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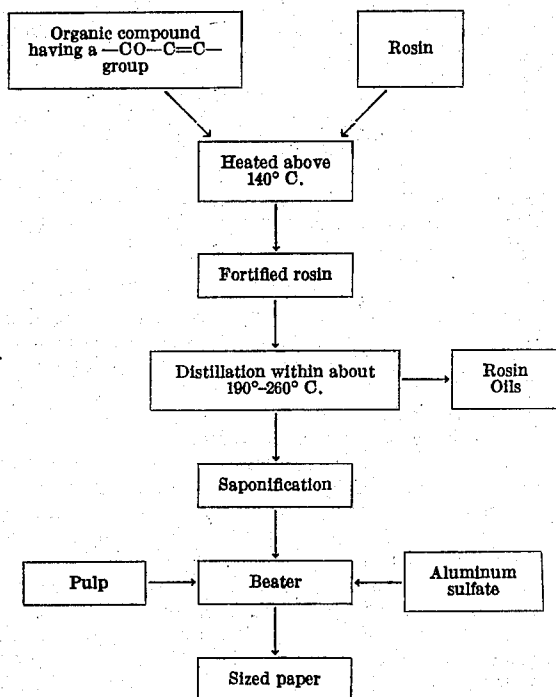
PAPER SIZING

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6 Claims. (Cl. 162-180)

This invention relates to the preparation of improved resins suitable for use in paper sizes, and particularly to resins of the type prepared from reaction products of rosin and an organic compound of acidic character containing a  $-\text{CO}-\text{C}=\text{C}-$  group, which reaction products are known as "fortified rosins," and to the use of the saponified product of these improved fortified rosins (i.e., a fortified rosin size) in the engine sizing of paper.

A simple flow diagram of the preparation and use of the improved fortified rosins is as follows:



The preparation and use of fortified rosins of this general type in paper sizes are known. However, certain difficulties have been encountered with the use of the saponified product of these rosins in paper sizing, including excessive foam formation and a tendency toward flotation of the pulp in the beaters and in subsequent operations, as in the refiners, pumps, agitators and screens.

It is accordingly a primary object of the present invention to produce rosins of the type described which, when saponified and employed in the engine sizing of paper pulp, utilizing sizing methods known to the art, do not cause appreciable foam formation and at the same time markedly reduce the tendency of the pulp solids to float on the surface of the pulp liquid.

It is a further object of this invention to provide a method for sizing paper utilizing fortified rosin sizes made according to the methods herein described, wherein the tendency of the paper pulp to float, during or after the incorporation of the fortified rosin size into said pulp, is reduced to a minimum without attendant loss of sizing efficiency of the fortified rosin size.

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

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Although the amount of foam and float which occurs in the beater sizing of paper with saponified rosin may be sufficient to somewhat disrupt the sizing operation, it is also known that heretofore, when using a saponified fortified rosin, the tendency of such fortified rosin to cause foam and float is increased.

It has now been found that, by removing rosin oils present in rosin used to prepare rosin sizes, the foam and float of a fortified rosin size of the type described can be so markedly reduced as to virtually eliminate the problem.

In general, the objects of this invention can be accomplished by reacting rosin and an organic compound of acidic character containing a  $-\text{CO}-\text{C}=\text{C}-$  group under conditions of time, temperature and pressure at which substantially no decarboxylation takes place and all, or substantially all, the rosin oils are removed. The resulting fortified rosins are exceedingly useful, when saponified, in the sizing of paper, as they are free of detrimental rosin oils and, at the same time, retain their original sizing efficiency. Rosins suitable for the purpose of this invention include gum rosin and wood rosin. Examples of suitable organic compounds of acidic character containing a  $-\text{CO}-\text{C}=\text{C}-$  group include alpha, beta-unsaturated polybasic organic acids or acid anhydrides, such as maleic, citraconic and fumaric acid, or maleic, citraconic and itaconic anhydride.

It is known, for example, that one method of separating turpentine from gum rosin is by steam stripping. This operation, however, is performed at lower temperatures (of the order of about 160° C.) than those contemplated by this invention and, as a result, rosin oils remain which contribute to high foam and float.

In the preparation of the resinous reaction products of this invention, it is usually preferable to first carry out the reaction between the rosin and the organic compound of acidic character containing a  $-\text{CO}-\text{C}=\text{C}-$  group, as this reaction will take place at temperatures below the temperature suitable for removing the float-producing oils. This order is not essential, however, as the rosin oils can be removed prior to reacting the rosin with said compound containing the  $-\text{CO}-\text{C}=\text{C}-$  group. Thus, said reaction can be performed at temperatures as low as about 140° C. but preferably at or above the melting point of the rosin. Although not absolutely necessary, it is usually preferable to remove the rosin oils at reduced pressures, such as 15 to 200 mm. of Hg, as this permits completion of the removal of the oils in shorter periods of time than otherwise, and also permits removal of the rosin oils at lower temperatures, thus avoiding excessive decarboxylation. When operating at such reduced pressures, the best results are obtained by heating the reaction mixture at temperatures between about 220° and 230° C. for about one hour. However, good results can be obtained under these conditions for longer or shorter periods varying from one-half to two hours. In addition, it has been found that at temperatures of about 220° to 230° C., pressures of 30 to 40 mm. of Hg are quite satisfactory. The removal of the float-producing oils does not seem to occur, within a practical length of time, below about 190° C. However, temperatures as low as 190° C. can be used, but in such case, four to five hours may be required for complete removal of the rosin oils, as well as the use of low pressures, no higher than about 15 mm. of Hg.

Conversely, although temperatures as high as 240° C. can be employed, the reaction time must then be shortened somewhat, for example, to about 15 minutes, in order to avoid excessive decarboxylation. Temperatures of 260° C. or higher can be used; however, in such case, the sojourn time at such temperature must be very short.

The rosin oils can also be removed by steam distilla-

tion or distillation at atmospheric pressure within the conditions of time and temperature hereinbefore stated; for example, rosin or fortified rosin is heated to temperatures within the range of about 190° C. to about 260° C., but preferably from about 190° C. to about 230° C., and at the same time said rosin or said fortified rosin is sparged with steam (i.e., steam is passed into intimate contact with and through said rosins) to remove by steam distillation rosin oils originally present in said rosins, thereby producing a substantially rosin oil-free rosin or fortified rosin. Thus, it is seen that the invention lies in the discovery that by removing rosin oils under conditions of time, temperature and pressure as to avoid substantial decarboxylation, a fortified rosin size can be prepared from gum rosin, wood rosin or tall oil rosin, which fortified rosin is used to produce a size having superior qualities of low foam and float.

Many techniques have been used in the laboratory to study the foaming tendency in sizes. Most of such techniques have been based on foam or froth formation, and the results have often been misleading. Large voluminous bubbles are not harmful, it is the small, opaque dense bubbles that cause the trouble. The test which is used to determine float, which has been proven to correlate with mill experience, is briefly as follows:

Standard bleached-sulfite pulp is beaten to a predetermined freeness, diluted to a standard consistency, and aerated by an electric mixture. Size and later alum are added at exact times. After aeration, the slurry is transferred to a graduate. The number of cc. of clear water under the floating pulp after 16 hours is a quantitative measure of the tendency of that size to cause air stabilization (and thus produce float). The value is called an air stabilization factor, or A.S.F.

A guide to A.S.F. values is given below:

0 to 25—Excellent. Very low air stabilization.  
25 to 50—Good. Seldom troublesome.  
50 to 75—Fair. Troublesome on some machines.  
75 to 100—Poor. Frequently troublesome.

A further understanding of the invention will be obtained from the following examples:

#### Example 1

Fifteen hundred grams of molten gum rosin and 42 grams of maleic anhydride were charged to a suitable reaction vessel. The mixture was then heated to about 220° C. and held at that temperature for about 15 minutes. The acid number of the mixture was then determined and sufficient 50% sodium hydroxide was added to result in a size having an acid number of 22, with the further addition of sufficient water to give a paste size containing about 70% solids. The float of the size thus prepared was determined to correspond to an A.S.F. value of about 100. This example demonstrates the undesirable high float of fortified rosin sizes prepared according to an established practice of the art.

#### Example 2

Fifteen hundred grams of molten gum rosin and 42 grams of maleic anhydride were charged to a suitable reaction vessel. The mixture was heated to 220° C. with stirring and was then vacuum distilled for 70 minutes at a pressure of 30 to 50 mm. of Hg.

The resin obtained in the above reaction was dissolved in 371 grams of water with the aid of 278 grams of 50% caustic soda, which resulted in a 69% solution of neutralized rosin-maleic reaction product suitable for use in the engine sizing of paper. The float was found to correspond to an A.S.F. value of 5, which, when compared to the result obtained in Example 1, demonstrates the outstanding improvement to be gained by the practice of the invention herein described.

#### Example 3

Ten hundred and twelve grams of molten gum rosin and 30 grams of fumaric acid were charged to a suitable reaction vessel. The mixture was heated to 192° C. and was then steam distilled for about two hours, with the temperature gradually increasing to about 255° C.

The rosin obtained in the above reaction was dissolved in 320 grams of water with the aid of 174 grams of 50% caustic soda, which resulted in a 70% solution of neutralized product suitable for use in the engine sizing of paper. The float of this material was equivalent to an A.S.F. number of about 6.

#### Example 4

Eleven hundred and sixty-six grams of molten gum rosin and 50 grams of fumaric acid were charged to a suitable reaction vessel. The mixture was eventually heated to a temperature of 276° C., the time of heating from 200 to 276° taking about one hour.

The rosin obtained in the above reaction was dissolved in 371 grams of water with the aid of 278 grams of 50% caustic soda, which resulted in a 70% solution of neutralized product suitable for use in the engine sizing of paper. The float of this material was equivalent to an A.S.F. number of about 12.

#### Example 5

A fortified wood rosin size, prepared essentially like the fortified gum rosin size of Example 1, was determined to have a float corresponding to an A.S.F. value of 94. This example demonstrates the undesirable high float for fortified rosin sizes prepared according to an established practice of the art.

#### Example 6

Thirteen hundred and fifty-two grams of wood rosin were melted and heated in a suitable vessel capable of sustaining sub-atmospheric pressure to a temperature of about 160° C., at which temperature 54 grams of maleic anhydride were added.

The mixture of maleic anhydride and wood rosin was heated to about 200° C., and the rosin oil in the mixture was then removed by vacuum distillation over about 50 minutes while maintaining the temperature at about 200° to 220° C. and while maintaining the pressure at about 40 mm. of Hg absolute.

The rosin obtained above, 360 grams of 50% sodium hydroxide and 354 grams of water were mixed together in a suitable vessel, thereby effecting saponification, which resulted in a 70% solution of neutralized rosin product suitable for use in the engine sizing of paper. The float of the product was found to correspond to an A.S.F. value of 1.

#### Example 7

The distillate from Example 3 was collected and the rosin oils separated from the condensed steam. To portions of the size prepared in Example 3, varying amounts of the distilled rosin oils were then added and a float determination made. The results were as follows:

Weight percent oils added:	Float
0.5	6
1.0	26
1.5	85
2.0	87

#### Example 8

A paper pulp beater was charged with unbleached sulfite pulp suspension containing about 2% of dry pulp. To the charge was added a dispersion of rosin oil-free fortified rosin size prepared in Example 2 in an amount equal to about 2% of fortified rosin based on the weight of dry pulp. The dispersion was beaten into the pulp for about 15 minutes, after which aluminum sulfate, in

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an amount equal to about 3% based on the weight of the dry pulp, was added. After beating the above for an additional 15 minutes, the stock was made into paper. Throughout all the above operations there was no evidence of any tendency of the pulp to float, as would occur when using a fortified rosin size prepared by methods known to the prior art. Furthermore, from the degree of sizing in paper produced, it was demonstrated that the fortified rosin sizes prepared by the method herein described have a sizing efficiency equal to the sizing efficiency of fortified rosin sizes prepared by methods of the prior art.

In the above examples, the organic compound of acidic character containing a  $\text{—CO—C=C—}$  group is used in the ratio of 2.8 parts by weight per 100 parts by weight of rosin. However, the advantages of the invention are equally applicable to reaction products containing lower or higher proportions of such compounds; for example, as high as 1 part per 3 parts of rosin.

In order to obtain satisfactory results in using the resinous reaction products of this invention, it is important that substantially all of the rosin oil be removed from the reaction mixture. In order to determine when substantially all of the float-producing oils have been removed, a sample of fortified rosin is removed from the distillation vessel after about one hour from the start of the distillation, saponified, and a float determination is made. If the float has reached a satisfactory minimum, distillation is discontinued and, conversely, if the float is still too high, distillation is continued for a short period of time and another float determination is then made. Because of the wide range of concentration of rosin oils which rosins contain, due to such factors as geographic origin of the rosin, the season of the year when the rosin was collected, method of producing the crude rosin, etc., the time for continuing the distillation cannot be exactly defined but nevertheless will be obvious to those skilled in the art when employing the method of the invention to remove float-producing rosin oils without attendant decarboxylation.

From the above examples, it is seen that the removal of rosin oils by the method of this invention results in a fortified rosin size having superior qualities of very low foam and float. While either atmospheric or sub-atmospheric distillation (i.e., distillation under a pressure less than atmospheric or a distillation wherein the partial pressure of the rosin oils is below what their partial pressure would be for an atmospheric distillation) is satisfactory for removing the rosin oils, in the case of tall oil rosin, sub-atmospheric distillation with steam has been found to give the greatest reduction of float when said rosin is to be employed in the engine sizing of paper.

This application is a continuation-in-part of my earlier filed application, Serial Number 358,971, filed June 1, 1953, and now abandoned.

What is claimed is:

1. In a process for sizing paper, the steps comprising incorporating into paper pulp an improved fortified rosin size comprising the saponified product prepared by the steps comprising (1) heating at temperatures above  $140^{\circ}\text{C.}$  from about one to about ten parts by weight of an organic compound of acidic character containing a  $\text{—CO—C=C—}$  group, with 100 parts by weight of rosin to form a fortified rosin, (2) heating said fortified rosin to temperatures within the range of about  $190^{\circ}\text{C.}$  to about  $260^{\circ}\text{C.}$  and removing by distillation, float-producing rosin oils originally present in said rosin, thereby producing a fortified rosin substantially free of float-producing rosin oils, and (3) thereafter saponifying said fortified rosin by heating with an aqueous solution of alkali to form said fortified rosin size.

2. In a process for sizing paper, the steps comprising incorporating into paper pulp an improved fortified rosin size comprising the saponified product prepared by the steps comprising (1) heating at temperatures above

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$140^{\circ}\text{C.}$  from about one to about ten parts by weight of an organic compound of acidic character containing a  $\text{—CO—C=C—}$  group selected from the group consisting of maleic anhydride and fumaric acid, with 100 parts by weight of rosin to form a fortified rosin, (2) heating said fortified rosin under reduced pressures to temperatures within the range of about  $190^{\circ}\text{C.}$  to about  $260^{\circ}\text{C.}$  and removing by distillation, float-producing rosin oils originally present in said rosin thereby producing a fortified rosin, substantially free of float-producing rosin oils, and (3) thereafter saponifying said fortified rosin by heating with an aqueous solution of caustic to form said fortified rosin size.

3. In a process for sizing paper, the steps comprising incorporating into paper pulp an improved fortified rosin size comprising the saponified product prepared by the steps comprising (1) heating at temperatures above  $140^{\circ}\text{C.}$  from about one to about ten parts by weight of an organic compound of acidic character containing a  $\text{—CO—C=C—}$  group selected from the group consisting of maleic anhydride and fumaric acid, with 100 parts by weight of rosin to form a fortified rosin, (2) heating said fortified rosin to temperatures within the range of about  $190^{\circ}\text{C.}$  to about  $260^{\circ}\text{C.}$  while sparging said fortified rosin with steam to remove by steam distillation, float-producing rosin oils originally present in said rosin, thereby producing a fortified rosin substantially free of float-producing rosin oils, and (3) thereafter saponifying said fortified rosin by heating with an aqueous solution of caustic to form said fortified rosin size.

4. In a process for sizing paper, the steps comprising incorporating into an aqueous suspension of paper pulp an improved fortified rosin size comprising the saponified product prepared by the steps comprising (1) heating at temperatures above  $140^{\circ}\text{C.}$  from about one to about ten parts by weight of an organic compound of acidic character containing a  $\text{—CO—C=C—}$  group selected from the group consisting of maleic anhydride and fumaric acid, with 100 parts by weight of rosin to form a fortified rosin, (2) heating said fortified rosin to conditions of temperature and pressure whereby float-producing rosin oils in said fortified rosin are removed by distillation, thereby producing a fortified rosin substantially free of float-producing rosin oils, and (3) thereafter saponifying said fortified rosin by heating with an aqueous solution of alkali to form said fortified rosin size.

5. In a process for sizing paper, the steps comprising incorporating into an aqueous suspension of paper pulp an improved fortified rosin size comprising the saponified product prepared by the steps comprising (1) heating at temperatures above  $140^{\circ}\text{C.}$  from about one to about ten parts by weight of maleic anhydride with 100 parts by weight of rosin to form a fortified rosin, (2) heating said fortified rosin to temperatures within the range of about  $190^{\circ}\text{C.}$  to about  $260^{\circ}\text{C.}$  while sparging said fortified rosin with steam to remove by steam distillation, float-producing rosin oils originally present in said rosin, thereby producing a fortified rosin substantially free of float-producing rosin oils, and (3) thereafter saponifying said fortified rosin by heating with an aqueous solution of sodium hydroxide to form said fortified rosin size.

6. In a process for sizing paper, the steps comprising incorporating into an aqueous suspension of paper pulp an improved fortified rosin size comprising the saponified product prepared by the steps comprising (1) heating at temperatures above  $140^{\circ}\text{C.}$  from about one to about ten parts by weight of fumaric acid with 100 parts by weight of rosin to form a fortified rosin, (2) heating said fortified rosin to temperatures within the range about  $190^{\circ}\text{C.}$  to about  $260^{\circ}\text{C.}$  while sparging said fortified rosin with steam to remove by steam distillation, float-producing rosin oils originally present in said rosin, thereby producing a fortified rosin substantially free of float-producing rosin oils, and (3) thereafter saponifying said fortified rosin by

heating with an aqueous solution of sodium hydroxide to form said fortified rosin size.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 2,995,483

August 8, 1961

Francis A. Bonzagni

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 3, line 68, for "371" read -- 495 --; same line 68, for "278" read -- 335 --; column 4, line 32, for "for" read -- of --; column 6, line 20, for "theg roup" read -- the group --.

Signed and sealed this 9th day of January 1962.

(SEAL)

Attest:

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