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(71) Applicant *(for all designated States except US)*: **KEMIRA KEMI AB** [SE/SE]; Box 902, S-251 09 Helsingborg (SE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **BISBAL TUDELA, Josep, Lluis** [ES/ES]; Ps. Torre Blanca 16, 4-1, E-08190 Sant Cugat Del Vallés (ES). **GYTEL, Ulla** [SE/SE]; Villa Linnéa, Ramlösa Brunnspark, S-256 54 Helsingborg (SE).

(74) Agent: **AWAPATENT AB**; Box 5117, S-200 71 Malmö (SE).

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(54) Title: SIZING COMPOSITION

(57) Abstract: A sizing composition and a method of sizing a cellulosic fibre material, such as paper, board or paper board, are described. The sizing composition comprises an aqueous dispersion of a rosin material and is characterised in that it also contains (a) 0.05-20 % by weight, based on the dry weight of the composition of a dicarboxylic acid derivative with the general formula (I): $R_1OOC\text{-}Q\text{-}COOR_2$; where R_1 and R_2 which are the same or different represent H, M, where M is a metal of Groups IA or IIA, or a straight or branched alkyl or alkenyl group having 1-30 carbon atoms; Q represents (i) R_3 which is a straight alkylene group or alkenylene group of the formula: $-C_nH_{2n-2z}-$, where n = 0-12 and z = 0-3; (ii) Formula (II), where R_3 is as defined above and R_4 is a straight or branched alkyl or alkenyl group having 1-30 carbon atoms; with the proviso that the compound of formula (I) includes at least 6 and at most 34 carbon atoms in total; and (b) an aluminium compound which is selected from the group consisting of: aluminium sulphate; aluminium polymers of the general formula (III): $[Al(OH)_x(A)_{(3-x)}]_n$; aluminium polymers of the general formula (IV): $[Al(OH)_x(H_3PO_4)_y\ (A)_{(3-x)}]_n$; where A = Cl^-, NO_3^-, $HCOO^-$, CH_3COO^-; aluminium polymers of the general formula (V): $[Al(OH)_x(SO_4)_{(3-x)/2}]_n$; aluminium polymers of the general formula (VI): $[Al(OH)_x(H_3PO_4)_y\ (SO_4)_{(3-x)/2}]_n$; where "x" is in the range 0.03 to 2.7, "y" in the range 0.01 to 0.8 and n ≥ 2; and mixtures of these. According to the method the sizing composition is added to a cellulosic fibre material in an amount of 0.01-10 % by weight, calculated as dry sizing agent on dry cellulosic fibres.

$$-R_3-R_4 \qquad \text{(II)}$$

SIZING COMPOSITION

Field of Invention

The present invention relates to a sizing composition comprising an aqueous dispersion of a rosin material as well as to a method of sizing a cellulosic fibre material, such as paper, board or paper board.

Background Art

One of the main properties of paper, board, paperboard and similar products is hydrophobation or resistance to penetration by water and other liquids, such as lactic acid, hydrogen peroxides solutions, etc. Hydrophobation also plays an important role in the ink jet properties of the paper, affecting the way inks are absorbed in the paper. The two main methods for conferring hydrophobic properties to paper products are internal sizing, which gives a hydrophobic effect in the entire paper structure, surface sizing, which is more or less limited to the actual surface structure, and a combination of both methods. The most common hydrophobic agents in internal sizing are rosin, synthetic sizing agents, such as alkyl ketene dimers, isocyanates, acid anhydrides and carbamoyl chlorides and combinations of both components.

It has recently been discovered, however, that dispersions of such sizing agents can exhibit stability problems, the practical consequences of which are a marked increase in the viscosity, agglomeration and phase separation which lead to depositions, difficulty in dosing and a loss of sizing efficiency. Moreover, deficient ink jet properties, i.e. drying time, colour appearance, wicking, colour-to-colour bleed, etc, may imply serious problems for the final user.

It has been shown that internal sizing with a cationic rosin size (CRS), such as those disclosed in ES-8900750, GB-2,159,153, EP-A-0 200 002, US-A-3,966,654 and US-A-4,199,369, or with a conventional anionic rosin

size (emulsion, paste or soap) gives the finished paper good resistance to penetration by water but it also has some drawbacks, such as some limitations in pH and temperature, the difficulty of giving the paper a good resistance to penetration by acid liquids or the need to be used in comparatively large amounts to give a satisfactory sizing effect. On the other hand, rosin dispersions are widely used and cannot in all circumstances be replaced by synthetic sizing agents; rosin dispersions give, for example, a good adhesion to yankee cylinders.

Synthetic sizing agents react with the cellulose to give an irreversible bond. Although these sizing agents generally lead to a very good sizing effect, both to water and other liquids, they do also have some disadvantages. For example, sizing must be carried out at neutral or slightly alkaline pH values (between 7 and 8.5) to be effective, there is a risk of hydrolysis in water and synthetic sizing agents cannot give the finished paper a good resistance to penetration by hot peroxides. Moreover, although synthetic sizing agents give good ink holdout and brighter colours, some other ink jet properties are relatively poor.

It is known to combine rosin and some synthetic sizing agents to obtain a more widely useful sizing agent, which makes it possible to overcome some of the above-mentioned disadvantages when they are used alone. For example, EP-A-0 074 544 discloses a method of sizing using cationic dispersions which contain as the dispersed phase particles of fortified rosin as well as particles of a synthetic sizing agent. EP-A-0 275 851 discloses a method of sizing utilising the above cationic and anionic dispersions which further contain a polyaluminium compound. EP-A-0 693 589 discloses a method of sizing paper and similar cellulose products containing precipitated calcium carbonate as a filler using the above dispersions. In WO 96/35841 a water-soluble inorganic alkali metal salt is added to improve the stability

of cationic dispersions of sizing agents based on rosin and cellulose reactive material. US-A-4,522,686 discloses a sizing composition in the form of an aqueous dispersion containing a cellulose-reactive sizing agent, fortified rosin and a water-soluble, nitrogen-containing dispersing agent, the last two components forming the elements of a CRS. EP-A-0 292 975 discloses a method for use in producing liquid packaging board. However, in the above publications there is no suggestion that there is a particular problem caused by a poor stability of the sizing dispersion or deficient ink jet properties.

US-A-4,919,725 relates to a sizing composition comprising an active sizing agent and a dispersant therefor. The active sizing agent may be an alkyl or alkenyl succinic anhydride prepared by reacting olefins having from 6 to 22 carbon atoms with maleic anhydride. Other active sizes include ketene dimers. The dispersant comprises a polyalkoxylate of a rosin or fortified rosin. The rosin derivative does not usually exhibit sizing properties, i.e. it is only used as a dispersant. Further, the composition does not include any aluminium compound.

US-A-5,639,812 relates to an alkenylsuccinic acid (ASA) emulsion sizing agent. The sizing agent comprises the ASA in a major amount of 50-100 parts by weight and may further comprise 0-50 parts by weight of one or more other components such as rosin or rosin derivatives. No aluminium compound is included in the sizing agent.

US-A-5,219,912 relates to an emulsified alkenylsuccinic acid (ASA) sizing agent comprising the ASA as a sizing agent in a high amount of not less than 25 parts by weight, such as 25-95 parts by weight. The sizing agent composition further comprises a hydrocarbon resin having no acid group and an anionic polymer dispersant. The composition may also include a component such as a rosin or a rosin derivative in a minor amount of, such as 5-50 parts by weight of rosin and 95-50 parts by weight

of ASA. The composition does not include any aluminium compound.

WPI/Derwent accession no. 1980-77008c (JP 1979-0038419) relates to a process for the preparation of a rosin sizing agent from an emulsion of a non-water-soluble organic solvent. The addition of a water-soluble alkenyl succinic acid salt to the emulsion facilitates the removal of the organic solvent by distillation. No inclusion of an aluminium compound is disclosed.

Summary of the Invention

It is an object of the present invention to provide a sizing composition and a method of sizing a cellulosic fibre material that reduce or eliminate the above problems associated with the prior art. This is achieved by including a specific dicarboxylic acid derivative, preferably a succinic acid derivative, and an aluminium compound in the sizing composition indicated above. Preferably also a synthetic sizing agent is included in the sizing composition.

According to one aspect, the present invention thus provides a sizing composition comprising an aqueous dispersion of a rosin material, characterised in that it also contains

(a) 0.05-20 % by weight, based on the dry weight of the composition of a dicarboxylic acid derivative with the general formula (I)

$$R_1OOC\text{-}Q\text{-}COOR_2 \qquad (I)$$

where

R_1 and R_2 which are the same or different represent H, M, where M is a metal of Groups IA or IIA, or a straight or branched alkyl or alkenyl group having 1-30 carbon atoms;

Q represents

(i) R_3 which is a straight alkylene group or alkenylene group of the formula $-C_nH_{2n-2z}-$, where n = 0-12 and z = 0-3;

(ii) $-R_3-R_4$, where R_3 is as defined above and R_4 is

a straight or branched alkyl or alkenyl group having 1-30 carbon atoms;

with the proviso that the compound of formula (I) includes at least 6 and at most 34 carbon atoms in total; and

(b) an aluminium compound which is selected from the group consisting of:

aluminium sulphate;

aluminium polymers of the general formula (III)

$$[\ Al\ (OH)_x(A)_{(3-x)}\ ]_n \qquad (III);$$

aluminium polymers of the general formula (IV)

$$[\ Al\ (OH)_x(H_3PO_4)_y\ (A)_{(3-x)}\ ]_n \qquad (IV)$$

where A = Cl^-, NO_3^-, $HCOO^-$, CH_3COO^- ;

aluminium polymers of the general formula (V)

$$[Al(OH)_x(SO_4)_{(3-x)/2}]_n \qquad (V);$$

aluminium polymers of the general formula (VI)

$$[\ Al\ (OH)_x(H_3PO_4)_y\ (SO_4)_{(3-x)/2}\ ]_n \qquad (VI)$$

where "x" is in the range 0.03 to 2.7, "y" in the range 0.01 to 0.8 and $n \geq 2$; and mixtures of these.

According to another aspect, the present invention provides a method of sizing a cellulosic fibre material, such as paper, board or paper board, characterised in that the above sizing composition is added to the cellulosic fibre material in an amount of 0.01-10 % by weight, calculated as dry sizing agent on dry cellulosic fibres.

These and other advantages and characterising features of the present invention will appear from the following specification and the appended claims.

Detailed Description of the Invention

From the above definition of the dicarboxylic acid derivative with the general formula (I) according to the invention, it is evident that it includes dicarboxylic acids as well as the salts of metals of Groups IA or IIA, i.e. the alkaline metal or alkaline earth metal salts thereof, or alkyl or alkenyl carboxylates thereof. The dicarboxylic acid derivative may contain unsaturation.

As examples of dicarboxylic acids encompassed by the present invention, mention can be made of oxalic acid (n = 0 in formula (I)), malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, azelaic acid and sebacic acid (n = 8 in formula (I)). Of these various acids succinic acid (i.e. n = 2 in formula (I)) is a particularly preferred dicarboxylic acid in the present invention.

As defined above, R_1 and R_2 may represent M, where M is a metal of Groups IA or IIA, i.e. an alkali metal or alkaline earth metal. It is preferred that M is an alkali metal, particularly Na or K.

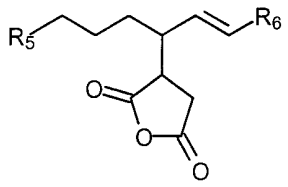
When R_1 and/or R_2 in formula (I) represents a straight or branched alkyl or alkenyl group, this group has 1-30 carbon atoms, preferably 1-6 carbon atoms. Also, preferably the group is a saturated, straight alkyl group.

In formula (I) above it is preferred that the dicarboxylic acid derivative includes a pending hydrocarbon group on the dicarboxylic acid main chain, i.e. that Q in formula (I) represents (ii) as defined above. The pending hydrocarbon group (R_4) is a straight or branched alkyl or alkenyl group having 1-30 carbon atoms, preferably 12-18 carbon atoms. It is particularly preferred that the pending hydrocarbon group R_4 is iso-octadecenyl.

When the dicarboxylic acid derivative according to the present invention includes unsaturation, this unsaturation may be in α position or in other positions. With regard to the alkyl and alkenyl groups mentioned, such as R_1 and R_2, these may comprise blends of isomeric alkylene or alkenyl groups, respectively, with different chain lengths, such as C_{16}-C_{18} groups.

Although the present invention encompasses several different dicarboxylic acids as explained above, for the sake of simplicity it will be illustrated and explained below with reference to succinic acid without being restricted thereto.

The alkyl or alkenyl dicarboxylic acids of the present invention are preferably obtained in a conventional manner by hydrolysis of the corresponding acid anhydrides, namely, by the reaction of such acid anhydrides with water. The corresponding alkyl or alkenyl dicarboxylates are obtained by saponification or estherification of the corresponding acids or acid anhydrides with a base, usually sodium hydroxide, potassium hydroxide or an alcohol. The acid anhydrides mainly used are alkenyl dicarboxylic acid anhydrides, such as alkenyl succinic anhydrides (ASA, formula (II)) and particularly iso-octadecenyl succinic anhydride.



(II)

where R_5 and R_6 are hydrocarbon groups having up to 24 carbon atoms.

Although the number of carbon atoms of each of R_1 to R_4 in formula (I) above may vary within wide limits, it is a requirement of the invention that the total number of carbon atoms of the dicarboxylic acid derivative of formula (I) be at least 6 and at most 34. This requirement

is based on the proviso that the dicarboxylic acid derivative of formula (I) should be water soluble.

It has been found that incorporation of the dicarboxylic acid derivatives of formula (I) in the sizing composition of the invention strongly increases the stability and the sizing efficiency thereof. Such dispersions have a low tendency to agglomerate and separate on storage.

In the sizing composition of the present invention the dicarboxylic acid derivative of formula (I) is present an amount efficient to enhance the stability and the sizing efficiency of the composition. The amount of the dicarboxylic acid derivative is at least 0.05 % by weight and up to 20 % by weight, preferably 0.05-10% by weight, more preferably between 0.5 and 3 % by weight, based on the total dry weight of the sizing composition.

Moreover, the dispersions of the invention allow work within a broad pH range (between 5 and 8). These surprising effects are even more unexpected since it was found that the use of a synthetic sizing agent, such as AKD, rosin size and alum or, alternatively, the use of combinations of rosin and synthetic sizing agents, such as those described in the above-mentioned patents, did not give the same sizing effects.

The sizing composition is added to the cellulosic fibre material in an amount of 0.01-10% by weight, calculated as dry sizing agent on dry cellulosic fibres.

As indicated above, the sizing dispersion of the present invention, besides the above-mentioned rosin material and dicarboxylic acid derivative, also comprises an aluminium compound.

The aluminium compound is chosen from a group consisting of:

aluminium sulphate;

aluminium polymers of the general formula (III)

$$[\ Al\ (OH)_x(A)_{(3-x)}\ ]_n \qquad (III);$$

aluminium polymers of the general formula (IV)

$$[\ Al\ (OH)_x(H_3PO_4)_y\ (A)_{(3-x)}\ ]_n \qquad (IV)$$

where A = Cl^-, NO_3^-, $HCOO^-$, CH_3COO^- ;

aluminium polymers of the general formula (V)

$$[Al(OH)_x(SO_4)_{(3-x)/2}]_n \qquad (V);$$

aluminium polymers of the general formula (VI)

$$[\ Al\ (OH)_x(H_3PO_4)_y\ (SO_4)_{(3-x)/2}\ ]_n \qquad (VI)$$

where "x" is in the range 0.03 to 2.7, "y" in the range 0.01 to 0.8 and $n \geq 2$; and mixtures of these compounds. Preferably, "x" lies in the range of 0.2-2.2 and "y" in the range of 0.02-0.3. Depending on the type of aluminium polymer the value of "n" may vary widely so that in some cases it lies in the range of 2-3, whereas in other cases it may be up to about 500.

In addition to the phosphate ions, polyaluminium compounds described in formulae (IV) and (VI) also include hydroxide, chloride, nitrate, formate, acetate and sulphate ions as counter ions.

The presence of phosphate in the above formulae (IV) and (VI) is shown as phosphoric acid even if in strongly basic or in diluted polyaluminium phosphate salt solutions some of the phosphate may be present as $H_2PO_4^-$. The factors "x" and "y" in the formulae hold irrespectively of in which form the phosphate is present.

Depending on the method used when producing the polyaluminium phosphate compound, it may also contain a neutral salt such as Na^+, K^+, NH_4^+, Ca^{2+} or Mg^{2+} sulphate, chloride, nitrate, acetate or formate. The polyaluminium phosphate compound of the present invention can be prepared by the addition of aluminium metal to the corre-

sponding aluminium salt, refluxing the mixture and finally adding phosporic acid to the mixture.

The number of aluminium atoms in the polymers of general formulae (III)-(VI) depends, among other factors, on the concentration and the pH. The molar ratio of aluminium to counter ion, with the exception of hydroxide ions, should be at least 0.34:1,preferably at least 0,50:1, and more preferably at least 0.65:1. They differ substantially from the ones described, for example, in WO 94/01619 and EP-A-0 062 015, especially polyaluminium sulphates, which are not stable enough, as well as the corresponding sizing dispersions.

In the sizing composition of the invention, the aluminium component is preferably present in an amount of at least 5 per cent by weight, more preferably 20-60% by weight, calculated as aluminium on the amount of rosin material in the sizing composition.

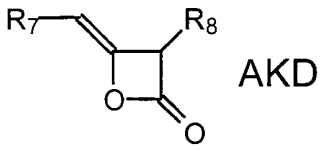
The rosin material used in the sizing composition according to the invention should have a high content of free rosin, i.e. not saponified rosin. The rosin material is derived from known types of rosin, such as gum rosin, wood rosin, tall oil rosin and mixtures thereof. The rosin material can be selected from rosin, modified rosin, fortified rosin and mixtures thereof. Modified rosin is rosin that has been modified in a known manner, such as for example disproportionated rosin, hydrogenated rosin, polymerised rosin, esterified rosin, etc. The rosin material is preferably fortified rosin, i.e. a Diels Alder adduct obtained in a known manner by the reaction between rosin, optionally modified as above, and an α,β-unsaturated carbonyl compound, i.e. pentaerythrite, fumaric acid, maleic acid or their anhydrides or half esters, acrylic acid and methacrylic acid. In combinations according to the present invention the degree of fortification of the rosin material can reach up to about 18 % by weight of adducted α,β-unsaturated

carbonyl compound, based on the total weight of the fortified rosin.

The amount of rosin component present in the rosin material is preferably in the range of from about 25 to about 80% by weight based on the total amount of rosin material. Preferably the rosin component is present in an amount of from about 40% to 60% by weight.

Finally, the sizing dispersion of the present invention may preferably also comprise a synthetic sizing agent. Synthetic sizing agents are well known in the art and preferably include at least one member selected from the group consisting of ketene dimers, acid anhydrides, organic isocyanates, carbamoyl chlorides and mixtures thereof. Ketene dimers (AKD) are preferred.

Ketene dimers (AKD) have the general formula:



AKD

wherein both R_7 and R_8 represent hydrocarbon groups having about 6 to about 30 carbon atoms, usually being alkyl groups having 12 to 20 carbon atoms, such as hexadecyl and octadecyl groups.

The dispersed phase of the sizing composition consists of particles either of rosin material; dicarboxylic acid derivative; optionally of synthetic sizing agent; or of a mixture thereof, whereby the mixture contains from 5 to 95 per cent by weight of rosin. As the particles contain a homogeneous mixture of the active sizing agents, the weight ratio in each particle in the dispersion will thus be in this range. The amount of synthetic sizing agent preferably is in the range from 2 to 75 % by weight, more preferably from 10 to 60 % by weight, based on the total dry weight of the sizing composition.

The dry content of the dispersions of the invention is at least 1% and preferably at least 5% by weight. The

upper limit depends on the type of sizing agent used and usually is about 60% by weight.

Dispersions of mixed particles are prepared without using dispersing agents or using one or several dispersing agents from the groups anionic, cationic or non-ionic dispersing agents. The amount of dispersing agent should be sufficient to give the dispersion the desired additional storage stability. The upper limit is not critical, but normally it is seldom necessary to use more than 5 % by weight of dispersing agent, based on the total dry weight of the sizing composition.

Cationic dispersing agents can, for example, be selected from nitrogen-containing dispersing agents such as quaternary ammonium compounds and salts of tertiary amines. Protective colloids or retention agents, such as cationic starch, casein, cellulose derivatives, guar gum, polyvinylalcohol, polyacrylamide, polyethyleneimine, polyamine, polyamidoamine, polyethyleneamine or polyacrylate can also be included in the dispersions. Anionic surfactants can be selected from alkyl sulphates, alkyl sulphonates, alkylarene sulphonates, i.e. sodium lauryl sulphate or sodium lignosulphonate. Nonionic dispersing agents can, for example, be alkoxylated alcohols, alkylphenols and fatty acids, partial fatty acid esters of polyvalent alcohols with 2 to 8 carbon atoms, or anhydro derivatives of these, and alkoxylated derivatives of these.

The aqueous cationic dispersion of rosin material can be prepared by homogenising the active substance in water in the presence of a dispersing agent using high shear forces and high temperatures so that fine particles are obtained as the dispersed phase. The active substance which is homogenised is a rosin component or a rosin component and a dicarboxylic acid derivative of formula (I). In this case, the homogeneous mixture is prepared preferably by means of intensive stirring of the melted rosin, to which the dicarboxylic acid derivative is added. The

active substance is dispersed in water in the presence of a dispersant under satisfactory stirring. The warm dispersed phase is then cooled and preferably mixed with an aluminium compound. The final dispersion is homogenised.

Aqueous dispersions or emulsions of synthetic or cellulose-reactive sizing agents are known in the art and commercially available and such dispersions can be prepared in per se conventional manner, e.g. by mixing the synthetic sizing agent with an aqueous solution of a dispersing agent or emulsifier and passing the mixture through a homogeniser.

The dispersion according to the invention can contain dispersed particles of rosin material, dispersed particles of dicarboxylic acid derivative and dispersed particles of synthetic sizing agent, or dispersed particles containing a mixture of rosin material, dicarboxylic acid derivative and synthetic sizing agent, or a combination of the mentioned dispersed particles. Dispersions containing discrete particles of rosin material and synthetic sizing agent can be prepared by mixing a preformed dispersion of rosin material and a dicarboxylic acid derivative and a preformed dispersion of synthetic sizing agent. They can also be prepared by mixing a dispersion of rosin material, a dispersion of synthetic sizing agent and a solution of the corresponding dicarboxylic acid derivative. Modifications of the above procedures are also suitable and within the skill of the art to which the invention pertains.

The present dispersions are particularly suitable for sizing of paper, board, paper board and similar cellulose fibre products. The dispersions can be used for internal and surface sizing. The dispersions are preferably used for internal sizing and are added in a conventional manner to a cellulose stock and conventionally used chemicals in paper production, such as drainage and/or retention agents, aluminium compounds, fillers, wet

strength resins, dyes, optical brightening agents, etc, can of course be used with the present dispersions. The dispersions can be used in an amount corresponding to 0.01 to 10% by weight of sizing agent, counted as dry on dry cellulose fibres, suitably in an amount corresponding to 0.025 to 1% by weight of sizing agent.

The invention is further illustrated in the following examples, which, however, are not intended to limit the same. Parts and percentages relate to parts by weight and per cent by weight, respectively, unless otherwise stated.

Example 1

100 parts of wood rosin and 15 parts of maleic anhydride were heated at 200°C during 2 h under agitation. The temperature was lowered to 160-170°C and 5 parts of 20% sodium hydroxide were added under slow agitation. Finally, 50 parts of 10% caseine were added under vigorous agitation. The final concentration was adjusted with water and the resulting emulsion was allowed to cool.

Example 2

100 parts of wood rosin and 15 parts of maleic anhydride were heated at 200°C during 2 h under agitation. The temperature was lowered to 160-170°C and 5 parts of 20% sodium hydroxide were added under slow agitation. Finally, 50 parts of 10% caseine solution and 2.5 parts of 50% iso-octadecenyl disodium succinate were added under vigorous agitation. The final concentration was adjusted with water and the resulting emulsion was allowed to cool.

Example 3

50 parts of emulsion according to Example 2 were mixed under vigorous agitation with 50 parts of solution of polyaluminium phosphate sulphate containing 4% aluminium. The resulting emulsion was stirred for 1 hour.

Example 4

50 parts of emulsion according to Example 1 were mixed under vigorous agitation with 50 parts of solution of polyaluminium phosphate sulphate containing 4% aluminium. The resulting emulsion was stirred for 1 hour.

Example 5

50 parts of emulsion according to Example 2 were mixed under vigorous agitation with 50 parts of solution of polyaluminium chloride containing 9% aluminium. The resulting emulsion was stirred for 1 hour.

Example 6

50 parts of emulsion according to Example 1 were mixed under vigorous agitation with 50 parts of solution of polyaluminium chloride containing 9% aluminium. The resulting emulsion was stirred for 1 hour.

Example 7

15 parts of rosin sizing emulsion according to Example 3 were mixed with 85 parts of an AKD emulsion containing 7% AKD wax at 35°C. The resulting emulsion was stirred for 1 hour.

Example 8

15 parts of emulsion according to Example 4 were successively mixed with 85 parts of an AKD emulsion containing 7% AKD wax and 5 parts of 50% iso-octadecenyl disodium succinate at 40°C under vigorous agitation. The final sizing emulsion was stirred for 1 additional hour.

Example 9

15 parts of emulsion according to Example 4 were mixed with 85 parts of an AKD emulsion containing 7% AKD wax at 40°C under vigorous agitation. The final sizing emulsion was stirred for 1 additional hour.

Example 10

50 parts of rosin sizing emulsion according to Example 3 were mixed with 50 parts of an AKD emulsion containing 15% AKD wax at 40°C. The resulting emulsion was stirred for 1 hour.

Example 11

50 parts of rosin sizing emulsion according to Example 4 were mixed with 50 parts of an AKD emulsion containing 15% AKD wax at 40°C. The resulting emulsion was stirred for 1 hour.

Example 12

50 parts of rosin sizing emulsion according to Example 5 were mixed with 50 parts of an AKD emulsion containing 15% AKD wax at 40°C. The resulting emulsion was stirred for 1 hour.

Example 13

50 parts of rosin sizing emulsion according to Example 6 were mixed with 50 parts of an AKD emulsion containing 15% AKD wax at 40°C. The resulting emulsion was stirred for 1 hour.

Example 14

The stabilities of the dispersions were evaluated by measuring their viscosities immediately and after storage at 20°C for 45 days. The viscosities were measured in a Brookfield viscosimeter, Mod. LVDV-II+, equipped with a small sample adapter (10 ml sample volume), using the SC18 spindle at 100 rpm. The results are listed in Table I.

Table I

Time / days	Viscosity (cP)				
	Example 3	Example 4	Example 7	Example 8	Example 9
0	10.2	12.5	6.0	7.1	8.5
15	11.3	(*)	7.2	7.5	25
30	12.1		8.5	8.1	40
45	15.2		10.2	8.9	57

(*) Phase separation

It is evident from Table I that the emulsions containing iso-octadecenyl disodium succinate had lower viscosities, both initially and after storage, thus showing a better stability.

Example 15

The stabilities of the dispersions were evaluated by measuring particle sizes immediately and after storage at 40°C for 45 days. The particle sizes were measured in a Coulter® Multisizer device, with a particle size range of 0.4 to 1200 µm and orifice tube sizes of 15 to 2000 µm. The results are listed in Table II.

Table II

Time / days	Particle size (CUM5) / µm			
	Example 10	Example 11	Example 12	Example 13
0	4.3	5.1	4.7	4.9
15	4.6	(*)	4.8	5.5
30	4.9		5.1	8.3
45	5.3		5.5	(*)

(*) Phase separation

It is evident from Table II that the emulsions containing iso-octadecenyl disodium succinate had a lower particle size both initially and after storage, thus showing a better stability.

Example 16

Paper sheets with a basis weight of 120 g/m^2 were prepared from recycled unbleached softwood sulphate pulp, at a head-box pH of 5-7.2, according to Tappi standard practice T205 sp-95 for laboratory scale. Table III shows Cobb-values measured according to Tappi standard T 441 om-90. Sizing dispersions were added to the thick stock just prior to dilution at the sheet former. No additional chemicals were added. Sizing level refers to

the level of sizing agent in % by weight, based on dry cellulose fibres.

Table III

Sizing dispersion	Sizing level (%)		Head-box pH	$Cobb_{60}$ (g/m^2)
	Emulsion	Rosin		
Example 3	2	0.24	7.2	65
Example 3	3	0.36	"	34
Example 4	2	0.24	"	76
Example 4	3	0.36	"	47
Example 5	2	0.24	"	24
Example 5	3	0.36	"	20
Example 6	2	0.24	"	30
Example 6	3	0.36	"	26
Example 3	2	0.24	5.0	41
Example 3	3	0.36	"	28
Example 4	2	0.24	"	46
Example 4	3	0.36	"	35
Example 5	2	0.24	"	23
Example 5	3	0.36	"	19
Example 6	2	0.24	"	28
Example 6	3	0.36		23

The emulsions containing iso-octadecenyl disodium succinate had lower Cobb values, both at acidic and neutral pH, thus showing a better sizing performance.

Example 17

Paper sheets with a basis weight of 80 g/m^2 were prepared from a mixture of bleached softwood and hardwood sulphate pulp (10:90 by weight), at a head-box pH of 7.2, according to Tappi standard practice T205 sp-95 for laboratory scale. Table IV shows Cobb-values measured according to Tappi standard T 441 om-90. Sizing dispersions were added to the thick stock just prior to dilution at the sheet former. No additional chemicals were added.

Sizing level refers to the level of sizing agent in % by weight, based on dry cellulose fibres.

Table IV

Sizing dispersion	Sizing level (%)			$Cobb_{60}$ (g/m^2)
	Emulsion	AKD	Rosin	
Example 7	0.5	0.03	0.01	41
Example 7	1	0.06	0.02	26
Example 8	0.5	0.03	0.01	45
Example 8	1	0.06	0.02	28
Example 9	0.5	0.03	0.01	76
Example 9	1	0.06	0.02	45

A trend similar to that of Example 16 can be noticed: emulsions containing iso-octadecenyl disodium succinate had lower Cobb values and therefore a better sizing degree.

CLAIMS

1. A sizing composition comprising an aqueous dispersion of a rosin material, characterised in that it also contains

(a) 0.05-20 % by weight, based on the dry weight of the composition of a dicarboxylic acid derivative with the general formula (I)

$$R_1OOC\text{-}Q\text{-}COOR_2 \qquad (I)$$

where
R_1 and R_2 which are the same or different represent H, M, where M is a metal of Groups IA or IIA, or a straight or branched alkyl or alkenyl group having 1-30 carbon atoms;
Q represents

(i) R_3 which is a straight alkylene group or alkenylene group of the formula $-C_nH_{2n-2z}-$, where n = 0-12 and z = 0-3;

(ii) $-R_3-R_4$, where R_3 is as defined above and R_4 is

a straight or branched alkyl or alkenyl group having 1-30 carbon atoms;
with the proviso that the compound of formula (I) includes at least 6 and at most 34 carbon atoms in total; and

(b) an aluminium compound which is selected from the group consisting of:

aluminium sulphate;

aluminium polymers of the general formula (III)

$$[\ Al\ (OH)_x(A)_{(3-x)}\ ]_n \qquad (III);$$

aluminium polymers of the general formula (IV)

$$[\ Al\ (OH)_x(H_3PO_4)_y\ (A)_{(3-x)}\ ]_n \qquad (IV)$$

where A = Cl^-, NO_3^-, $HCOO^-$, CH_3COO^- ;

aluminium polymers of the general formula (V)

$$[Al(OH)_x(SO_4)_{(3-x)/2}]_n \qquad (V);$$

aluminium polymers of the general formula (VI)

$$[\ Al\ (OH)_x(H_3PO_4)_y\ (SO_4)_{(3-x)/2}\ ]_n \qquad (VI)$$

where "x" is in the range 0.03 to 2.7, "y" in the range 0.01 to 0.8 and $n \geq 2$; and mixtures of these.

2. A sizing composition according to claim 1, wherein the composition comprises the dicarboxylic acid derivative of formula (I) in an amount of 0.05-10 % by weight, based on the dry weight of the composition.

3. A sizing composition according to claim 1 or 2, wherein M is selected from Na and K.

4. A sizing composition according to any one of claims 1-3, wherein Q represents $-R_3-R_4$, where R_3 is a straight alkylene group of the formula $-\overset{|}{C}H\overset{|}{C}H_2-$ and R_4 is a straight or branched alkyl or alkenyl group having 1-30 carbon atoms.

5. A sizing composition according to any one of claims 1-4, wherein R_4 is a straight or branched C_{12}-C_{18} alkyl or alkenyl group.

6. A sizing composition according to claim 5, wherein R_4 is iso-octadecenyl.

7. A sizing composition according to any one of claims 1-6, wherein the dicarboxylic acid derivative is iso-octadecenyl disodium succinate.

8. A sizing composition according to any one of the preceding claims, wherein the composition further comprises a synthetic sizing agent.

9. A sizing composition according to claim 8, wherein the synthetic sizing agent is selected from the group

consisting of ketene dimers, acid anhydrides, organic isocyanates, carbamoyl chlorides, and mixtures thereof.

10. A sizing composition according to claim 8 or 9, wherein the composition comprises the synthetic sizing agent in an amount of 2-75 % by weight, based on the dry weight of the composition.

11. A sizing composition according to any one of the preceding claims, wherein the aluminium compound comprises 20-60 % by weight, calculated as aluminium on the amount of rosin material of the sizing composition.

12. A method of sizing a cellulosic fibre material, such as paper, board or paper board, c h a r a c t e r i s e d in that the sizing composition according to any one of the preceding claims is added to the cellulosic fibre material in an amount of 0.01-10 % by weight, calculated as dry sizing agent on dry cellulosic fibres.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 01/00289

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21H 17/16, D21H 17/62, D21H 21/16
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Patent Abstracts of Japan, abstract of JP 55-131053 A (SEIKO KAGAKU KOGYO CO LTD), 11 October 1980 (11.10.80), & WO 8002147 --	1-13
A	GB 1547282 A (AMERICAN CYANAMID COMPANY), 6 June 1979 (06.06.79), page 1, line 27 - line 39, claims 1-5 --	1-13
A	US 5639812 A (YASUSUKE TAKEDA ET AL), 17 June 1997 (17.06.97), column 1, line 48 - column 3, line 11; column 4, line 42 - line 50, claim 1 --	1-13

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 June 2001	06 -06- 2001
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 01/00289

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 4919725 A (MERVYN F. JONES), 24 April 1990 (24.04.90), column 1, line 28 - line 37; column 5, line 26 - line 32, claims 1 and 22, abstract --	1-13
A	US 5219912 A (YOSHIO TAKAHASHI ET AL), 15 June 1993 (15.06.93), claim 4 --	1-13
A	EP 0074544 A1 (HERCULES INCORPORATED), 23 March 1983 (23.03.83), page 2, line 2 - page 4, line 5; page 7, line 5 - page 8, line 10, claim 1 -- --------	1-13

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