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SIZE EMULSION AND METHOD OF PREPARING THE SAME

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This invention relates to rosin dispersions or emulsions and to methods of producing the same. More particularly, the invention relates to an improved high free rosin dispersion or emulsion, and to a method of producing the emulsion.

Emulsions comprising rosin or rosinates and water are used extensively for sizing paper and the like. In such emulsions saponified rosin is present and the rosin is only partially dispersed or suspended as free rosin. It has been established that, under certain conditions, the sizes having a high free rosin content impart better sizing than neutral or low free rosin sizes. This is due to the drastic action of hard water on neutral or low free rosin sizes, which causes rosin to floc or precipitate in dilute solution and fail to properly size the paper efficiently.

In order to increase the free rosin content of sizes, it has been customary to add acidic materials, such as, boric acid, to rosinate solutions. A difficulty of this procedure was that relatively large quantities of boric acid were required to free the rosin and that the addition of boric acid did not lower the pH value an appreciable extent. The addition of such quantities of boric acid increased the cost of the size and the use of this size required a relatively large amount of alum to be added to the paper stock, which further increased the cost of sizing. Another objection is that a relatively large quantity of protein stabilizing agent was used. Also, the electrolite materials remaining in the stock were objectionable in some cases.

The present invention aims to overcome the above difficulties by providing an improved, stable, high free rosin size emulsion and methods of producing the same.

An object of the invention is to provide a rosin emulsion or dispersion having a relatively high free rosin content.

Another object is to provide a rosin emulsion which can be utilized more economically.

Another object is to provide a rosin emulsion which is not affected adversely by variations in the hardness of the water and condition of the paper pulp.

Another object is to provide high free rosin emulsion which can be prepared by treating low free rosin size emulsions with materials which usually are wasted.

Another object is to provide a high free rosin emulsion containing an electrolite which is readily freed from the paper stock.

Another object is to provide a method of producing a rosin emulsion having the foregoing characteristics.

Another object is to provide a method for converting rosin emulsions having low free rosin content into stable emulsions or dispersions having a high free rosin content.

A further object is to provide a method of preparing and stabilizing high free rosin content emulsions.

Other and further objects will be obvious upon an understanding of the illustrative embodiment about to be described, or will be indicated in the appended claims, and various advantages not referred to herein will occur to one skilled in the art upon employment of the invention in practice.

These objects are accomplished by dispersing or emulsifying in water, substantially or completely saponified rosin sizes which normally provide a dispersion or emulsion having a relatively low free rosin content, that is, about 35% or less free rosin by titration methods, or about 45% or less by extraction methods. A stabilizing agent may be either added to the concentrated size or to the emulsions, and after thorough mixing an acidic gas is passed through the mixture while continuing agitation, whereby the mixture is converted into a high free rosin emulsion. This emulsion may be added to the beater, beater chest, to the Jordan engine, the head box, or any other suitable location.

In accordance with the invention, I have found that any grades of gum or wood rosins or the like, saponified to produce sizes having a low free rosin content, can be advantageously converted to a high free rosin emulsion. In practice, I may employ any water-soluble alkali metal rosinate, such as a paste size, a dry size, or a cold saponified size. The stabilizing agents I found to be suitable are, for example, casein, soya bean protein, animal glue, or other known protective colloids which are readily available on the market.

The acidific gases which are suitable, are of the class which when passed through water dissolve and unite with the water to form acids. Such gases, for example, are carbon dioxide (CO_2), sulphur dioxide (SO_2), acetic acid fumes, and chlorine or hydrochloric acid gas. I prefer the use of carbon dioxide because it is relatively inexpensive and is available in flue gas which is ordinarily wasted; does not endanger the health of the operators; does not corrode the paper plant equipment; and does not react unfavorably with compounds in the rosin or with the casein. As a source of carbon dioxide, I may use compressed carbon dioxide gas supplied in cylinders or dry ice (solid carbon dioxide). Sulphur dioxide may also be used, but because of its chemical activeness and its ability to form a relatively stronger acid more caution is necessary to prevent local coagulation. Acetic acid fumes, chlorine or hydrochloric acid gas, when diluted with air or relatively inert gases produce the desired acidification and freeing of the rosin.

In carrying out the invention, I add to a suit-

able volume of water a quantity of rosin paste or dry size which may contain rosin substantially or completely saponified, and while agitating, heat the water sufficiently preferably to about 165° F. to facilitate dissolving or emulsifying the rosin soap and dispersing the free rosin. The mixture may contain between about 1 and 20% solids, but usually a concentration between 5 and 15% is used. To this mixture, if so desired, I may add a colloidal stabilizer such as casein, soya bean protein, or animal glue. Between about 1 and 25% colloid based on the solid rosin content of the mixture may be used, the actual amount used depending on and being determined by specific paper mill conditions.

These colloids may be in alkaline solutions previously prepared by adding about 10% colloid to water containing, for example, 7% of sodium carbonate or other weak alkali which facilitates dissolving or emulsifying the colloid. If desired, the dissolved colloids may be added to the paste size or to the diluted size solution before or after being treated with the acidific gas. Also, the colloid may be ground and mixed with dry alkali adapted to be added to the paste or to the dilution thereof. Also the colloid may be mixed in dry form as a powder or other physical state with dry size which subsequently is dissolved.

I then pass acidific gas or acid fumes through the mixture, either with or without mechanical agitation of the mixture. The gas dissolves in the water to form an acid which will ionize to give hydrogen ions adapted to react with the alkali rosinate (alkali abietate) to give free rosin (abietic acid) suspended in finely divided, minute particles. When sufficient gas has passed through the mixture, the original translucent appearance of the mixture, which characterizes a low free rosin emulsion, gradually changes to an opaque, and in some instances where a light colored rosin is used, to a milk white appearance characteristic of a high free rosin emulsion.

In other words, the soluble or emulsifiable rosin soap, characterized by a clear mixture or solution was thrown out of solution by the acidific gas into an insoluble state to form a free rosin dispersion containing between 65% and 95% free rosin by extraction. The resulting dispersion may then be used as a paper size in any usual manner.

Example I

A quantity of 144 pounds of commercial rosin paste size, mostly sodium rosinate, containing 70% total solids and 13.1% free rosin by titration, was heated in a size heating and measuring kettle to 165° F. A quantity of 20.2 pounds solution of 20% casein which had been cut with 4% sodium carbonate based on the weight of casein was stirred into the size and heated therewith for 15 minutes. The resulting casein-rosin size was diluted at 168° F. with water at 166° F. to give 16% solids rosin emulsion containing about 4% casein based on solids in the emulsion. Cold water was used for the dilution of the 16% emulsion to 6%.

Carbon dioxide was then passed from a cylinder into the emulsion while at 110° through perforated spray heads placed adjacent the bottom of the tank and the emulsion was agitated. Carbon dioxide was added at the rate of about 5 pounds per hour for thirty minutes and then at a rate of about 3 pounds per hour, and at a net pressure of 12.5 pounds per square inch. While adding the carbon dioxide, the cylinder was weighed at intervals to determine the weight of gas added.

The emulsion prepared by the above procedure was then diluted to .075% solids, first by using water No. 1, having a hardness of 20 grains per gallon (calculated as calcium and magnesium) and then by using water No. 2, having a hardness of 15 grains per gallon. As presented in the following table, tests were made on emulsions taken at various times when increasing amounts of carbon dioxide had been added to determine per cent carbon dioxide, total solids, free rosin; pH value and stability.

Properties of alkali rosinate (alkali abietate) size containing 4% casein, after treatment with carbon dioxide gas.

Sample No.	Addition time of CO_2	Percent CO_2 added	pH	Emulsion		Stability upon dilution in H_2O	
				Total solid	Free rosin extraction	No. 1	No. 2
	Minutes			*Percent*	*Percent*	*Hours*	*Hours*
A	70	5.0	8.92	6.0	68.3	44 to 73	
B	105	7.5	8.71	6.0	78.2	44 to 73	44 to 73
C	140	10.0	8.43	6.2	79.7	44 to 73	44 to 73
D	170	12.0	7.73	6.1		44 to 73	44 to 73
E	215	16.5	7.13	6.1		44 to 73	44 to 73
F	255	20.5	7.07	6.2		44 to 73	44 to 73

The samples of the size were also examined microscopically and it was found in all cases that between 95 and 99% of the particles of the size did not exceed one micron and in each instance no particles greater than three microns were found. This indicated that the size contained finely divided and minute particles which could be readily dispersed or emulsified. Also, a very stable emulsion is provided by these particles which requires a small amount of stabilizing colloid. The tests also indicated that the size emulsions remained stable for more than 44 hours when diluted with hard waters to a concentration of about .075%. This stability is adequate to accomplish a satisfactory degree of sizing by virtue of the fact that it by far exceeds the maximum time pulp is in process in a paper mill.

A batch sizing emulsion corresponding to sample E was added to a patch of paper pulp in a beater and it was found that a smaller quantity of alum than usually required was necessary to give good sizing results. This is due to the fact that the size has a relatively low pH (as compared with sizes employed heretofore) and less additional materials are, therefore, required to lower the pH.

From the foregoing table, it will be observed that high free rosin size emulsions can be economically prepared. For example, a size emulsion having between 78 and 81% free rosin and a pH between 7.5 and 8.5 can be prepared by adding between 10 and 12% carbon dioxide to a low free rosin size solution.

Example II

A quantity of rosin paste size calculated to contain 150 pounds of size on a dry basis was heated to a temperature of about 165° to 170° F. and was mixed with a quantity of water at about 165° F. to provide an emulsion containing about 16% solids. This emulsion was diluted with cold water to contain 8% solids and 6 pounds of casein in 14% solution, and cut with 6% sodium carbonate (based on weight of casein) was added and stirred in for 15 minutes. While continuing agitation 18 pounds of solid carbon dioxide

(dry ice) was added in small pieces over a period of an hour and a half, the rate of addition being slower at first.

Five batches were prepared in this manner. The final pH varied between 8.5 and 8.6 and the solids, on a dry basis, between 6.66 and 7.15%. A sample of each batch was examined microscopically and it was found that 99% of the particles of the size did not exceed one micron and in no case particles greater than 3 microns were found. The size emulsion was diluted with hard water to .075% solids, and was found to be stable and non-floccing.

By using dry ice as a source of carbon dioxide, the carbon dioxide can be handled, weighed and added to the emulsion very conveniently.

Example III

To 200 grams of water at 165° F. were added 30 grams of liquified size paste (70% solids) which had about 20% free rosin on a dry basis. To the mixture was added 10 grams of a 10% casein solution which was previously cut with 7% sodium carbonate. While thoroughly agitating the mixture, sulphur dioxide gas was passed therethrough for five minutes and caused to dissolve in the emulsion. A suitable size emulsion having a high free rosin content was provided.

From the foregoing description and examples, it will be seen that the present invention provides an improved high free rosin size which can be economically made and can be used more efficiently as a size emulsion. The emulsion is not affected adversely by variations in the hardness of the water when diluted and does not flock at low concentration when diluted with relatively hard water. By using an acidific gas which can be driven from the paper pulp in the latter stages of the paper manufacture, a better paper is provided. Also, the acidific gas lowers the pH considerably without the use of large amounts, and further decreases the amount of materials such as alum required for sizing the pulp. The size emulsions prepared in accordance with the present invention remain stable for long periods without sacrificing any advantages thereof. A further feature is that carbon dioxide in the form of stack gas, which is ordinarily wasted, can be utilized.

It will be understood that the details and examples hereinbefore set forth are illustrative only, and that the invention as broadly described and claimed is in no way limited thereby.

What I claim and desire to protect by Letters Patent is:

1. The process which comprises passing an acidific gas into an aqueous dispersion comprising saponified rosin to partially decompose said saponified rosin and liberate free rosin of extremely fine particle size and in highly dispersed form, whereby there is formed an aqueous rosin sizing dispersion containing a high proportion of free rosin on the dry basis and being stable against flocking when diluted with hard water for a period of time greater than the normal time elapsed between adding the sizing dispersion to the paper pulp and the addition of a size precipitant.

2. The process which comprises passing gaseous carbon dioxide into an aqueous dispersion comprising saponified rosin to partially decompose said saponified rosin and liberate free rosin of extremely fine particle size and in highly dispersed form, whereby there is formed an aqueous rosin sizing dispersion containing a high proportion of free rosin on the dry basis and being stable against flocking when diluted with hard water for a period of time greater than the normal time elapsed between adding the sizing dispersion to the paper pulp and the addition of a size precipitant.

3. The process which comprises passing gaseous sulfur dioxide into an aqueous dispersion comprising saponified rosin to partially decompose said saponified rosin and liberate free rosin of extremely fine particle size and in highly dispersed form, whereby there is formed an aqueous rosin sizing dispersion containing a high proportion of free rosin on the dry basis and being stable against flocking when diluted with hard water for a period of time greater than the normal time elapsed between adding the sizing dispersion to the paper pulp and the addition of a size precipitant.

4. The process which comprises adding solid carbon dioxide to an aqueous dispersion comprising saponified rosin to partially decompose said saponified rosin and liberate free rosin of extremely fine particle size and in highly dispersed form, whereby there is formed an aqueous rosin sizing dispersion containing a high proportion of free rosin on the dry basis and being stable against flocking when diluted with hard water for a period of time greater than the normal time elapsed between adding the sizing dispersion to the paper pulp and the addition of a size precipitant.

5. The process which comprises passing gaseous carbon dioxide into an aqueous dispersion comprising saponified rosin and a stabilizing colloid to partially decompose said saponified rosin and liberate free rosin of extremely fine particle size and in highly dispersed form, whereby there is formed an aqueous rosin sizing dispersion containing a high proportion of free rosin on the dry basis and being stable against flocking when diluted with hard water for a period of time greater than the normal time elapsed between adding the sizing dispersion to the paper pulp and the addition of a size precipitant.

6. The process which comprises passing gaseous carbon dioxide into an aqueous dispersion comprising sodium rosinate and casein and containing from about 1 to about 20% by weight of solids to partially decompose the sodium rosinate and liberate free rosin of extremely fine particle size and in highly dispersed form, whereby there is formed an aqueous rosin sizing dispersion containing between about 65 and about 95% by weight of free rosin on a dry basis and being stable against flocking when diluted with hard water for a period of time greater than the normal time elapsed between adding the sizing dispersion to the paper pulp and the addition of a size precipitant.

7. The process which comprises passing gaseous carbon dioxide into an aqueous dispersion comprising saponified rosin and casein to partially decompose said saponified rosin and liberate free rosin of extremely fine particle size and in highly dispersed form, whereby there is formed an aqueous rosin sizing dispersion containing a high proportion of free rosin on the dry basis and being stable against flocking when diluted with hard water for a period of time greater than the normal time elapsed between adding the sizing dispersion to the paper pulp and the addition of a size precipitant.

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