



US 20090095431A1

(19) **United States**(12) **Patent Application Publication**
Fallmann et al.(10) **Pub. No.: US 2009/0095431 A1**(43) **Pub. Date: Apr. 16, 2009**(54) **PAPER-SIZING EMULSION, PROCESS FOR
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(2), (4) Date: **Sep. 24, 2008**(30) **Foreign Application Priority Data**

Dec. 23, 2005 (AT) A2065/2005

Publication Classification(51) **Int. Cl.**
D21H 21/16 (2006.01)(52) **U.S. Cl.** **162/179; 106/287.24; 106/287.17**(57) **ABSTRACT**

Aqueous paper-sizing emulsions for bulk and surface sizing with a content of fatty acid anhydrides are described in which the fatty acid anhydrides are derived from unsaturated or saturated fatty acids or their mixtures with chain lengths of C₁₂-C₂₄ and are liquid under 50° C. The paper sizing emulsions additionally may contain another reactive or non-reactive sizing agent and/or a fixing agent containing aluminum ions. The new emulsions are suitable for the finishing of paper and cardboard.

PAPER-SIZING EMULSION, PROCESS FOR PREPARING IT AND USE THEREOF

[0001] The present invention relates to new aqueous emulsions for paper sizing, using fatty acid anhydrides (FAA).

[0002] The use of fatty acid anhydrides as sizing agents for paper has long been known, cf. U.S. Pat. No. 1,996,707. Thus, Patent DE 1 213 221 describes the preparation of dispersions of fatty acid anhydrides for paper sizing. The fatty acid anhydrides are then emulsified above their melting point in cationic starch in the presence of anionic agents. The method suppresses formation of anhydride aggregates, which could lead to precipitation in the dispersion. Stearic anhydride is mentioned as example, which is present as solid particles at room temperature, and therefore less exposed to hydrolysis. Nevertheless, rapid hydrolysis must be taken into account due to the high reactivity of anhydrides.

[0003] U.S. Pat. No. 3,409,500 describes a method for sizing with fatty acid anhydrides, together with a water-soluble cellulose-substantive cationic polyamine. Here too, the form of anhydride used consists of a solid-in-liquid dispersion, which is formed by rapid cooling of an emulsion. Stearic anhydride is mentioned as fatty acid anhydride. Storage stability is only conditionally present in this production method as well. This limitation is also decisive, in that fatty acid anhydrides, in addition to the more stable, but also less reactive alkyl ketene dimers (AKD), are not claimed in the application as sizing agents.

[0004] The use of resin acid anhydrides as sizing agents is described in U.S. Pat. No. 3,582,464. The dispersions, which, similar to the above described fatty acid anhydride dispersions, are formed as an emulsion at elevated temperatures and stabilized by cooling, also exhibit the drawback of continuing hydrolysis, which restricts the activity of the product.

[0005] Alkenylsuccinic anhydrides (ASA) are also very efficient sizing agents. Their high reactivity prevents transport as a ready-to-use emulsion. However, because of their liquid state of aggregation, ASA can be directly emulsified and used at the machine. This makes the use of a homogenizer necessary on site, but has the advantage that, in addition to high efficiency, the active substance is transported pure and emulsifiers, stabilizers or biosides for protection of dispersions can be eliminated. By hydrolysis and when calcium carbonate is used as filler, deposits can form from ASA, which can interfere with system cleanness by their adhesiveness.

[0006] It has now been found that the use of liquid fatty acid anhydrides (FAA) produces very effective sizing systems. Because of the liquid state of aggregation, the FAA can be emulsified right before use on the paper machine. Contact time with the aqueous system can thereby be minimized and undesired hydrolysis suppressed. The FAA can be added directly to the aqueous phase and emulsified via an appropriate homogenizer, as used in the ASA metering systems. Emulsifiers can be used, but are not absolutely necessary. An aqueous phase containing starch during emulsion formation has a positive effect on cellulose substantivity.

[0007] The following can be used as liquid fatty acid anhydrides: anhydrides of unsaturated and saturated fatty acids or their mixtures with chain lengths of C_{12} - C_{24} ; mixed anhydrides from these fatty acids or fatty acid mixtures and acetic acid; anhydrides produced from mixtures of the mentioned fatty acids and resin acids.

[0008] The invention is not restricted to the origin of the employed fatty acids. Possible raw material sources are: tall oil fatty acids, plant fatty acids from sunflower oil, rapeseed oil, soybean oil, linseed oil, animal oil. Resin acids may consist, for example, of balsam resin, tall resin, wood rosin or mixtures thereof.

[0009] The invention is also not restricted to a specific preparation of the fatty acid anhydrides. A simple and known method is conversion of fatty acids with acetic anhydride with subsequent elimination of acetic acid. The acetic acid can be worked up again into anhydride and circulated.

[0010] Liquid FAA can be used together with another sizing system. Because of the liquid form, the FAA is miscible in any ratio with ASA. A synergistic effect can be observed in the sizing effect by the use of combinations of ASA and FAA. Adjustment of the desired end product properties can therefore be produced via a mixing ratio.

[0011] Aluminum salts have an unexpectedly positive effect on the sizing effect of FAA. These include, inter alia, aluminum sulfates or polyaluminum chloride (PAC).

[0012] FAA are compatible with calcium-loaded water systems. At the usual pH values in paper-making, no buildup of deposits of a tacky consistency occurs, as is known of ASA under certain circumstances.

[0013] The sizing system of the invention is based on raw materials that are present in the original paper raw material, the wood. The sizing agent therefore once again assumes this task in modified form, a task is inherent to it for achieving the original plant properties.

[0014] The following examples will further explain the invention.

EXAMPLE 1

Preparation of Fatty Acid Anhydrides

[0015] In a typical experiment, tall oil fatty acid and acetic anhydride are added in equimolar amounts to the reactor and converted at 120° C. After 5 hours, the formed acetic acid is withdrawn under vacuum, in which a temperature of 150° C. is not exceeded. Yield of fatty acid anhydride: 91.6%.

EXAMPLE 2

Testing of Anhydride Sizes for Their Sizing Effect

[0016] To test the size, a laboratory sheet former, the Rapid Köthen System, was used. The employed pulp was a bleached kraft pulp with a 70% long fiber and 30% short fiber percentage, ground to a Schopper-Riegler angle of 30°.

[0017] Aluminum sulfate was added as fixing agent. The optimal amount of aluminum sulfate was determined beforehand by recording a concentration curve for each sizing agent. In the experiments with the filler calcium carbonate, 20% of it was used, with reference to dry paper.

[0018] 1 part anhydride size was added to 99 parts of a 4% cationic starch solution, and the emulsion emulsified with a shear device (Ultraturrax) at 10,000 rpm for one minute. The resulting size emulsions were stable for about 2 hours. Before sizing, it was diluted with water 1:10.

[0019] As a comparison, a traditional cationic resin size dispersion based on tall oil resin acid was used. Addition to the paper stock occurred as dilute commercial product.

[0020] The Cobb 60 value describes water absorption in g/m² in 60 seconds.

Size 1: Anhydride from 100% tall oil fatty acid

Size 2: Anhydride from 50% tall oil fatty acid and 50% tall oil resin

Size 3: Usual cationic resin dispersion for paper sizing

Size 4: Solid anhydride from tall oil resin according to U.S. Pat. No. 3,582,464.

[0021] The active content of the sizing agent is stated with the amount of size. The amounts relate to t of dry paper.

Size	Amount of size	Al sulfate	Chalk	Cobb 60
1	0.9 kg/t	1 kg/t	no	32
2	0.9 kg/t	1 kg/t	no	33
3	1.0 kg/t	2.3 kg/t	no	38
1	1.3 kg/t	5.5 kg/t	yes	38
2	1.3 kg/t	5.5 kg/t	yes	42
3	4.6 kg/t	13.6 kg/t	yes	80
3	6.4 kg/t	13.6 kg/t	yes	38

EXAMPLE 3

Use of FAA Together with ASA

[0022] Size 2, prepared from tall oil fatty acid and tall oil resin, was mixed with C18-ASA in different concentrations and tested for sizing effect, as described in example 2.

ASA	Size 2	Al sulfate	Cobb 60
0.7 kg/t	0	3 kg/t	28
0.47 kg/t	0.23 kg/t	3 kg/t	26
0.23 kg/t	0.47 kg/t	3 kg/t	27
0 kg/t	0.7 kg/t	3 kg/t	54
0.35 kg/t	0 kg/t	3 kg/t	91

[0023] A synergistic effect can be observed when mixtures of FAA together with ASA are used.

EXAMPLE 4

Influence of Mixed Anhydrides Together with ASA

[0024] Anhydride sizes, prepared from mixtures of tall oil fatty acid and tall oil resin, were mixed with C18-ASA 1:1 and tested for sizing effect as described in example 2. The aluminum sulfate amounts were optimized here too relative to the sizing agent. The contents pertain to anhydride size compositions.

Size	Percentage of fatty acid	Percentage of resin acid	Cobb 60
1	100%	0%	32
2	50%	50%	34
4	0%	100%*	83

*Resin acid anhydride as described in U.S. Pat. No. 3,582,464.

EXAMPLE 5

Anhydride Sizes in Combination with Aluminum Salts

[0025] Size 2 was used with different aluminum salts, as in example 2.

Size	Amount of size	Al salt	Amount Al salt	Cobb 60
1	0.9 kg/t	—	—	47
1	0.9 kg/t	Al sulfate	0.07%	30
1	0.9 kg/t	PAC	0.07%	29
1	1.2 kg/t	—	—	30
2	0.7 kg/t	—	—	54
2	0.7 kg/t	Al sulfate	0.07%	29
2	0.7 kg/t	PAC	0.08%	29
2	1.2 kg/t	—	—	30

1. Paper-sizing emulsion with a content of fatty acid anhydrides, characterized by the fact that the fatty acid anhydrides are derived from unsaturated or saturated fatty acids or their mixtures with chain lengths of C₁₂-C₂₄ and are liquid under 50° C.

2. Paper-sizing emulsion according to claim 1, characterized by the fact that the fatty acid anhydrides are present as mixed anhydrides from the mentioned fatty acids or fatty acid mixtures and acetic acid.

3. Paper-sizing emulsion according to claim 1, characterized by the fact that the fatty acid anhydrides are formed from mixtures of the mentioned fatty acids and resin acids.

4. Paper-sizing emulsion according to one of the claims 1 to 3, characterized by the fact that the fatty acids originate from tall oil, sunflower oil, rapeseed oil, soybean oil, linseed oil or animal oil.

5. Paper-sizing emulsion according to claim 3 or 4, characterized by the fact that the resin acids originate from balsam resin, tall oil resin, wood rosin or their mixtures.

6. Paper-sizing emulsion according to one of the claims 1 to 5, characterized by the fact that it additionally contains at least one other reactive sizing agent or non-reacting sizing agent.

7. Paper-sizing emulsion according to one of the claims 1 to 6, characterized by the fact that it additionally contains aluminum salts, like aluminum sulfate or polyaluminum chloride.

8. Method for production of a paper-sizing emulsion, characterized by the fact that the fatty acid anhydrides, according to claim 1 to 7, are emulsified in an aqueous phase by shear forces or vigorous agitation.

9. Method according to claim 8, characterized by the fact that emulsifiers are used for emulsion formation.

10. Use of the paper-sizing emulsion prepared according to the method of claim 8 or 9 for direct, continuous sizing of paper stock.

11. Use of the paper-sizing emulsion prepared according to the method of claim 8 or 9 for surface treatment of paper in the sizing press.

12. Paper produced using the paper-sizing emulsion according to claims 1 to 7.

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