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2,797,167

HYDROPHOBIC BLENDS COMPRISING FORTIFIED ROSIN AND WAX

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The present invention relates to homogeneous blends of fortified rosin and wax suitable for conversion into paper sizing dispersions. More particularly, the invention relates to homogeneous fortified rosin-hydrophobic wax blends containing a higher alcohol as coupling agent, that is, as agent rendering the fortified rosin and wax mutually compatible. The invention includes aqueous dispersions of the blends and paper sized therewith, as well as the several methods involved.

In the past, heavily sized paper for use as ice cream, cottage cheese, margarine, and butter containers and as oyster pails has been made by a process which comprises forming an aqueous slurry of papermaking cellulosic fibers, adding thereto an aqueous rosin-wax sizing dispersion (such as is formed by emulsifying a homogeneous rosin-wax hot melt in water), sheeting the fibers, and drying the web thus formed at a convenient temperature within the range of about 190°–260° F. The rosin-wax particles melt and flow during the heating step, thus conferring sizing to each fiber as a whole. In papers for the uses described, lactic acid resistance is particularly important.

In such sizes the rosin is present in unsaponified form, that is, in the form of a free organic acid. Molten rosin has excellent compatibility for wax and will form a homogeneous solution therewith in any ratio.

More recently it has been found that the lactic acid resistance of liquid rosin size (that is, rosin predominantly in the form of sodium rosinate) can be increased by first condensing rosin with a small amount of a compound of acidic character containing a $-\text{CO}-\text{C}=\text{C}-$ linkage usually maleic anhydride (cf. U. S. Patents Nos. 2,383,933, 2,628,918 and 2,684,300) thereby forming "fortified rosin," and then saponifying with aqueous caustic. Such size is now sold on a large commercial scale.

The reaction occurring is well-known Diels-Alder condensation, and is effected by heating the rosin with the acidic organic compound at 175°–200° C. for a few hours. The acidic organic compound is generally employed within the range of $\frac{1}{12}$ to $\frac{1}{4}$ mol per mol of rosin, and best fortification is usually obtained within the range of about $\frac{1}{10}$ to $\frac{1}{5}$ mol of the compound per mol of rosin. The melting point of the fortified rosins thus obtained is usually between about 140° and 200° F., depending principally on the amount and type of acid compound taken. For example, in place of maleic anhydride other compounds may be used such as itaconic acid, citraconic acid, and the mixture of acids or anhydrides obtained by heating citric acid at 200° C. A number of other means are known for preparing fortified rosin, and thus rosin may be reacted with a large amount of the organic acidic material, say 0.7–0.9 mol, and then diluted with ordinary rosin to bring the amount of combined organic acid within the range mentioned above.

When used in normal amounts, fortified rosin size usually causes increases of from 20% to 50% or more in the lactic acid values obtained over the values obtained in similar manner by the use of ordinary rosin size.

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Despite this foreseeable advantage, up to the present it has not been considered possible to employ fortified rosin in the manufacture of aqueous rosin-wax dispersions. The principal reason for this is that fortified rosin and wax are incompatible when melted together, the materials behaving as mutual non-solvents even when stirred together for extended periods of times. This is due to the more organophobic character which fortified rosin possesses resulting from the presence of the organic acidic material therein. As a result, when molten fortified rosin and wax are mixed, two layers form, the wax floating on the rosin layer and no significant solubilization occurs even after thorough stirring.

I have now discovered that the higher monohydric fatty alcohols such as stearic alcohol are coupling agents for molten fortified rosin-wax and that the presence of only a small amount of such alcohols permits formation of fortified rosin-wax hot melts which are completely homogeneous and free from any tendency to form two layers. I have further found that such homogeneous hot melts may be readily emulsified to form valuable sizing agents for paper.

It is of particular advantage that the alcohols referred to do not more than negligibly decrease the benefits expected from the presence of the fortified rosin.

In the preparation of the hot melts the fortified rosin and wax are taken in the amounts at which ordinary rosin and wax have heretofore been employed for the manufacture of paper sizes, that is, in weight ratio between about 40:60 and 60:40, so as to obtain maximum benefit from each component. According to one embodiment, the wax and fortified rosin are first melted together and the alcohol is then added in solid or liquid form. The amount of alcohol added need be no more than that sufficient to cause the wax and fortified rosin to form a unitary, homogeneous mixture. The precise amount of fatty alcohol needed is not the same in each instance as it depends upon such variables as the number of anhydride groups in the fortified rosin, the fortified rosin:wax weight ratio, the chain length of the fatty alcohol selected, and the temperature of the melt. The amount is most easily found by trial, and so far less than 5% based on the weight of the melt has generally proved sufficient. Since normal melt temperatures do not exceed 200° F. and half an hour of mixing is ample to form the melt, no substantial esterification of the alcohol takes place.

As coupling agents any of the normally solid monohydric alkanols may be employed as well as mixtures thereof, that is alkanols which melt at temperatures above about 70° F. Such alcohols include dodecanol, myristyl alcohol, octadecanol already mentioned, and the mixtures of higher alcohols produced from oxidized petroleum. Preferably the alcohols have melting points below 190° F. so as not to increase emulsification temperatures. The primary alcohols having 16 to 20 carbon atoms give excellent coupling effect, are readily available, and melt below about 120° F. Such alcohols are therefore preferred.

From the foregoing it is apparent that the compositions of the present invention consist essentially of homogeneous blends of fortified rosin and a wax in weight ratio between 40:60 and 60:40 together with a small but effective amount of a normally solid monohydric primary fatty alcohol as coupling agent therefor. The fortified rosin is most conveniently described as corresponding to the mixture formed by reacting one mol of rosin with between about $\frac{1}{12}$ and $\frac{1}{4}$ mol of a compound of acidic character containing a $-\text{CO}-\text{C}=\text{C}-$ linkage. The invention includes the blends both in solid and also in molten form.

The method of the present invention principally comprises the stirring together of fortified rosin and wax of

the above-stated types in the above-stated proportions in molten form with a suitable higher fatty alcohol as coupling agent.

The hot melts may contain other materials customarily present in rosin-wax sizes including wax-soluble dyes, and organophilic fillers and pigments including organic polysiloxane-coated titanium dioxide pigment. U. S. Patent No. 2,717,246 discloses pigment of this description.

The fortified rosins may be prepared from any of the rosins heretofore used in the manufacture of paper sizes. Such rosins include gum rosin, wood rosin, and tall oil rosin. Such rosins may and often do contain small amounts of special additives such as phenothiazine, diphenylamine, or N-phenyl-2-naphthylamine as antioxidants; phenolic compounds such as saligenins as crystallization inhibitors; and sulfur or sulfur acid salts as residual catalysts.

The waxes in the compositions of the present invention are preferably hydrocarbon waxes having a melting point between about 115° and 190° F. these being the waxes customarily employed as sizing agents for paper. Specific waxes frequently used are slack wax (a petroleum wax containing residual oil and having a melting point of about 120° F.), crude scale wax having a melting point of about 130° F., microcrystalline waxes melting at about 130° to 150° F., and the highly refined petroleum waxes from which oil has largely been removed and which melt sharply at about 150° to 160° F. Although they have not been tried it is believed that any water-insoluble hydrophobic wax melting below about 200° F. is benefited by the present invention including carnauba wax, candillilla wax, bees wax, montan wax and ozocerite, and such waxes are therefore included within the scope of the present invention. In practice we prefer to use waxes melting between about 115° and 160° F. since they permit comparatively low emulsification temperatures while affording sizes which confer excellent water-resistance to paper. Aqueous dispersions of the foregoing blends may be prepared by any of the methods heretofore employed for the preparation of paper sizes from rosin-wax blends. However, we have found the following general method to be particularly advantageous in that the dispersions obtained are quite stable to alum acidity and therefore on sheeting are more uniformly distributed through the web. The procedure involves two principal steps.

The first step consists in forming an aqueous phase by dissolving a hydrophilic colloidal gum and one or more alum-stable anionic dispersing agents of the sulfonate or sulfate type in water. The weight of the water is sufficient so that the final dispersion contains 30 to 60% solids by weight. The combined weight of the gum and dispersing agent should be determined as described below but is generally between about ¼% and 10% of the hot melt to be added. The temperature of the water should be above the flow point of the hot melt so as to insure formation of an emulsion of the liquid-in-liquid type.

In the second step the hot melt is slowly poured into the aqueous phase with vigorous agitation. An emulsion rapidly forms which is homogenized hot and then rapidly cooled to preserve the colloidal size of the particles.

The dispersing agents referred to are characterized in that 0.5% by weight aqueous solution thereof do not precipitate or flocculate at 20° C. in the presence of 500 p. p. m. of alum as aluminum sulfate tetradecylhydrate. Representative members of the group include sodium propyl naphthalene sulfonate condensed with formaldehyde; sodium isopropyl naphthalene sulfonate; sodium tetrahydronaphthalene sulfonate; sodium octylsulfobenzoate condensed with formaldehyde; sodium lignin sulfonate; sodium octyl sulfate; the sodium salt of N-oleyl-N-methyl-taurine, and the commercial agents known as Triton 720, Tanak KL, and Nacconal NR. Triton 720 is the sodium sulfonate of octylphenol-ethylene oxide reaction product;

Tanak KL is the di-sodium salt of methylene-bis-naphthalene sulfonic acid; and Nacconal NR is sodium keryl benzene sulfonate.

As gums, any of the commercially available hydrophilic (i. e., water-soluble) materials may be used which have heretofore been employed as protective colloids for oil-in-water dispersions including gum arabic, methylcellulose, sodium carboxymethyl cellulose, gum ghatti, and sodium alginate.

Sufficient of the anionic dispersing agent or agents should be employed to insure rapid and complete emulsification of the hot melt. The amount will vary with the precise agent selected, the amount of combined organic acid in the fortified rosin, the temperature, and solids content of the batch, and can be most easily determined by trial. Sufficient of the gum should be used to prevent flocculation when one volume of the resulting dispersion at 50% solids is cooled to 20° C. and diluted with 20 volumes of water. The several gums vary in their effectiveness and the optimum amount is likewise most conveniently determined by trial. So far, the total weight of gum and dispersing agent required has in no instance amounted to more than 10% of the weight of the hot melt.

The preferred dispersions of the present invention are uncommon in that they are not directly substantive towards cellulosic fibers and cannot be precipitated on the fibers by addition of alum, at least in conventional amounts. They are most conveniently deposited by the action of subsequently-added liquid rosin and alum, the flocculated rosin size appearing to carry the fortified rosin-wax particles to the fibers.

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

Example 1

The following illustrates the preparation of a homogeneous hot melt and an alum- and acid-stable paper sizing dispersion therefrom.

The hot melt was prepared as follows: 170 gm. of fortified gum rosin (prepared by heating gum rosin with 0.25 mol of maleic anhydride at 200° C. for four hours) was melted on a steam bath. To this 170 gm. of molten refined petroleum paraffin wax (M. P. 155° F.) was slowly added with stirring. Two layers formed when stirring was momentarily stopped, showing that the two materials were incompatible, the wax floating as a very light tan layer on the rosin. Molten stearic alcohol was then slowly added with continued stirring. When 10 gm. of stearic alcohol had been added, the solution became homogeneous and did not separate on standing.

The sizing dispersion was prepared by heating 600 gm. of water to 195° F., adding 40 gm. of gum arabic and 10 gm. of sodium lignin sulfonate, and slowly flowing in the hot melt with vigorous agitation. A creamy emulsion resulted which was homogenized at once and rapidly cooled to about room temperature by flowing through a laboratory heat exchanger.

The size gave satisfactorily high lactic acid resistance values when added to paper pulp in the beater and precipitated by addition of rosin size and alum.

Example 2

The procedure of Example 1 was repeated except that 1 gm. each of pentachlorophenol (Dowicide #7) and the sodium salt of pentachlorophenol (Dowicide G) were added as mold-growth inhibitors to the hot water prior to addition of the fortified rosin-wax melt. These materials caused no change in the lactic acid values obtained.

Example 3

Two comparative sizing dispersions were prepared to illustrate the jump in lactic acid resistance which occurs

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when ordinary rosin is replaced with fortified rosin according to the present invention. The hot melts were prepared by the method of Example 2, except that the fortified rosin was prepared by the reaction of gum rosin with only 4% of its weight ($\frac{1}{2}$ mol) of maleic anhydride, and slack wax (M. P. 120° F.) was used in place of the refined paraffin wax. The hot melts were emulsified by the method of Example 1, both emulsions being emulsified hot and rapidly cooled in the same manner. The amount of stearyl alcohol used in size 3-B was about the minimum needed to render the fortified rosin compatible with the wax. The materials used were as follows:

	Size	
	3-A	3-B
Hot melt:	Percent	Percent
Gum rosin.....	24.01	Nil
Fortified gum rosin.....	Nil	24.01
Slack wax.....	24.01	24.01
Stearic alcohol.....	Nil	0.50
Aqueous phase:		
Gum arabic.....	0.50	0.50
Sodium lignin sulfonate.....	1.20	1.20
Dowicide 7.....	0.12	0.12
Dowicide G.....	0.16	0.16
Water.....	50.00	49.50
Total.....	100.00	100.00

The resulting dispersions were diluted to 5% solids with water and applied to paper as follows. A suspension of beaten 60% sulfite-40% soda fibers was diluted to a consistency of 2% with water and 2 aliquots withdrawn. To each aliquot was added first 0.5% of one of the above described sizing dispersions, then 1.5% of liquid gum rosin size, and finally 2% of alum (solids in each instance based on the dry weight of the fibers) the pulps were sheeted on a British handsheet machine, dried at 190° F. for 2 minutes, conditioned for 24 hours at 73° F. and 50% relative humidity, and tested. Results are as follows:

Sizing Dispersion	Thin Sheets			Thick Sheets	
	Sheet Basis Wt. ¹	Resistance to—		Sheet Basis Wt. ¹	Lactic Acid Resist. ⁴ (Sec.)
		Water ² (Sec.)	Ink ³ (Sec.)		
Ex. 3-A.....	46.4	55	310	194.0	190
Ex. 3-B.....	45.9	59	375	193.5	300

¹ Lb. per 25" x 40" 500 ream.

² By Currier test (slack scale).

³ By BKY method.

⁴ By penescope.

The results show that the paper containing fortified gum rosin exhibited a jump in lactic acid resistance of 58%. This increase is wholly ascribable to the fortified rosin content of the size. The data also show very pronounced increases in the water and ink resistance values. The results further show that the stearyl alcohol present had at most only a negligible effect upon the sizing results.

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Example 4

The stability of the sizing dispersion of Example 1 was demonstrated by stirring 10 gm. of the emulsion obtained into 200 cc. of water and adjusting the pH first to 5.0 by addition of hydrochloric acid and then to 8.5 by addition of sodium hydroxide. The dispersion remained stable throughout. A second test showing its alum stability was made by stirring 5 gm. of the emulsion into 100 cc. of water and adding sufficient alum solution to decrease the pH to 4.5. The dispersion also remained stable for a period.

I claim:

1. A homogeneous blend consisting essentially of fortified rosin and wax in weight ratio between about 40:60 and 60:40 and a small but effective amount of a normally solid mono-hydric fatty alcohol having a melting point below 190° F. as coupling agent therefor, said fortified rosin corresponding to that formed by reacting rosin with from about $\frac{1}{2}$ to $\frac{1}{4}$ of a mol of an organic compound of acidic character containing a $-\text{CO}-\text{C}=\text{C}-$ linkage, and said wax having a melting point between 100° and 180° F.

2. A homogeneous blend consisting essentially of fortified rosin and a hydrocarbon wax in weight ratio between 40:60 and 60:40 together with a small but effective amount of a $\text{C}_{16}-\text{C}_{20}$ monohydric fatty alcohol as coupling agent therefor, said rosin corresponding to that formed by reacting 1 mol of rosin with between $\frac{1}{10}$ and $\frac{1}{5}$ mol of maleic anhydride, said wax having a melting point between about 115° F. and 160° F.

3. A blend according to claim 2 wherein the alcohol is stearic alcohol.

4. A method of forming a homogeneous blend from fortified rosin and wax in weight ratio between about 40:60 and 60:40 which consists essentially of stirring said rosin and said wax in molten form with a small but effective amount of a normally solid monohydric fatty alcohol having a melting point below 190° F. as coupling agent therefor, said fortified rosin corresponding to that formed by reacting rosin with from about $\frac{1}{2}$ to $\frac{1}{4}$ of a mol of an organic compound of acidic character containing a $-\text{CO}-\text{C}=\text{C}-$ linkage, and said wax having a melting point between 100 and 180° F.

5. A colloidal aqueous dispersion of a blend according to claim 1 containing from 30% to 60% solids by weight.

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