June 30, 1942. F. ARLEDTER ET AL 2,288,060

SOLID WATER-IN-ROSIN PAPER SIZE

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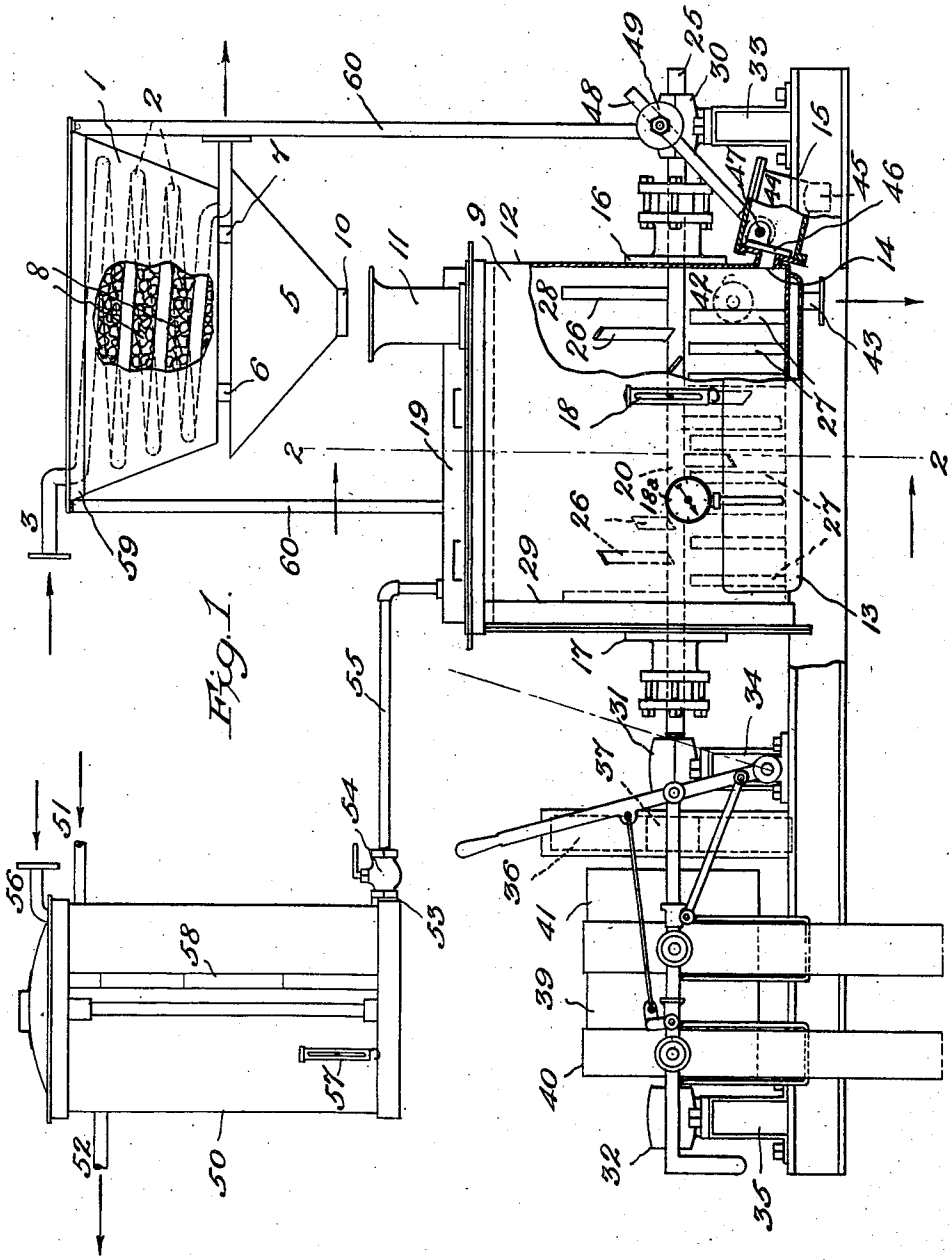


Fig. 1.

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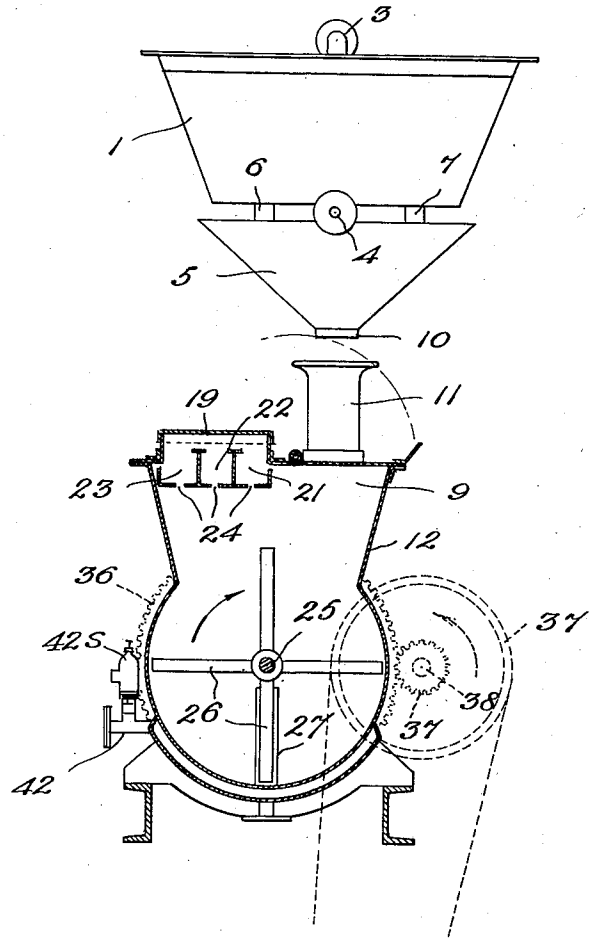


Fig. 2.

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UNITED STATES PATENT OFFICE

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SOLID WATER-IN-ROSIN PAPER SIZE

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Application September 2, 1938, Serial No. 228,080

4 Claims. (Cl. 106—238)

The present invention relates to rosin paper size and, more particularly, to a process for producing a solid, substantially non-saponified rosin paper size readily dispersible in water and the product thereof and to a process for producing a dilute size solution from the aforesaid concentrated solid rosin size.

In the sizing of paper, two types of rosin size, generally speaking, have been in common use. The type which has been in use for the longest time has been commonly known as neutral size and the other has been known as free rosin size. By reducing the amount of alkali used to saponify the rosin, the amount of free rosin present in a size can be increased from about 8.2% in completely saponified rosin to about 52.6% in the free rosin size. The minimum of 8.2% free rosin in completely saponified rosin size has been obtained as a result of the presence of about 8.8% of unsaponifiable material in the original rosin. However, it is to be noted that as the proportion of free rosin increases, difficulties arise in the utilization of the size in the paper mill. This was especially true of rosin sizes containing more than about 35% free rosin. Unless the dilution of sizes containing more than 35% free rosin was controlled with meticulous care, the size decomposed with the formation of a coarse suspension of rosin which was not only inefficient, but was certain to cause trouble.

Since the sizing of paper may be considered to be an operation in which the fibers of the paper have been given a coating of water-insoluble material, it is manifest that the smaller the particles of the coating substance, the greater surface of paper will be coated with a given amount of size. This is readily proven mathematically by considering the comparative surface of two globules of rosin one with a diameter of 1 centimeter and the other with a diameter of 0.25 centimeter. The first will have a surface area of about 3.142 square centimeters and a volume of about 0.5236 cubic centimeter, while the second will have a surface area of about 0.197 square centimeter and a volume of about 0.0082 cubic centimeter. Thus, if the first globule be divided into about 63.8 globules each having a diameter of about 0.25 centimeter, the combined surfaces of the 63.8 globules will be about 12.372 square centimeters. In other words, the same volume or weight of rosin if subdivided into particles having 0.25, the diameter of the original globule will cover a surface 3.97 times as great. The above calculations hold whether the diameter of the first globule be 1 centimeter or 1 micron.

A paper size solution of the class of free rosin sizes having up to about 45% free rosin has been described in U. S. Patent No. 1,882,680 to Wieger. This patentee describes a process in which 98 kilograms of a rosin having a saponification number of 165 are melted and to which small quantities of water are added to cool the material. If desired, small amounts of alkali, say about 0.1 to 3% are added. At a temperature of about 80 to 90° C., a hot solution of 2% casein in 25 liters of water containing 200 grams of caustic soda is added. More water is added in order to cool the material. This process produces a size which usually contains about 55% water and therefore must be shipped in expensive water-tight drums. Furthermore, when this size is dispersed in water, the diameter of the particles on the average is of the order of 1 micron, although there are often particles having a diameter of 2 to 10 microns.

While Wieger's paper size has been accepted by the paper industry to a certain extent, the solution must be shipped in water-tight barrels which are expensive. For every 45 pounds of rosin on which the consumer pays freight, he also must pay freight on 55 pounds of water. Due to the comparative coarseness of the particles, the maximum sizing effect cannot be obtained. In addition, the rosin sizes of the prior art are very sensitive to local mill conditions of salt content of the water, pH of the water, and similar variables which are well known to those skilled in the art.

A more recent development in the art of producing paper size is the process and product described in several foreign patents notably the British Patent No. 424,230. These foreign patents disclose a process for the production of a solid, readily soluble rosin which is supposed to be an improvement on Wieger. The process involves melting rosin and then cooling the melted rosin to about 100° C. To the cooled rosin an amount of water equivalent to about 10% of the weight of the rosin is added, followed by the addition of an amount of casein equal to about 3% of the rosin and an amount of ammonia equal to about 1.2% of the weight of the rosin. While soluble rosin was not known prior to this disclosure, these patentees claim to produce a product which is a solid form and capable of being kept indefinitely, but which as distinct from natural rosin, is soluble in water. Thus, the art has been confronted with the problem

of providing a more efficient rosin size and process and apparatus of using the same, including a rosin size, of which a unit weight would size a greater weight of paper and require less alum and the like than prior art sizes. The art has likewise been confronted with the problem of the sensitivity of conventional prior art sizes to local sizing conditions and of the complexity and difficulties of operations. Although many attempts have been made to solve these problems, none, so far as we are aware, has resulted in a wholly satisfactory solution especially when carried into practice on an industrial scale.

We have discovered a process for preparing size rosin in the solid state which is insoluble in water and is readily dispersible therein as a dispersion of extremely fine particles. A smaller amount of our improved size rosin will coat a given weight of paper and permit less penetration of ink as determined by standard methods than prior art products. A given weight of our improved size rosin requires a smaller amount of alum for precipitation in the paper being sized. The sizing process in the paper mills may be carried out at higher pH values with the same margin of safety when using our improved size rosin than is conventional practice. Our improved size rosin likewise is capable of producing rosin size emulsion containing from 40 to 90% unsaponified resin acids or free rosin. Thus, the disadvantages of the prior art products, such as the necessity of using water-tight barrels and containers, the costly excess weight due to the presence of water of solution, and the sensitivity of prior art size rosins containing appreciable amounts of free rosin to local sizing conditions, are overcome by the product of our new process. In addition, the saving in the quantity of size rosin consumed and the amount of alum used is appreciable when our improved size rosin is used.

It is an object of the present invention to provide a process for producing a water-insoluble, solid size rosin containing appreciable amounts of unsaponified resin acids and readily dispersible in water.

It is another object of the present invention to provide a process for producing a water-insoluble, solid size rosin containing at least 40% free rosin and readily dispersible in water.

It is a further object of the present invention to provide a process for producing water-insoluble, solid size rosin containing over 40% free rosin and readily dispersible in water to form a sizing solution having particles of free rosin size with an average diameter of less than 1 micron.

The present invention also contemplates the provision of a process for producing a dilute aqueous emulsion from the concentrated solid size "gel" and an apparatus therefor.

It is also within the scope of the present invention to provide a sized paper having a thinner film of rosin size than prior art papers of comparable weight and of comparable constituents, having equivalent resistance to ink penetration.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a side elevational view of a converter embodying the principles of the present invention with parts broken away for the sake of clarity, and

Fig. 2 is a sectional view of a converter embodying the principles of the present invention taken on line 2—2 of Fig. 1 looking in the direction of the arrow.

Generally speaking, our improved process for the production of size rosin in the solid state and readily dispersible in water to form a sizing solution having particles the average diameter of which is less than about 1 micron, comprises emulsifying a small amount of water in rosin in the molten state in the presence of carefully regulated critical amounts of protective colloids, and then reversing the type of emulsion to a rosin in water emulsion at the time of sizing paper.

In accordance with the principles of the present invention, a water-in-rosin emulsion is formed by melting collophony with or without additions of natural or synthetic resins, fatty oils, saponified stearine, paraffin, and the like. The resinic material is cooled to slightly above its melting point and between about 70° and about 120° C. Small amounts of water, say up to 5%, either in the liquid state or the vapor state, are slowly pumped preferably through a distributor placed in the bottom of a tank or autoclave containing the resinic material, into the collophonic material. The liquid resinic material is stirred to ensure intimate and homogeneous mixing of the water with the rosin. Small amounts of alkali, say about 0.1 to about 0.5% by weight, are introduced either before the addition of the water, with the water, or immediately after the addition of the water. With the slow addition of the water and the thorough stirring and mixing of the water in the resinic material, a water-in-rosin emulsion is formed. After the formation of the water-in-rosin emulsion, the temperature of the emulsion is preferably cooled to about 75 to about 90° C., and additions of one or more protective colloids are made. The total amount of protective colloid added is between about 3 and about 20% and preferably about 4 to about 10%. The protective colloids may be added individually or in combination and as a powder or in solution. The addition of the protective colloid must be carried out with care to ensure that the water-in-rosin emulsion takes up the colloid at practically the same rate with which the colloid is introduced into the emulsion. We have found that satisfactory results are obtained by introducing the colloid into the emulsion of water-in-rosin through a distributor located in the bottom of the tank. During the introduction of the colloid, the water-in-rosin emulsion should be stirred so that the colloid is thoroughly mixed with the emulsion to form a homogeneous mass. Care should be exercised to prevent the addition of the colloid at temperatures at which the colloid denatures or at a rate at which the undistributed colloid agglomerates and forms lumps in the water-in-rosin emulsion. The temperature of the colloid should be about 40 to 60° C. When all the colloid has been added, a quantity of ammonia and/or ammonium salts equivalent to about 0.4% to about 2.5% of the weight of the rosin is pumped into the homogeneous mixture of water, rosin and colloid. We have found that very satisfactory results are obtained by introducing the ammoniacal solution through a distributor similar to the aforementioned distributor which is especially constructed for this purpose, care being taken that the pressure does not rise above about ten atmospheres. Excess ammonia may be withdrawn from the mixing vessel and recovered for further use. We have found that less than about 50%

of the total ammonia added to the resinic material is retained in the solid rosin size product; the remainder being vaporized and recovered if desired. Analysis of the solid rosin size with a determination of the alkali content, has shown only that amount of total alkali present which would combine with all the protective colloid and about 20 to about 45% of the rosin. Thus, solid rosin sizes have been produced which, by calculation based upon the analytically determined alkali content, contained from about 55% to about 80% free rosin. Such solid rosin sizes are capable of producing rosin size emulsions containing up to about 93% free rosin.

We have found that satisfactory results are obtained when starch, dextrines, animal glue, gelatine, and casein are used as protective colloids. Good results are likewise obtained by the use of synthetic emulsifiers, such as triaethanolamine stearate. Of course, combinations of two or more of the various colloids and/or emulsifiers referred to hereinabove may be used, and in fact exceptionally good results have been obtained with mixtures, such as the following: a mixture of protective colloids amounting to about 3 to about 20% of the weight of the resinic material and containing about 2.8% starch, about 1.9% animal glue or gelatine, and about 3.0% casein. An alkaline solution containing 40% solids and containing a quantity of animal glue or gelatine equivalent to about 2.3% of the weight of the rosin and a quantity of casein equivalent to about 4.5% of the weight of the rosin produces a very good result, while other combinations include one containing 2.5% starch and 3.5% casein, and another 5.3% starch and 2.5% animal glue or gelatine, wherein all quantities are based on the weight of the rosin. The use of different protective colloids or combinations has a marked effect upon the size of the particles and the distribution of particles in groups having various diameters and also upon the size of the precipitated particles after the addition of alum in the sizing process. For example, in the presence of starch, animal glue, gelatine, and the like in the emulsion, the particles flocculated by the addition of alum in the sizing process are very fine. On the other hand, the use of casein alone results in the flocculation of the rosin in particles of comparatively large size. Casein can also assist in the flocculation in the presence of alum of materials which otherwise would stay in solution or suspension.

As alkaline agents in the formation of the water-in-rosin emulsion, soda ash, caustic soda and sodium aluminate, and similar alkaline substances may be used. Ammonium carbonate may be substituted for a portion, up to about 50%, of the aqua ammonia.

To obtain special effects, it is often advisable to incorporate small amounts of phenol and formaldehyde in the emulsion.

The saving in consumption of alum will be appreciated by consideration of the following facts. It is conventional practice to maintain a pH of about 5.5 to 4.7 in sizing with the prior art products. However, when sizing with our improved size rosin, it is only necessary to reduce the pH to about 5.5 to about 6.5 in order to size with the same safety as when using conventional prior art products.

For the purpose of giving those skilled in the art a better understanding of the process for producing our improved water-insoluble, solid size rosin, in accordance with the principles of the present invention, the following illustrated examples are given:

Example No. 1

About 1000 kilograms of molten rosin are thoroughly mixed in a container, for example, an autoclave, with about 5 kilograms of soda ash (Na_2CO_3) or a mixture of about 2.5 kilograms of caustic soda and about 2.5 kilograms of sodium aluminate. About 10 kilograms of water in either aqueous or vapor form are introduced preferably through a distributor located at the bottom of the container and provided with numerous small openings. The temperature is adjusted to about 80° to about 100° C. and the water thoroughly incorporated in the resin in the presence of the alkali to form a water-in-rosin emulsion. The temperature of the water-in-rosin emulsion is then reduced to below about 100° C. and about 90 kilograms of a starch solution containing about 45%–55% starch is stirred into the resinic material. The starch solution may be made up of equal parts of corn starch and potato starch hydrolyzed by 150 grams of biolase, the activity of which has been reduced by the addition of inhibitors such as 5% alkali or acid salts, that is salts which in aqueous solution have a markedly acid reaction. The starch solution is added slowly and not at a rate at which it cannot be taken up by the emulsion. Usually 5 to 30 minutes is required to introduce this amount of starch solution into the emulsion. The introduction of the starch should be accompanied by thorough stirring. When all the starch solution has been added, about 100 kilograms of an alkaline solution containing about 45 kilograms of a mixture of about 30 kilograms of casein and about 15 kilograms animal glue or gelatine and about 1.5 kilograms of caustic soda is introduced with the same precautions as were exercised in the introduction of the starch. In addition, the temperature of the protective colloids should be maintained at about 55° C. and extreme care exercised to introduce the colloids at approximately the rate at which the colloids are dispersed in the emulsion. After the introduction of the colloids, the speed of agitation may be increased (the viscosity of the emulsion decreases and thus the expenditure of power does not become prohibitive) and the stirring continued for a short time, say about 20 minutes. Then about 50 kilograms of aqua ammonia containing about 33% ammonia is introduced under pressure through the aforementioned distributor. After the whole of the ammonia has been introduced and has reacted to a desired extent with the contents of the container, the excess is withdrawn and the rosin size run off into containers. By analysis it has been determined that only about 0.8 to about 1.0% of the ammonia (NH_3) added to the rosin remains in the product.

Example No. 2

To about 1000 kilograms of rosin having a saponification value of about 165 and in the molten state, about 7 kilograms of water and 120 kilograms of alkaline casein or other protective colloid solutions are added. The rosin is thoroughly agitated or stirred during the introduction of the casein wtih the same precautions as were observed in Example No. 1. Then, 15 kilograms of ammonia gas are introduced through a distributor located at the bottom of the tank or autoclave and subsequently about 10

kilograms of an ammonium salt, such as ammonium carbonate in about 10 kilograms of water, are introduced through the distributor. After the addition of the ammonium salt, at least 40 kilograms of a 30% starch solution is mixed with the water-in-rosin emulsion and thoroughly dispersed therein. During the introduction of the starch solution, the temperature is regulated to about 50° C. After the addition of the starch, the resin emulsion is drawn off into containers.

Example No. 3

About five kilograms of caustic soda and about 20 kilograms of water are thoroughly incorporated in about 1000 kilograms of liquid rosin at about the melting temperature of the rosin. The mixture is stirred vigorously until a water-in-rosin emulsion is obtained, whereupon about 80 kilograms of casein, or casein and starch or casein, animal glue and starch in the powder form are mixed with the water-in-rosin emulsion. After the colloid has been added to the emulsion and dispersed therein, about 15 kilograms of caustic soda in about 60 liters of water are thoroughly mixed with the emulsion. After a further stirring for a short time, say about 20 minutes, 50 kilograms of aqua ammonia containing about 33% ammonia are mixed with the emulsion and thoroughly dispersed therein with vigorous stirring. The size rosin is then drawn off into containers and allowed to solidify.

Example No. 4

A modified process for producing solid size rosin in accordance with the principles of the present invention includes the production of the size rosin in accordance with Examples Nos. 1 to 3 and the addition of about 20 kilograms of triaethanolamine stearate or the like immediately after the addition of the ammonia.

Example No. 5

A further modification comprises the addition of about 50 kilograms or more of saponified stearine, fatty acid products, waxes, paraffin and/or similar products to the molten rosin.

The diameter of the particles of the solid size rosin produced in accordance with the principles of the present invention, when dispersed in water, will average less than 1 micron. In fact, solid rosin sizes made in accordance with the principles of the present invention will often disperse in water to form suspensions in which about 50% more or less of the particles are such size that they are invisible under the ultramicroscope and a major portion of the remainder have an average diameter of about 0.25 to 0.5 micron.

We have found that the diameters of the particles of rosin size are critically affected by the amount or concentration of the protective colloid. For example, from a solid rosin size "gel" containing about 7% to about 9% or more casein, a rosin size "sol" or suspension, commonly called "size milk" may be made in which nearly all the particles of the size are of such diameters as to be invisible when examined at a magnification of 2500 diameters. On the other hand, a rosin size "sol" or suspension may be made from a solid rosin size "gel" having a concentration of about 5% to about 6% casein, in which the visible particles of the size have diameters of about 0.25 micron to about 1 micron.

While the solid rosin size "gel" may be converted into a dilute aqueous "sol" or suspension in various types of apparatus or mixers, we have found that a particular apparatus gives the best results. In our preferred apparatus the melting of the solid rosin size is carried out in such a manner that the solid rosin size "gel" is subjected to the necessary temperatures for melting for the shortest time possible. When the solid rosin size "gel" produced in accordance with the principles of the present invention is subjected to temperatures reached in the vicinity of steam coils, for example, for any extended period of time, and the critical volume of the particles of rosin size is affected adversely. Thus, it is necessary to provide a means for melting the solid rosin size in which it is possible to remove the size from the zone of relatively high temperature as soon as the size is fluid enough to flow.

The rate of the introduction of the necessary diluent water into the molten rosin size must be controlled within critical limits to insure that the rosin particles will not flocculate. In addition, the temperature of the water and the temperature of the rosin-water mixture during the transition from the "gel" stage to the "sol" stage must be controlled within critical limits. Furthermore, the temperature of the mixture of rosin size and water must be controlled within critical limits during the transition from the "gel" stage to the "sol" stage and during dilution to avoid flocculation of the rosin size particles.

In addition to the importance of maintaining the fine state of division in which the rosin size is present in the "gel" stage during the transition to the "sol" stage or condition, the power consumption is also an important factor, particularly from a practical and industrial point of view. For example, the power consumed in bringing one of the conventional concentrated aqueous size solutions or suspensions to the dilute condition of a dilute size suspension, i. e., a size milk, is considerably greater than that necessary to bring the solid rosin size "gel" of the present invention from the "gel" condition to the "sol" stage, and then to the dilute concentration suitable for use in the beater when the apparatus of the present invention is employed. As those skilled in the art know the power consumed in mixing varies as the cube of the rate of rotation. Thus, a mixer now in use for this purpose for the purpose of diluting concentrated rosin size operates at a rate of 150 R. P. M. (revolutions per minute), whereas the mixer of the converter hereinafter described operates at a rate of 20 to 80 R. P. M. and preferably at a rate of 40 R. P. M.

The time required to dilute a prior art concentrated aqueous suspension of rosin size or to convert the solid concentrated rosin size "gel" of the present invention to a dilute suspension likewise is an important industrial factor in the practical application of rosin to the sizing of paper. The fact that free rosin size is difficult to suspend in dilute suspension even when starting from concentrated suspensions is well known in the art. This difficulty has been overcome in a practical manner in the following way. It is known that when molten rosin is divided into strings, threads or filaments of small diameter while under warm water, a very small part of the rosin goes into suspension as small particles. However, in the presence of dispersants molten rosin readily goes into suspension in warm water.

We have taken advantage of this characteristic in the design of the mixer of the present invention. The advantage of obtaining dilute rosin size suspensions through the agency of this characteristic is clearly shown by a comparison of the time required to produce a dilute rosin size suspension (size milk) from a concentrated aqueous rosin size suspension in a conventional mixer with the time required to convert the concentrated rosin size "gel" of the present invention to a dilute aqueous suspension or "sol."

A mixing time of 120 minutes was required to produce a dilute size suspension from a concentrated size suspension in a conventional type of apparatus. On the other hand, dilute size "sols" or suspensions have been made from the solid concentrated rosin size "gel" embodying the present invention in about 30 to about 70 minutes in the apparatus described hereinafter. In other words, an equivalent amount of dilute size suspension or size milk can be made from the concentrated solid size "gel" in 25 to about 50% of the time heretofore required.

In general, the preparation of dilute size ready for use in the beater from solid concentrated size "gel" of the present invention is advantageously carried out in an apparatus, such as is shown in Figs. 1 and 2.

The concentrated solid rosin size "gel" is melted in the hopper and flows into the mixing tank. Water for dilution is added at critical rates and at a critical temperature from a supply tank. The rate of mixing may be increased as the viscosity of the size-water mixture decreases as the size passes from the "gel" stage to the "sol" stage.

For the purpose of giving those skilled in the art a better understanding of the principles of the present invention, the apparatus for making dilute rosin size suspensions from solid concentrated rosin size "gels" and the operation thereof will be described in conjunction with the accompanying drawings.

The solid concentrated rosin size "gel" in a more or less comminuted condition is placed in hopper or melting pot 1 supported in a ring 59 mounted on vertical members 60. Hopper 1 is provided with a steam coil 2 equipped with an inlet 3 and an outlet 4 for condensate. The melting pot or hopper 1 is supported over a feed hopper 5 by a plurality of members 6 and 7. Rosin size 8 in hopper 1 rests on and against steam coil 2. As soon as the rosin size has been brought to a temperature at which it is fluid, it drips or flows into a feed hopper 5. In this way the water-in-rosin "gel" is not exposed to the de-emulsifying effect of the relatively high temperatures existing in the vicinity of the steam coil long enough to result in breaking down the emulsion. For best results, the temperature of the water-in-rosin emulsion should be maintained between about 55° C. and about 65° C., and preferably at about 55° C. The molten size "gel" passes from the feed hopper 5 into converter 9 by means of feed hopper outlet 10 and converted inlet 11.

The converter 9 comprises a casing 12 provided with an inlet 11, a steam jacket 13, an outlet 14, a dump valve 15, and shaft seals and bearings 16 and 17. A means for determining the temperature of the contents of the converter, such as a thermometer 18, and a pressure gauge 18a are also provided. The converter is likewise provided with a water manifold or distributor 19 and an agitator 20. The water manifold or distributor is divided into a plurality of compartments, preferably three, 21, 22 and 23. These compartments are provided with a plurality of orifices or outlets 24 for the purpose of controlling the rate of introduction of the diluent water into the molten rosin size gel or suspension. For example, one compartment is provided with sufficient orifices to permit a unit quantity of diluent water to flow into the converter in a given period, say about 15 to 20 minutes. A second compartment is provided with sufficient effluent capacity to allow the unit quantity of diluent water to flow into the converter in, say 0.5 the time. A third compartment is provided with sufficient effluent area to permit the passage of the unit quantity of water into the converter in, say 0.33 to 0.25 the time required for the emptying of the first compartment. By controlling the addition of the diluent water in this critical manner, the transition of the concentrated molten rosin size "gel" to the "sol" stage and then to the dilute "sol" stage is accomplished without de-emulsifying the suspension and without the flocculation or agglomeration of the size particles. By combining this critical control of the rate of addition of the diluent water, viz., the rate at which the "gel" is capable of taking up water and passing to the "sol" stage, with the critical control of the temperature of the water, of the rosin and of the resulting suspension, it is possible to produce rosin size emulsions (sols) embodying the present invention and having rosin size particles averaging less than 1 micron in diameter and having 50% or more of the particles invisible at a magnification of 2500 diameter.

An important feature of the converter 9 is the means for agitating and mixing the molten size and the diluent water. It is of major importance, as those skilled in the art appreciate, to produce size suspensions with uniform texture, i. e., size suspensions which have a uniform concentration of size particles of uniform diameters. This uniformity of texture is obtained readily, rapidly and consistently as a result of the unique form of mixing or agitating elements. Converter 9 is provided with an agitator 20 comprising shaft 25 and a plurality of blades 26. From the bottom of the converter 9 a series of stationary blades 27 rise between which the movable blades 26 pass. The blades 26 are disposed around the axis of the shaft 25 in such a manner that a line drawn through the outer extremities of the blades describes a curve around the shaft as an axis similar to the conventional "sine" curve. The blades 26 also are disposed on the shaft 25 with the horizontal axes of the blades forming an angle less than a right angle with the horizontal axis of the shaft 25. Due to the positioning of the blades with respect to the shaft and to each other, the rosin-water mixture is constantly moved from the ends 28 and 29 of the converter to the center thereof and flows back to the ends to pass through the cycle again and again.

The agitator shaft 25 is supported in bearings 30, 31 and 32 and bearing seals 16 and 17. The bearings 30, 31 and 32 are mounted on supports 33, 34 and 35, respectively. The shaft 25 is driven by means of gear 36 keyed thereto which in turn is driven by spur gear 37 keyed to countershaft 38. On countershaft 38 are mounted pulleys 39, 40 and 41, of which 39 is keyed to the countershaft 38, while pulleys 40 and 41 are free to revolve thereon. Pulleys 39, 40 and 41 are preferably of the same diameter and predetermined

speeds of rotation of pulley 39, are provided by means of pulleys of different diameter mounted on the mainshaft (not shown). Of course, other means of varying the speed of rotation may be provided, but we have found that the method herein described above gives satisfactory results. Since the gears 36 and 37 have a fixed ratio, the pulleys of the main driving shaft are proportioned to give the desired R. P. M. of the agitator, viz., 20 to 80 R. P. M., and preferably 20 to 40 R. P. M.

The steam jacket 13 is provided for the preparation of modified sizes containing components having a higher melting point than the unmodified concentrated solid size, and for such emergencies as the stoppage of the converter through power outage and the like. By introducing steam into the jacket 13 by means of inlet 42, the contents of the converter may be maintained within the critical limits required to avoid agglomeration of the rosin size and to avoid solidification of the molten rosin size or to raise the contents of the converter to the higher temperatures required by the elevated melting points of some special ingredients added to the unmodified size for special effects. The condensate produced by the steam escapes through outlet 43. A safety valve 42s and a pressure gauge 18a are also provided.

To avoid spattering and splashing of the dilute size suspension and to provide a valve which does not "freeze" and is readily cleaned, we have found that a dump valve similar to that illustrated in Fig. 1 meets all requirements. Valve 15 comprises a splash box 44 having an outlet 45 and a converter closure plate 46. The valve is pivoted on shaft 47 and actuated by lever 48. Slidably mounted on lever 48 is counterbalancing weight 49. By this construction, a readily cleaned closure control and rapidly opened valve is provided, and likewise the splashing and spattering of the size-milk is avoided.

The diluent water may most conveniently be heated and stored in a supply tank 50 erected near, and preferably over, the converter. The supply tank is provided with a water inlet 51, a water overflow 52, and a discharge 53. The discharge 53 is preferably provided with a three-way valve 54 providing three different rates of discharge. A flexible conduit 55 is provided to carry the diluent water from the valve to the water manifold 19. Of course, other means for providing different rates of discharge, such as three separate valves serving three separate conduits and similar means, may be employed. The flexible conduit 55 may be moved from one compartment of the manifold 19 to another as the operation proceeds. The supply tank 50 is provided with a steam inlet 56 for the introduction of steam into the diluent water for the purpose of raising the temperature of the water when necessary. Of course, a steam coil could replace the open steam line if desired. A thermometer 57 and a gauge glass 58 are also included in the equipment of the supply tank.

We have found that the solid concentrated size "gel" produced in accordance with the principles of the present invention can best be diluted in the following manner. Comminuted size is placed in the melting hopper 1 and steam introduced into the coil 2. The size on melting immediately flows or drips down into the feed hopper 5 and thence through the hopper outlet 10 and the converter inlet 11 into the converter 9. As soon as size is introduced into the converter 9, the agitator is started. Meanwhile the required amount of diluent water has been heated, if necessary, to a temperature of about 36° C. to about 40° C. in the supply tank. The temperature of the diluent water is regulated to be just sufficient to maintain a temperature of about 40° C. to about 60° C. in the finished dilute size suspension. The temperature of the water is preferably about 36° and that of the molten rosin size about 55° C. at the start of the mixing process in order to obtain the best particle size in the dilute rosin-in-water suspension.

The water is introduced preferably in three portions of approximately equal volume. For example, for best results the first third of the diluent water is introduced through the compartment of the manifold 19 having the smallest effluent area in about 15 to about 20 minutes with the agitator revolving at a rate of about 40 R. P. M. At the end of about 15 to about 20 minutes, the discharge conduit 55 is transferred to the compartment having an intermediate effluent area and the valve 54 turned to the position in which the discharge of the second portion of the diluent water will take place in an intermediate period, say 7 to 10 minutes. When the second third of the diluent water has been introduced into the converter, the flexible conduit 55 is transferred to that compartment of the manifold 19 which has the largest effluent area and the valve 54 turned to the position in which the final third of the diluent water is discharged in the least time, say 3 to 5 minutes. With greater amounts of size gel and correspondingly greater amounts of diluent water, the time increases. However, for practical purposes, the solid concentrated rosin size "gel" may be converted to a "sol" and diluted to a dilute aqueous size suspension (size milk) in from 25 to 70 minutes. This time of conversion from the concentrated solid size "gel" to the dilute size suspension may be compared with the time of 120 minutes given hereinabove for the conversion of a concentrated aqueous size suspension to a dilute aqueous size suspension in conventional equipment.

As exemplary of the practical advantages accruing from the use of the concentrated solid rosin size "gel" of the present invention converted into a dilute rosin size suspension or size milk by the hereinafter described process in the hereinabove described apparatus, the following tabulation of the sizing effect secured with the dilute size suspension of the present invention as compared with two other commercial size preparations is given.

As those skilled in the art recognize a smooth wood-free paper stock of the 60 gram grade is very difficult to size on one side. Such a paper weighing 63 grams per square meter was sized under controlled conditions with two commercial sizes in comparison with the size milk of the present invention. The composition of the size milks or dilute size suspensions is given below:

Table I

Size	Total rosin (rosin acids+unsaponifiable) in size milk	Per cent free rosin per 100 parts size milk	Per cent free rosin per 100 parts total rosin
A	43.3	34.0	78.2
B	54.4	13.8	25.5
Present invention	29.5	27.8	90.0+

The sizing of the hereinabove mentioned 60-gram wood-free paper was carried out with the above size milks and the sizing effect determined by means of the conventional ink penetration test. A comparison of the sizing effect of the three size milks referred to in Table I is given in Table II:

Table II

Test No.	Size A, percent size referred to the weight of the pepar stock	Size B, percent size referred to the weight of the paper stock	Present size, percent size referred to the weight of the paper stock	Sizing effect
1	3.0			(2)
2	2.7			(2)
3	2.55			(2)
4	2.25			(2)
5		2.03		(1)
6	1.95			(1)
7		1.83		(1)
8		1.63		(1)
9			1.62	(2)
10	1.50			(1)
11			1.42	(1)
12			1.22	(1)

[1] Designates "Unsatisfactory."
[2] Designates "Satisfactory."

The sizing effect secured with 1.62 grams of the present size is equivalent to the sizing effect of 2.25 grams of size A. Size B is so greatly inferior to the present size that no absolute values have been determined. However, it can be readily seen from the above tabulation that size B at least is no better than size A when compared with the present size. This tabulation clearly shows that the use of an amount of the size of the present invention equivalent to about 72% of the amount of size A or B produces equivalent sizing effects. This represents a saving of 28% in the amount of size required.

A tabulation of the sizing effect of the size of the present invention on a one sided 80-gram wood-containing paper shows similar results:

Table III

Test No.	Size A, percent size referred to the weight of the paper stock	Size B, percent size referred to the weight of the paper stock	Present size, percent size referred to the weight of the paper stock	Size effect
1	0.65			(1)
2	1.03			(1)
3			1.23	(1)
4	1.29			(1)
5			1.31	(1)
6			1.38	(2)
7	1.60			(1)
8		1.84		(1)
9	1.92			(3)

[1] Designates "Absolutely unsatisfactory."
[2] Designates "Unsatisfactory."
[3] Designates "Satisfactory."

While the results obtained with 1.38% of the rosin size of the present invention were not completely satisfactory, they were very close to the results obtained with 1.92% of size A: Again the tests show that sizing effects can be obtained with the size of the present invention equivalent to those of competitive sizes when using only about 70% as much size.

A comparison of the amount of alum required by the optimum amounts of size A and the size of the present invention is clearly shown in Table IV:

Table IV

Size	63 gram paper		80 gram paper	
	Grams size per 100 grs. paper to produce satisfactory size effect	Grams of alum per 100 grams paper	Grams size per 100 grs. paper to produce satisfactory size effect	Grams of alum per 100 grams paper
A	2.25	1.13	1.92	2.25
B	2.03	1.25	1.84	1.88
Present size	1.62	0.88	1.38	1.75

The above tabulation shows that the size of the present invention requires only about 78% as much of alum as other commercial sizes. Furthermore, in view of the fact that the dilute rosin-in-water size suspensions of the present invention contain not more than 10% saponified rosin in comparison with about 75% saponified rosin in prior art sizes (see Table I), it follows that when paper is sized at the highest pH (most alkaline, say pH 6.5) commensurate with satisfactory sizing, the amount of alum required will be less than that required by the prior art sizes and in some instances as much less as 30 to 50%. This highly practical advantage has been confirmed by actual tests.

The sizing effect of the size of the present invention probably is dependent in a large measure upon the size of the particles of rosin in the solid concentrated rosin size "gel" of the present invention and the fact that through the critical control of the various factors during conversion, the rosin particles do not agglomerate or flocculate. In this manner, the rosin size particles are suspended in as finely divided form as possible and thus the maximum sizing effect from a given weight of size is obtained.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, it is to be understood that variations and modifications can be made. Such variations and modifications are understood to come within the purview of the specification and the scope of the appended claims. Thus, it is to be understood that wherever the term "free rosin" is used in the present specification and the appended claims, it is to be understood that the difference between the total rosin content and the saponified rosin content is meant. In other words, "free rosin" as used herein designates the total of unsaponified resin acids and unsaponifiable components of rosin contained in the rosin "gels" and "sols" embodying the present invention. Similarly, the term "alkaline reagents" as used in the present specification and the appended claims refers to those reagents which form water-soluble compounds with the components of the solid rosin size in the amounts present.

We claim:

1. The process for making aqueous dilute rosin size suspensions having a free rosin concentration of at least about 40% and having practically all size particles invisible at a magnification of 2500 diameters which comprises mixing up to about 15% by weight of water with molten rosin in the presence of about 1.0 to about 3.5% by weight of alkali to form a water-rosin mixture, introducing into said mixture during agitation about 7 to about 9% by weight of casein at a rate approximating that at which said casein is taken up by the water-rosin mixture to form a water-in-rosin emulsion, adding water at a predeter-

mined rate to said water-in-rosin emulsion to convert said water-in-rosin emulsion into a concentrated rosin-in-water emulsion, maintaining the temperature of said concentrated rosin-in-water emulsion at about 55° C. to prevent occlusion of the casein by the rosin, and adding diluent water to said concentrated rosin-in-water emulsion at a predetermined rate to prevent the breaking down of said concentrated rosin-in-water emulsion and to obtain a dilute rosin-in-water emulsion whereby dilute rosin-in-water emulsions are obtained containing at least about 40% of the total rosin content in the free rosin state and having practically all rosin particles invisible at a magnification of 2500 diameters.

2. The process of making concentrated solid water-in-rosin size gel suitable for making dilute aqueous sizing suspensions having practically all size particles less than about 1 micron in diameter which comprises establishing a body of molten rosin having a temperature of about 80 to about 100° C., slowly introducing into said molten rosin up to about 5% by weight of water and about 0.1 to about 0.5% by weight of soluble alkali to form a fluid water-rosin mixture, agitating and reducing the temperature of said water-rosin mixture to about 75 to about 90° C., introducing during agitation at least two protective colloids selected from the group consisting of starches, dextrins, animal glue, gelatine and casein at a temperature of about 40 to about 60° C. in an amount equivalent to about 3 to about 20% of the weight of the rosin and at a rate not greater than that at which said colloids are taken up by the water-rosin mixture, continuing the agitation until a homogeneous water-in-rosin emulsion is formed, slowly introducing into said water-in-rosin emulsion up to about 2% of ammonia by weight in the form of about 33% aqua ammonia, allowing an amount of said ammonia equal to about 0.8% to about 1.0% by weight of the rosin to react with said water-in-rosin emulsion, and then allowing said water-in-rosin emulsion to cool to form a concentrated water-in-rosin gel containing an amount of total alkali only sufficient to combine with all the protective colloids present and about 20% to about 45% of the rosin present and suitable for the preparation of dilute aqueous rosin suspensions having practically all size particles less than about 1 micron in diameter and containing up to about 93% free rosin.

3. The process set forth in claim 2 wherein triethanolamine stearate is employed as one of the protective colloids.

4. The process of making concentrated solid water-in-rosin size gel suitable for making dilute aqueous sizing suspensions having practically all size particles less than about 1 micron in diameter which comprises mixing about 1000 kilograms of molten rosin with about 5 kilograms of soda ash, introducing about 10 kilograms of water into said rosin alkali mixture, adjusting the temperature of said rosin mass to about 80 to about 100° C. and thoroughly incorporating said water in said rosin in the presence of said alkali to form a water-in-rosin emulsion, reducing the temperature of said water-in-rosin emulsion below about 100° C., introducing into said water-in-rosin emulsion about 90 kilograms of a starch solution containing about 45 to about 55% starch at a rate no greater than that at which the water-in-rosin emulsion takes up the starch solution, then adding about 100 kilograms of an alkaline solution containing about 45 kilograms of a mixture of about 30 kilograms of casein and about 15 kilograms of animal glue and about 1½ kilograms of caustic soda at a rate not exceeding that at which said alkaline solution is taken up by the water-in-rosin emulsion containing starch, the temperature of said starch solution and said alkaline solution of casein and animal glue being maintained at about 55° C., increasing the speed of agitation and continuing the agitation for a short time, introducing about 50 kilograms of aqua ammonia containing about 33% ammonia into the water-in-rosin emulsion, allowing a portion of said ammonia to react with said water-in-rosin emulsion, removing excess ammonia and allowing said water-in-rosin emulsion to cool to form a solid gel containing about 0.8% to about 1.0% of the ammonia whereby a concentrated water-in-rosin gel containing an amount of total alkali only sufficient to combine with all the protective colloids present and about 20 to about 45% of the rosin present is produced, said solid concentrated water-in-rosin gel being suitable for the preparation of dilute aqueous rosin suspensions having practically all size particles less than about 1 micron in diameter and containing up to about 93% free rosin.

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