating period may frequently be reduced.

In charging the beater with the above resin, it is necessary to first form an alkaline dispersion of the resin in water to facilitate thorough mixing of the resin with the pulp. This is preferably accomplished by first forming a preliminary dispersion of relatively high concentration, after which the concentrated dispersion may be diluted to the desired extent. In general, the rosin maleic resin, caustic soda or other alkali and water are heated and simultaneously stirred in any suitable reaction vessel at temperatures between about 140° and 200° C. The various materials used may be added in amounts varying from about 50 to 80% of resin, 4 to 14% of alkali, and 6 to 46% of water, although it is preferable to use the smaller proportions of resin as the resulting dispersions may be more readily removed from the reaction vessels. The charge is finally cooled down to 60 to 90° C., depending upon the amount of resin employed, and is then removed, whereupon it cools to a consistency varying from a viscous fluid mass to a hard and brittle solid, which may be ground to a powder. In all instances, the amount of alkali used is sufficient only to partly neutralize the resinous reaction product.

In preparing the secondary or dilute dispersion from the primary dispersion, the latter dispersion is diluted with from 1500 to 4000 parts by weight of water for each 100 parts by weight of the dispersion depending upon the amount of resin in the dispersion. The mixing is preferably accomplished with the aid of vigorous stirring and at temperatures varying from 10 to 65° C., depending upon the amount of resin present in the primary dispersion. In all instances, the resulting product is in the form of a milky dispersion which does not settle to any great extent upon standing.

In using the above milky dispersion as a sizing adjuvant, the beater is first charged with a predetermined amount of pulp, after which the rosin size is added in the form of a dilute aqueous and partially or wholly neutralized dispersion in amounts capable of supplying from about ¼ to 4% of rosin based on the weight of the dry pulp used. The dilute dispersion of rosin maleic resin prepared as described above is then added to the pulp suspension in an amount sufficient to supply from 5 to 40% of the rosin maleic resin based on the weight of the rosin used. After thoroughly beating the mixture, the pulp is then ready for the addition of aluminum sulfate or like fixing agent, which may be added in amounts varying from about 1 to 5% based on the dry pulp weight, depending upon the type of paper which it is desired to make. As previously indicated, however, the various materials employed may be added in any desired order, or simultaneously.

A further understanding of the invention will be obtained from the following specific examples of methods of using the sizing adjuvants of the invention:

Example I

A paper beater was first charged with 40,000 pounds of a sulfite pulp suspension containing about 5% of dry pulp. To the charge was then added about 30 pounds of rosin in the form of a rosin dispersion which was 70% neutralized and contained 0.29 pound of rosin per gallon of dispersion. The rosin dispersion was beaten into the pulp for about one-half hour, after which an alkaline dispersion of rosin-maleic anhydride resin, prepared by reacting rosin with maleic-anhydride, partially neutralizing the reaction product and dispersing the neutralized product in sufficient water to produce a dispersion containing 0.29 pound of resin per gallon, was added in an amount sufficient to provide about 6 pounds of the resin. The resulting mixture was beaten for about one-half hour, after which about 5% of aluminum sulfate based on the weight of the dry pulp was added. After a further half hour of beating, the stock was made into paper, which upon being tested by the standard ink penetration test showed 28 minutes sizing. The same stock sized with 62 pounds of rosin in the form of a 70% neutralized rosin dispersion, but without the addition of the rosin-maleic anhydride resin showed 26 minutes sizing. Thus, it was possible to obtain better sizing by using rosin-maleic anhydride resin in conjunction with the rosin, even though more than twice as much rosin was used in the absence of the resin.

The extent to which a given sheet of paper is sized is generally expressed in units of time, as for example, the number of seconds or minutes required for a given liquid, such as water, ink or the like, to penetrate the sheet to a predetermined degree. The liquid used, the end point taken, and the method of determining the arrival of the end point vary, and as a result the numerical values obtained by different observers vary quite widely. It is noteworthy, however, that the comparative values for different kinds or samples of paper are very nearly the same, regardless of the test method employed.

Example II

A small paper beater was charged with 132 grams of an alpha pulp suspension containing about 1.7% of dry pulp. To the charge was then added about 2 grams of rosin, or 1.5% based on the weight of the dry pulp, in the form of a rosin dispersion which was 70% neutralized and contained 10 grams of rosin per liter of dispersion. The rosin dispersion was beaten into the pulp for about 15 minutes, after which an alkaline dispersion of rosin-maleic anhydride resin was added in an amount sufficient to provide about 0.4 gram of the resin, or 20% based on the weight of the rosin used. The resulting mixture was beaten for about 15 minutes, after which about 1% of aluminum sulfate based on the weight of the dry pulp was added. After another 15 minutes of beating, the stock was made into paper, which upon being tested by the standard ink penetration test showed 35 seconds sizing. The same stock sized with 2 grams of rosin in the form of a 70% neutralized rosin dispersion, but without the addition of the rosin-maleic anhydride resin, showed only 29 seconds sizing.

Example III

One hundred and thirty-two grams of an alpha pulp suspension containing about 1.7% of dry pulp were treated in the manner described in Example II, but using 1 gram of rosin, or 0.75% based on the weight of the dry pulp, and 0.2 gram of the rosin-maleic anhydride resin, or 20% of the weight of the rosin used. After making paper of the resulting stock, the paper was tested by the standard ink penetration test and showed 61 seconds sizing. The same stock sized with 1 gram of rosin in the form of a 70% neutralized rosin dispersion, but without the addition of the rosin-maleic anhydride resin, showed only 5 seconds sizing.

Similar tests were made on alpha pulp, using rosin alone as well as rosin in combination with other resinous reaction products of the general class hereinbefore described, but otherwise following the methods of Examples II and III. The amount of sizing obtained with the various sizing agents or combinations of sizing agents used is given in the following table:

Sizing Agent	Seconds Sizing	
	0.75% rosin	1.5% rosin
Rosin alone	5	29
Rosin + 20% rosin-itaconic acid resin	24	41
Rosin + 20% rosin-citraconic acid resin	38	65
Rosin + 20% rosin-fumaric acid resin	58	76

It is to be understood that the per cents of rosin referred to in the above table are based on the weight of the dry pulp being treated, while the per cents of resinous reaction product are based on the weight of the rosin used.

In order to show further the effectiveness of

the sizing adjuvants of the present invention, comparative tests were made with various kinds of pulp and with varying amounts of the sizing agent, using the standard ink penetration method. This method, which is one of the most commonly used, involves making a "boat" of a test sheet of previously sized paper, floating the same upon a bath of ink, and noting the time (usually in seconds) which passes before a shade of coloration appears on the upper surface of the sheet. In each instance certain samples of the test papers were sized with a rosin dispersion alone, while other samples of the same kinds of paper were sized with the rosin dispersion and proportional amounts of the rosin-maleic resin dispersion prepared as hereinbefore described. To reduce variables to a minimum, the tests were made in each instance with a dispersion of G grade rosin which had been 70% neutralized, with the use of 1% of aluminum sulfate based on the weight of the dry pulp, and with the final pulp suspension (after the sulfate addition) at a pH of 4. In each of those instances where the rosin-maleic resin was used in conjunction with the rosin, it was employed in an amount equal to 20% of the weight of the rosin employed.

The results of the various tests are given in the following tables:

BLEACHED KRAFT PULP

Rosin Alone		Rosin + Rosin-Maleic Resin	
Percent Rosin	Seconds Sizing	Percent Rosin	Seconds Sizing
0.2	15	0.2	15
1	45	0.5	50
2	57	1	74
3	63	1.5	84
4	55	2	80

SULFITE PULP

Rosin Alone		Rosin + Rosin-Maleic Resin	
Percent Rosin	Seconds Sizing	Percent Rosin	Seconds Sizing
0.2	2	0.3	2
1	21	0.8	50
2	40	1	65
3	57	1.5	89
4	70	2	102
5	75	3	105
6	65	4	85

RAG PULP

Rosin Alone		Rosin + Rosin-Maleic Resin	
Percent Rosin	Seconds Sizing	Percent Rosin	Seconds Sizing
0.8	0	0.5	2
1.2	4	1	12
1.6	7	1.5	19
2	10	2	25

ALPHA PULP

Rosin Alone		Rosin + Rosin-Maleic Resin	
Percent Rosin	Seconds Sizing	Percent Rosin	Seconds Sizing
0.2	2	0.2	2
1	6	0.5	40
2	22	1	74
3	43	1.5	85
3.2	45	2.5	48
4	35	3.5	24

The above tables clearly show that the efficiency of rosin as a sizing material is markedly increased, when rosin-maleic resin is employed therewith to the extent of 20% by weight of the rosin. Thus, it is possible to obtain either a much larger amount of sizing with an equivalent amount of rosin, when the rosin-maleic resin is employed, or the same degree of sizing may be obtained with considerably less rosin. This is of great advantage to the papermaker, particularly in those instances where it is desired to obtain a maximum amount of sizing at minimum cost.

In the preparation of the dispersions of rosin or the resinous reaction products of the invention, it is usually necessary to first prepare a relatively concentrated dispersion, as it is difficult to form dilute dispersions directly without employing excessive amounts of alkali. Moreover, the preparation of a preliminary concentrated dispersion is of considerable advantage to the papermaker, who usually does not make his own sizing agents, as it permits considerable saving in freight. It is possible in some instances to add the concentrated dispersion directly to the beater without first forming a dilute dispersion, but in general, it is preferable to dilute the dispersion before adding it to the beater. In preparing dispersions of the resinous reaction products, the resin is partly neutralized with caustic soda, caustic potash, soda ash or other alkali metal base.

Although it is possible to employ the resinous adjuncts of the invention in widely varying amounts, it is usually not practical to employ less than 5% or more than 40% of the resin based on the weight of the rosin used. Moreover, from the standpoint of cost, it is preferable to use amounts of the resin between 10 and 25%, as smaller amounts do not increase the sizing efficiency as much as is usually desired, while larger amounts give less and less increase in sizing as the amount is increased.

As an alternative to the procedures described above, the rosin-maleic anhydride resin can be used to size the paper in one step without the separate addition of rosin size. In such a case the resin employed is prepared with a larger proportion of rosin than previously described, that is, the resin is prepared as previously herein described, but the amount of maleic anhydride employed in the preparation of the resin is less than one-quarter mol per mol of rosin and may be as low as one-twentieth of a mol per mol of rosin.

As an example of this alternative procedure, a small paper beater was charged with 23,000 grams of unbleached sulfite pulp suspension containing about 2% of dry pulp. To the charge was then added about 8.5 grams of rosin-maleic anhydride resin (prepared by heating maleic anhydride with rosin at 165° C. in the proportion of 0.15 mol of maleic anhydride per mol of rosin), or 2% based on the weight of the dry pulp, the resin being added in the form of a resin dispersion which was 85% neutralized and contained 27 grams of resin per liter of dispersion. The resin dispersion was beaten into the pulp for about 15 minutes, after which about 14 grams of aluminum sulfate, or 3% based on the weight of the dry pulp, was added. After another 15 minutes of beating, the stock was made into paper, which upon being tested by the standard ink penetration test showed 648 seconds sizing. The same stock sized with 2% of conventional rosin size and with 3% of aluminum sulfate in a similar manner, but without the use of rosin-maleic

anhydride resin, showed only 253 seconds sizing.

This application is a continuation-in-part of our prior application Serial No. 764,022, filed July 26, 1947, which is a continuation-in-part of our prior application Serial No. 452,670, filed July 28, 1942, now both abandoned.

What is claimed is:

1. A paper sizing agent consisting of an aqueous dispersion of the unesterified reaction product of one-twentieth to one mol of an organic compound of acidic character containing a

$$—CO—C=C$$

group with one mol of rosin, said dispersion being partly neutralized with an alkali metal base and containing at least 54% total solids.

2. A paper sizing adjunct consisting of an aqueous dispersion of the unesterified reaction product of one-quarter to one mol of an organic compound of acidic character containing a

$$—CO—C=C$$

group with one mol of rosin, said dispersion being partly neutralized and containing between 50 and 80% of said reaction product, between 4 and 14% of an alkali metal base and between 6 and 46% of water.

3. A paper sizing agent consisting of an aqueous dispersion of the unesterified reaction product of one mol of rosin and one-twentieth to one-quarter mol of maleic anhydride, said dispersion being partly neutralized with an alkali metal base and containing at least 54% total solids.

4. A paper sizing adjunct consisting of an aqueous dispersion of the unesterified reaction product of one mol of rosin and one-quarter to one mol of fumaric acid, said dispersion being partly neutralized with an alkali metal base and containing at least 54% total solids.

5. A paper sizing adjunct consisting of an aqueous dispersion of the unesterified reaction product of one mol of rosin and one-quarter to one mol of citraconic acid, said dispersion being partly neutralized with an alkali metal base and containing at least 54% total solids.

6. A paper sizing adjunct consisting of an aqueous dispersion of the unesterified reaction product of one mol of rosin and one-quarter to one mol of itaconic acid, said dispersion being partly neutralized with an alkali metal base and containing at least 54% total solids.

7. A paper sizing adjunct consisting of an aqueous dispersion of the unesterified reaction product of one mol of rosin and one-quarter to one mol of maleic anhydride, said dispersion being partly neutralized and containing between 50 and 80% of said reaction product, between 4 and 14% of an alkali metal base and between 6 and 46% of water.

8. A paper sizing adjunct consisting of an aqueous dispersion of the unesterified reaction product of one mol of rosin and one-quarter to one mol of maleic anhydride, said dispersion being partly neutralized and in the form of a viscous fluid containing about 57% of said reaction product, about 5% of caustic soda, and about 38% of water.

9. A paper sizing adjunct consisting of an aqueous dispersion of the unesterified reaction product of one mol of rosin and one-quarter to one mol of maleic anhydride, said dispersion being partly neutralized and in the form of a hard and brittle solid and containing about 80% of said reaction product, about 7% of caustic soda, and about 13% of water.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,063,540	Ellis	Dec. 8, 1936
2,081,889	Borglin	May 25, 1937
2,385,794	Chappell	Oct. 2, 1945