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3,578,477 PAPER SIZING COMPOSITION COMPRISING A CATIONIC WAX EMULSION, AN ANIONIC ROSIN AND AN ACID AMINE CONTAINING EMULSIFYING AGENT

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ABSTRACT OF THE DISCLOSURE

A paper sizing composition is provided comprising a mixture of an aqueous cationic wax emulsion and an anionic rosin size.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to paper sizing compositions and, in one of its aspects, relates to paper sizing compositions in the form of wax emulsions. More particularly, in this aspect, the invention relates to paper sizing compositions in the form of aqueous wax emulsions and a sizing agent. Still more particularly, in this aspect, the invention relates to paper sizing compositions in the form of aqueous wax emulsions and sizing agents specially adapted for use in improving high strength properties in the manufacture of so-called "fine" papers, such as book paper, writing and typing grade papers and other papers in which a marked degree of permanence is required.

(2) Description of the prior art

Wax emulsions, or wax emulsions in conjunction with rosin size, have heretofore been employed in the beater sizing of papers. In order to precipitate the wax or rosin, or both wax and rosin, on the paper fibers alum has been incorporated in such compositions as a precipitating agent. In such systems the pH range is so low (usually from about pH 4.5 to about pH 5.5) that papers of poor aging quality, and particularly poor strength properties, are produced. While for many uses such deficiency is not of prime significance, nevertheless in the so-called "fine" papers, a high degree of permanence is required and which is not obtainable with the use of such emulsions of the prior art in which both the aqueous wax emulsion employed and also the rosin size, are anionic in character, and in which alum is employed as a precipitating agent.

SUMMARY OF THE INVENTION

In accordance with the present invention improved paper sizing compositions are provided comprising a mixture of an aqueous cationic wax emulsion and an anionic rosin size, and which do not require the presence of a precipitating agent, such as alum, for depositing the wax and the rosin on the paper fibers. Where only moderately successful results have heretofore been obtained in employing a system comprising an anionic wax emulsion, anionic rosin size and alum, the sizing compositions of the present invention, comprising a cationic wax emulsion, employ the anionic rosin for precipitating the wax while maintaining a neutral system and still obtaining a good sizing, and which do not require the additional use of alum as a precipitating agent. The use of these novel sizing compositions is based on the advantage taken of the finding that there is a tendency for anionic and cationic systems to mutually precipitate each other. Both the cationic wax emulsion and the anionic rosin are sizing agents by themselves, and a synergistic effect is found to be obtained when they are employed in combination.

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Thus, no additional precipitating agent such as alum or other precipitants is required, and hence represents a marked improvement over the sizing compositions heretofore employed in paper making.

The cationic wax emulsions, employed in the paper sizing compositions of the present invention, may comprise a wide variety of waxy materials including, for example, petroleum wax, vegetable wax, mineral wax and other forms of waxy materials which can be employed in the form of cationic wax emulsions. The rosin size, as hereinbefore indicated, may comprise any anionic rosin which has been saponified to some degree (either partially or completely) to form a water-soluble soap material, e.g. a water-soluble soap obtained by saponification of abietic acid with an alkali. Thus, illustratively, a fortified rosin size may comprise the product obtained when rosin (unfortified) is reacted with maleic anhydride. Insofar as the rosin component is concerned, it may be employed in any desired amount in combination with the aqueous cationic emulsion, depending upon the nature of the manufactured paper desired. In general, the rosin size is employed, for most practical purposes, in an amount from about 5 to about 50 percent, and preferably in an amount from about 10 to about 35 percent, by weight, of the total weight of the paper sizing composition.

The cationic wax emulsions suitable for use in forming the paper sizing compositions of the present invention, in general comprise a dispersed phase containing the waxy material and a suitable cationic emulsifying agent. If so desired, an emulsion modifier may also be incorporated in the cationic wax emulsion.

In a preferred embodiment the cationic wax emulsion employed for forming the paper sizing compositions of the present invention may comprise (a) a dispersed phase comprising a petroleum wax; (b) an emulsifying agent comprising an amine salt of an acid selected from the group consisting of organic acids having from about 1 to about 18, and preferably from about 1 to about 6 carbon atoms and inorganic mineral acids, with an amine having from about 10 to about 40, and preferably from about 20 to about 40 carbon atoms; and, if so desired, (c) an emulsion modifier comprising an amine having up to 12 carbon atoms and having a molecular weight lower than that of the amine reactant employed for producing the aforementioned emulsifying agent.

The above-described exemplary cationic wax emulsion may be prepared, by reacting an aqueous mixture of the aforementioned amine, having from about 10 to about 40 carbon atoms, with the aforementioned organic acid or inorganic acid to produce the emulsifying agent, which comprises an aqueous solution of the corresponding amine salt; combining the aqueous solution of the amine salt thus produced with the aforementioned emulsion modifier (if its presence is desired) which, as previously described, comprises an amine having up to 12 carbon atoms and a molecular weight which is lower than that of the amine reactant employed for producing the aforementioned emulsifying agent; and dispersing the petroleum wax component in the thus-combined mixture; or by adding the emulsifying agent to the wax component and thereafter combining this mixture with the emulsion modifier. When the aforementioned aqueous cationic wax emulsions are employed as a component of the paper sizing compositions of the present invention, the petroleum wax component can be employed in an amount from about 10 to about 70 percent and preferably from about 40 to about 70 percent, by weight, based on the total weight of the emulsion. The emulsifying agent can be employed in an amount from about 0.5 to about 10, and preferably from about 1 to about 8 percent, by weight, based on the quantity of the petroleum wax component present. The emulsion modifier when so employed, is present in an amount from about 0.05 to about 3, and preferably from about 0.1 to about 2 percent, by weight based on the total quantity of the petroleum wax and emulsifying agent components present.

If the waxy material selected comprises a petroleum wax, such was may be present in various forms including a paraffin wax, scale wax or slack wax, as obtained from petroleum distillation processes, or microcrystalline wax, such as obtained from petroleum residual; also, petroleum waxes modified with various polymers, e.g. polyethylene, or copolymers, e.g. ethylene vinyl acetate copolymers and similar polymeric materials.

In producing the emulsifying agent, in the aforementioned cationic wax emulsions, the amine reactant, as previously described, can contain from about 10 to about 40, and preferably from about 20 to about 40 carbon atoms. In this respect, mono-amines having from about 10 to about 30 carbon atoms, and di-amines having from about 20 to about 40 carbon atoms have been found to be most desirable. Representative examples of the amine reactants that may be employed in producing the emulsifying agents of the novel wax emulsions, include propylene diamines, such as N-arachidyl-behenyl 1,3 propylene diamine, N-dodecyl amine, N-hexadecylamine, N-octadecylamine, N-eicosylamine, N-dodecyl 1,3 propylene diamine, N-hexadecyl 1,3 propylene diamine, alkyl trimethyl ammonium chlorides and dialkyl dimethyl ammonium chlorides having alkyl carbon chain lengths of 10 to 40 carbon atoms.

The organic acid employed for reaction with the aforementioned amine reactant, as previously described, may comprise any organic acid having from about 1 to about 18 carbon atoms. Representative examples of these acids include formic acid, acetic acid, propionic acid and butyric acid. Representative inorganic mineral acids employed for reaction with the amine reactant include hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, and similar inorganic acids. It should be noted that the organic or inorganic mineral acid is employed in an amount sufficient only to react with all of the amine employed for preparing the emulsifying agent.

The emulsion modifier of this wax emulsion, as previously stated, comprises an amine having up to 12 carbon atoms, but a molecular weight which is lower than that of the amine reactant employed for producing the above-described emulsifying agent. Thus, these modifiers may comprise any low-molecular weight amine having up to 12 carbon atoms, and can thus comprise aliphatic, cycloaliphatic, aromatic and primary, secondary or tertiary amines. Representative amines employed as the emulsion modifier, include dicyclohexylamine, n-heptyl B-amine, n-octyl amine, n-dodecylamine, n-dodecyl 1,3-propylene diamine, aniline, and N-dodecyl 1,3 propylene B-diamine. Particular emphasis, with respect to the efficacy of the wax emulsions of the present invention, is placed upon the emulsion modifier for the reason that this modifier lowers the viscosity and improves the shear stability of the emulsion. The use of this modifier alone, however, without the emulsifying agent, has been found not to result in the above-described advantages. The wax emulsions employed in accordance with the present invention, as previously indicated, are cationic in character. In essence, these emulsions contain an ion with a positive charge present after the amine has reacted with the acid to produce the emulsifying agent.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The following examples and comparative data will serve to illustrate the novel compositions of the present invention and their efficacy when employed for paper sizing. In accordance with these examples and the test data obtained, the preparation of paper handsheets and the testing of these handsheets for water absorption are carried out in accordance with the following procedures.

Preparation of paper handsheets

Bleached kraft pulp is beaten in a laboratory beater to a freeness of 20 (Schopper-Riegler scale). Portions of pulp suspension representing 2 grams of dry pulp are transferred to a beaker at about 0.5% pulp consistency, the sizing agents are added by pipette, and after stirring for 6 minutes, the sheets are formed on a sheet mold according to TAPPI Method T-205. The sheets are pressed between blotters at 50 p.s.i. pressure, dried on a hot plate at 230° F. for 10 minutes, and conditioned at 73° F. and 50 percent relative humidity for 24 hours before testing for water absorption.

Testing handsheets for water absorption

The water absorption test is carried out by the Cobb test procedure, TAPPI Method T-441. The dry, conditioned sheet is weighed to the nearest .01 gram, and placed in the specimen holder. Water is added to one side of the sheet to a depth of 1 cm. After a contact time of 1 minute the excess water is quickly removed, and the sheet is reweighed. The amount of water absorbed is multiplied by a factor (depending on specimen area), so that the results are expressed in grams per square meter of paper surface.

The cationic and anionic wax emulsions employed for comparative tests in accordance with the examples and corresponding data disclosed, have the following composition:

	Percent (wt.)
Emulsion A (anionic):	
Paraffin wax (128° AMP)	47.5
Vegetable gum	1.0
Emulsifier—	
Lignin sulfonate	1.0
Condensed naphthalene sulfonate	1.0
Water	49.5
	100.0
Emulsion B (cationic):	
Paraffin wax (128° AMP)	63.2
Emulsifier—	
Propylenediamine	1.5
Dicyclohexylamine	0.3
Acetic acid	0.3
Water	34.7
	100.0

The rosin size, employed in the following examples, comprises the product obtained in which unfortified rosin is reacted with maleic anhydride.

Sizing composition (based on total weight of pulp)	Weight percent	Water absorption (grams/m.[2])
Example 1:		
Rosin	1.0	(1)
Anionic wax emulsion (emulsion A)	1.0	
Example 2:		
Rosin	0.5	(1)
Anionic wax emulsion (emulsion A)	1.5	
Example 3:		
Rosin	1.5	(1)
Anionic wax emulsion (emulsion A)	0.5	(1)
Example 4:		
Rosin	2.0	16.2
Anionic wax emulsion (emulsion A)	0.5	
Alum	2.0	
Example 5:		
Rosin	1.5	15.4
Anionic wax emulsion (emulsion A)	0.5	
Alum	2.0	
Example 6:		
Rosin	0.5	14.1
Cationic wax emulsion (emulsion B)	1.5	
Example 7:		
Rosin	1.0	29.1
Cationic wax emulsion (emulsion B)	1.0	
Example 8:		
Rosin	1.5	(2)
Cationic wax emulsion (emulsion B)	1.0	

[1] Sheet completely penetrated because of absence of alum.

[2] Sheet completely penetrated because of inverse ratio of rosin and wax emulsion.

As will be noted from the foregoing Examples 1, 2 and 3, where the sizing composition comprises a rosin-anionic wax emulsion, with no alum being present, the degree of water absorption is so great that the sheet becomes completely penetrated. On the other hand, where alum is also present as a component of the sizing composition (as employed by the prior art and as shown in Examples 4 and 5), the degree of water absorption is reduced to a satisfactory level, rendering the sizing composition satisfactory for many applications.

On a comparative basis, it will be noted from Example 6 that where alum is eliminated from the sizing composition and cationic wax emulsion is substituted for anionic wax emulsion (thus providing a neutral system), a satisfactory level of water absorption is obtained; similarly, as shown by Example 7, where the rosin is employed in accordance with the aforementioned maximum of 50% by weight, a still satisfactory sizing composition is obtained and is useful for many applications. On the other hand, as shown by Example 8, where the ratio of rosin and cationic wax emulsion is inverted (i.e. more than 50% by weight of rosin is employed) the sheet becomes completely penetrated and thus is unsatisfactory for practical applications.

I claim:

1. A paper sizing composition comprising a mixture of an aqueous cationic wax emulsion and not more than about 50 percent, by weight, of an anionic rosin size which has been saponified to form a water-soluble soap, wherein said aqueous cationic wax emulsion comprises (a) a dispersed phase comprising a petroleum wax; and (b) emulsifying agent comprising a salt of an acid, selected from the group consisting of organic acids having from about 1 to about 18 carbon atoms and inorganic mineral acids, reacted with an amine having from about 10 to about 40 carbon atoms (c) an emulsion modifier comprising an amine having up to 12 carbon atoms and a molecular weight lower than that of the amine reactant employed for producing the aforementioned emulsion agent.

2. The composition of claim **1** wherein said rosin size comprises a water-soluble rosin soap obtained by saponification of abietic acid with an alkali.

3. The composition of claim **1** wherein said rosin size is present in an amount from about 5 to about 50 percent, by weight.

4. The composition of claim **1** wherein said rosin size is present in an amount from about 10 to about 35 percent, by weight.

5. The composition of claim **1** wherein the acid for producing the emulsifying agent is employed in an amount sufficient only to react with all of said first-mentioned amine.

6. The composition of claim **1** wherein said petroleum wax comprises a paraffin wax.

7. The composition of claim **1** wherein said petroleum wax comprises a microcrystalline wax.

8. The composition of claim **1** wherein said organic acid reactant employed for producing the emulsifying agent contains from about 1 to about 6 carbon atoms.

9. The composition of claim **1** wherein said organic acid employed for producing the emulsifying agent is acetic acid.

10. The composition of claim **1** wherein said inorganic acid employed for producing the emulsifying agent is hydrochloric acid.

11. The composition of claim **1** wherein said amine reactant employed for producing the emulsifying agent contains from about 20 to about 40 carbon atoms.

12. The composition of claim **1** wherein said amine reactant employed for producing the emulsifying agent is propylene diamine.

13. The composition of claim **1** wherein said amine reactant employed for producing the emulsifying agent is N-arachidyl-behenyl 1,3 propylene diamine.

14. The composition of claim **1** wherein said amine employed as the emulsion modifier is dicyclohexylamine.

15. The composition of claim **1** wherein said aqueous cationic wax emulsion comprises petroleum wax in an amount from about 10 to about 70 percent, by weight, based on the total weight of the emulsion; from about 0.5 to about 10 percent by weight of the emulsifying agent based on the quantity of the petroleum wax component present; and from about 0.05 to about 3 perccent by weight of the emulsion modifier based on the total quantity of the petroleum wax and emulsifying agent components present.

16. The composition of claim **1** wherein said aqueous cationic wax emulsion comprises petroleum wax in an amount from about 40 to about 70 percent, by weight, based on the total weight of the emulsion; from about 1 to about 8 percent by weight of the emulsifying agent based on the quantity of the petroleum wax component present; and from about 0.1 to about 2 percent by weight of the emulsion modifier based on the total quantity of the petroleum wax and emulsifying agent components present.

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