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(54) Paper sizing methods and compositions.

(57) The manufacture of sized paper, by adding a sizing agent and an aluminium compound to paper-making stock or by surface-sizing paper with a pre-blend of the agent and the compound, is carried out at a neutral or alkaline pH, typically a pH above 6, and so that the agent and the compound are added simultaneously to the paper-making stock or are applied simultaneously to the paper surface. If the agent and the compound are used as a one-shot pre-blend, this is made on or immediately before use.

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PAPER SIZING METHODS AND COMPOSITIONS

The present invention relates to paper sizing methods and is more particularly concerned with the sizing of paper using rosin-based sizing compositions at relatively high pH values. The invention also relates to sizing compositions per se, for use in carrying out such methods, and the resultant sized paper products.

Conventional paper sizing methods, using rosin in either its emulsified or soaped forms, involve the separate addition to one or more selected points in the paper machine wet-end of the rosin-based sizing composition and of an aluminium salt. This technique operates satisfactorily at pH values lying generally in the range from 4 to 6. When the pH is higher than about 6, to any significant extent, for example in the case where chalk is added to the paper pulp, sizing by this technique becomes erratic and very difficult to control. In view of these difficulties, when attempting to make sized paper or to surface size paper already made, using a pH value above the normal 4 to 6 range, it is common practice to resort to the use of non-rosin sizes, such as those based on alkyl ketene dimers.

Attempts to size generally at neutral or alkaline pH values or to use specific aluminium salts (e.g. polyaluminium chloride) in the two-shot mode in the presence of chalk have only given very poor results.

It is also known that if a one-shot mode of operation is used, namely a method involving use of a pre-mix of rosin and aluminium salt, made a considerable time before addition of the pre-mix to the machine, again only spasmodic control of sizing in an alkaline environment is obtainable. Such one-shot systems, operated so as to avoid these difficulties, are disclosed for instance in our pending Application No. 88304405.9 (Publication Number EP-A-0293119) and also in US-A-4333795.

It has now surprisingly been found that if a pre-mix of a rosin-based size and an aluminium salt is made, on an in-line basis just before its addition to the paper machine, much better and more controlled sizing is obtained with rosin, when the stock contains chalk or otherwise has a neutral or alkaline pH value. Thus, the present invention is based upon the unexpected discovery of a difference in behaviour if a pre-mix of rosin and an aluminium salt is made when or just before it is in fact used, as compared with known methods where it is made a considerable time before its use.

According to one aspect of the present invention therefore, a paper sizing method is provided, in which paper is made from a pulp system containing chalk or otherwise having a neutral or alkaline and therefore high pH, in which a pre-blended composition containing a rosin-based size and an aluminium compound is used or the rosin-based sizing composition and the aluminium compound are added separately but simultaneously and are pre-mixed just prior to addition at an appropriate selected point in the paper machine wet-end.

According to another aspect of the present invention, a pre-blended paper sizing composition, comprising a rosin-based size and an aluminium compound and suitable for use on or immediately after its formulation, is also provided. Particular optional but preferred features of the proposed one-shot paper sizing composition of the present invention may include the incorporation into the composition of a higher than normal amount of aluminium salt, a higher than normal amount of the rosin-based size or the inclusion of at least one polyelectrolyte.

According to a further preferred feature of the method and the composition of the invention, the weight ratio of the rosin size to the aluminium compound, used in carrying out the method and accordingly present in the one-shot composition, on a dry basis, lies in the ratio 1:0.01 to 5. According to a further preferred feature of the invention, the ingredients added to the paper machine wet-end in carrying out the method of the invention, either during operation or as a one-shot pre-mix, include at least one urea-based extender.

In addition to the stock sizing of paper, according to the invention, another aspect consists in the use of pre-mixed compositions and techniques, of the kind indicated above, in the surface sizing of paper which has already been manufactured, whether or not a rosin-based sizing composition has been used in its manufacture up to that stage. A further aspect of the present invention consists of any paper or paper-like product made by a method according to the present invention or made using a paper-sizing composition according to the invention.

In accordance with a preferred embodiment of the invention, a pre-mixed rosin-based sizing composition for use in carrying out the present invention may contain, in addition to the rosin and the aluminium compound, one or more other additives useful in the making of paper, for instance for optimising the sizing function of the rosin-based component per se. Such additional and optional additives include cationic and anionic polyelectrolytes, and also cationic starches. For example, the pre-mix can contain one or more of cationic and anionic polyacrylamides, polyethyleneimine, polydialkyl dimethyl ammonium chloride (DADMAC) or polyamide/epichlorohydrin condensates, as well as dicyandiamide/formaldehyde condensa-

tion products.

According to a further aspect of the invention, despite the fact that pre-mixed one-shot sizing products, such as are available commercially, in the form of products made and supplied by chemical companies, are difficult to use, particularly in neutral or alkaline pH circumstances, it is possible according to another aspect of the invention to effect modification of the in-line mixing technique indicated above, optionally with the addition of further aluminium salt and/or polymers, so that such pre-mixed commercial products can also be employed, in accordance with the principles of the present invention, whereby greater control and effectiveness than has previously been possible with such one-shot products.

In order to carry out the method of the invention in practical terms, it is necessary to employ some form of mixing device, so as to control the degree of dispersion of the aluminium salt and the rosin size, which in turn affects its distribution amongst the paper fibres, with optimisation of sizing efficiency. The mixing device is suitably associated with the wet-end of the paper machine and its proper use ensures that the dispersion serves to control the degree of agglomeration of the fibres in the pulp.

In carrying out the invention, the rosin-based size component employed, by being formulated into a pre-mix with an aluminium compound, can be based on rosin or rosin modifications, prior to conversion into a stable emulsion form. Thus, use can be made for this purpose of gum rosin, formaldehyde-treated gum rosin or tall oil rosin, fumaric acid-treated gum rosin or tall oil rosin, disproportionated rosin, maleic anhydride-treated gum rosin or tall oil rosin such as the compounds or any combination of untreated or treated rosin, such as the compounds of the kinds just mentioned. In addition, esters or part esters of any of any of the above-mentioned forms of rosin, formed with straight chain or polyhydric alcohols, can also be used. A third possibility is to use any appropriate mixture of any of the aforementioned untreated or treated forms of rosin, including disproportionated rosin and tall oil rosin, together with any one or more of the esters or part esters just described.

As a further aspect of the invention, it is possible to use resinous materials other than rosin per se or chemically-modified rosin compounds. For example, hydrocarbon resins, both of the aromatic and aliphatic varieties, can be used when suitably formulated, in order to carry out the paper-making methods of the present invention.

Paraffin waxes and microcrystalline waxes may be used in conjunction with any of the above-mentioned rosin or resin-based types of sizing compositions, the particular use of one or other of the possible waxes depending largely upon the properties which may be required in the eventual paper product.

Furthermore, any appropriate rosin-based sizing emulsion, derived from any one or more of the above-mentioned materials, may incorporate one or more extenders. By way of example, urea-based extenders may be employed for this purpose. Such extenders are disclosed for example in US-A-4022634, 4093779, 4141750, 4025354, 4437894 and 4605445. Any appropriate rosin emulsion may also be extended with emulsions of alkyl ketene dimers, prior to or subsequent to pre- mixing with the aluminium compound. The alkyl ketene dimer emulsions may be stabilised with either cationic starch or cationic or anionic polymers.

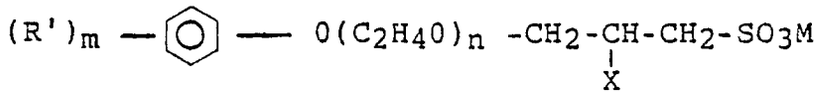
According to another aspect of the invention, the aluminium compound incorporated in the one-shot pre-mix of the invention or otherwise employed in carrying out paper sizing methods according to the present invention is selected from polyaluminium chlorides, aluminium chlorohydrate, aluminium sulphate (paper makers alum) and any mixture of two or more of the foregoing.

In putting the invention into practice, it is desirable to incorporate in the paper sizing composition, when made up in a one-shot form, at least one stabilising agent, which may take the form of one or more surface active agents or surfactants. Mixtures of stabilising agents or surfactants also can be used. A very wide range of possibilities is available as to the nature of such materials, which can be anionic, non-ionic, cationic or amphoteric.

One particular class of stabilised emulsion comprises essentially a rosin soap and a protective colloid. The rosin-based component, namely the rosin soap, can be a sodium, potassium or ammonium soap of rosin or of a modified rosin, together with amine salts of rosins or modified rosins, for instance the amine salts formed with mono-, di- or triethanolamine. These stabilisers can be added separately or formed in situ when making up the rosin-based emulsion composition. Colloids which can be used to stabilise the resultant product include casein, starch, soya protein and cellulose derivatives, the former being the most preferred, as well as certain polymers, such as polyvinyl pyrrolidone or polyvinyl alcohol (PVA). A preferred form of stabilised emulsion consists essentially of the potassium or sodium soap of the rosin or rosin derivative and casein as the stabilising colloid.

According to a further feature of the invention, surface active agents or surfactants which can be used in formulating the compositions of this invention include:

(i) salts of sulphonic acids having the general formula:



where R′ represents a hydrocarbon residue having from 4-18 carbon atoms, m is an integer having a value of 1 or 2, n is an integer having a value of 4 to 25, X represents a hydrogren atom or a hydroxyl group and M represents a monovalent cation and

(ii) salts of sulphuric acid half esters having the general formula:

wherein R^2 represents a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms, A represents a straight chain or branch chain alkylene group having 2 or 3 carbon atoms, p is an integer having a value of 4 to 25 and Q is a monovalent cation, including all those compounds described in US-A-4309388.

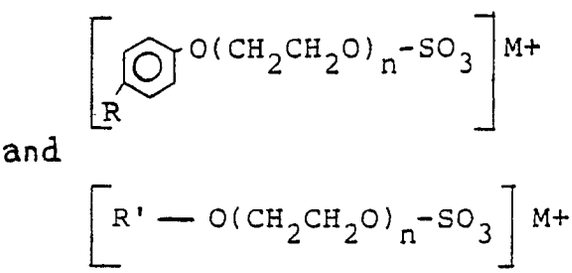
(iii) alkyl-benzene sulphonates wherein the alkyl substituent comprises from 8 to 24 carbon atoms, including all those compounds described in US-A-4157982.

(iv) sulphosuccinate half esters of fortified rosin having the formula:

H_{3-m}. R. $[(CH_2CH_20)_n$- $OC.C_2H_3SO_3Na$.- C00Na]

wherein R is a fortified rosin acid tricarboxylate group, m has an average value of 1.5 to 3 and n has an average value from 4.5 to 25 including all those described in EP-A-159794.

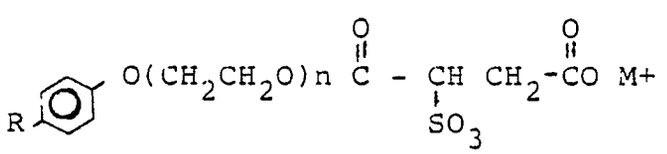
(v) compounds having one or other of the formulae:



and

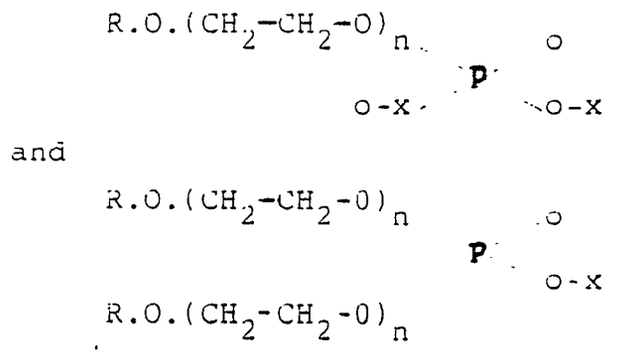
wherein R represents an alkyl group comprising from 4 to 18 carbon atoms, and R′ represents an alkyl or alkenyl group comprising from 4 to 18 carbon atoms and n is an integer having a value of 4 to 25, including all those described in US-A-4199367.

(vi) sulphosuccinate salts of ethylene oxide condensates having the general formula:-



wherein R represents an alkyl group comprising from 4 to 18 carbon atoms and n is an integer having a value of 4 to 25 including all those compounds described in US-A-4203776.

(vii) organic phosphate esters having one or other of the general formulae:



and mixtures thereof,
wherein R represents an alkyl or an alkyl-phenol, alkenyl or alkaryl group comprising from 5 to 20 carbon atoms, n has a value of 5 to 20 and X represents a monovalent cation or hydrogen.

Cationic resin dispersant systems may also be used to stabilise the rosin dispersions of this invention. Examples of suitable materials include water-soluble polyaminopolyamide/epichlorohydrin resins, water-soluble alkylene-polyamine/ephichlorohydrin resins and poly(diallylamine)/epichlorohydrin resins.

In order that the present invention may be fully understood and appreciated, the following examples of use of the paper sizing methods and compositions of the present invention are given, by way of illustration only. In the examples, all amounts are given as percentages by weight, unless otherwise indicated. In example 1, part A represents use of the invention, while part B represents use according to the prior art.

Example 1

Part 1

A pilot Fourdrinier paper machine was used which was operated to produce paper of 85 gsm at 16 kg per hour from softwood/hardwood Kraft furnish loaded with 10% chalk.

Pre-mixes of the rosin size and aluminium salt were made using a laboratory mixer and were metered just prior to the flow box.

The following results were obtained:-

Rosin Size Solids/fibre %	Polyaluminium chloride (as received)	1 min Cobb gsm	pH at Flow Box
1.0	0.5	68	7.8
1.0	1.0	29	7.6
1.0	1.5	29	7.6

Part B

For comparison with the practice exemplified in Part A, sheets were made using Kraft pulp containing 10% of chalk. The size and the PAC were added separately to the pulp and held for 30 minutes before sheets were made.

The following results were obtained:-

Rosin size Solids/fibre %	Polyaluminium chloride (as received)	1 min Cobb gsm	pH at Flow Box
1.0	0.5	146	7.4
1.0	1.0	156	7.2
1.0	1.5	154	7.3
2.0	0.5	154	7.4
2.0	1.0	144	7.3
2.0	1.5	137	7.2

Example 2

A commercial paper machine producing envelope paper at the rate of 6.8 tonnes per hour with a chalk content varying from 5.8 to 7.8 per cent was sized by pre-blending free rosin size and alum and adding the pre-mix to the forward side of the thick stock head-box. Throughout the run, the amount of size used (dry basis) was 0.45% and the amount of alum used (dry basis) was 1.93%.

Time	1 Min Cobb	Flow Box pH
12.30	26	8.0
12.45	20	8.0
13.45	20	8.0
13.50	22	7.5
14.25	21	7.7
14.59	21	7.6
15.34	21	7.7

Referring to example 1 above, it will be noted that, in part B, the Cobb values indicate that the sheets were close to saturation. Referring to the last three results in part B of example 1, double the amount of rosin size on a percent solid/fibre basis was used, as compared with the first three, but this made very little difference to the Cobb values obtained and none of those obtained in part B came anywhere near the much better results in terms of levels of sizing achieved in carrying out the invention, according to part A of example 1. A very satisfactory range of sizing is given by the last two results of example 1 part A in particular and throughout example 2. In these examples, "as received" in relation to the polyaluminium chloride means that it contained 10 percent Al_2O_3.

The invention thus represents a substantial and surprising advance on previous paper sizing methods and compositions.

Claims

1. A method of sizing paper using paper-making stock to which a rosin-based or resin-based sizing agent and an aluminium compound are added, characterised in that

(a) sizing is carried out at a neutral or alkaline pH and

(b) the sizing agent and the aluminium compound are added simultaneously to the paper-making stock at a selected point in the paper machine wet-end.

2. A method according to claim 1, wherein the paper pulp system contains chalk in an amount sufficient to produce a pH above 6.

3. A method according to claim 1 or 2, wherein a pre-blended composition comprising the rosin-based or resin-based sizing agent and the aluminium compound is added to the paper-making stock in the paper machine.

4. A method according to claim 1 or 2, wherein the rosin-based or resin-based sizing agent and the aluminium compound are added separately but simultaneously to the paper-making stock in the paper machine.

5. A method according to claim 3, wherein the sizing agent and the aluminium compound are pre-mixed just prior to addition to the paper machine.

6. A method according to any preceding claim, wherein a higher than normal amount of aluminium compound or a higher than normal amount of the sizing agent is incorporated in the composition.

7. A method according to any preceding claim, wherein the weight ratio of the sizing agent to the aluminium compound used in carrying out the method, on a dry basis, lies in the range from 1:0.01 to 5.

8. A method according to any preceding claim, wherein the ingredients added to the paper machine wet-end, either during operation or as a one-shot pre-mix, include at least one urea-based extender.

9. A method according to any preceding claim, wherein at least one polyelectrolyte is incorporated into the composition.

10. A method according to claim 9, wherein a pre-mixed rosin-based sizing composition, used in carrying out the method, also contains in addition to the rosin and the aluminium compound, one or more other additives for optimising the sizing function of the rosin-based component per se.

11. A method according to claim 10, wherein the one or more additives are selected from cationic and anionic polyelectrolytes and cationic starches.

12. A method according to claim 11, wherein the additives are selected from cationic and anionic polyacrylamides, polyethyleneimine, polydialkyl dimethyl ammonium chloride (DADMAC), polyamide/epichlorohydrin condensates and dicyandiamide/formaldehyde condensation products.

13. A method according to any preceding claim, wherein a pre-mixed composition comprising the sizing agent and the aluminium compound is used, at a neutral or alkaline pH, in the surface sizing of paper which has already been manufactured, whether or not a rosin-based sizing composition was used in its manufacture up to that stage.

14. A method according to any preceding claim, wherein the sizing agent is based upon rosin or a rosin modification selected from gum rosin, formaldehyde-treated gum rosin or tall oil rosin, fumaric acid-treated gum rosin or tall oil rosin, disproportionated rosin, maleic anhydride-treated gum rosin or tall oil rosin, esters or part esters of any such rosin or rosin modification with straight chain or polyhydric alcohols, and mixtures of such untreated and treated forms of rosin with any one or more of such esters or part esters.

15. A method according to any of claims 1 to 13, wherein the sizing agent is based upon resinous materials selected from aromatic and aliphatic hydrocarbon resins.

16. A method according to any preceding claim, wherein the aluminium compound is selected from polyaluminium chlorides, aluminium chlorohydrate, aluminium sulphate and mixtures thereof.

17. A method according to any preceding claim, wherein at least one stabilizing agent selected from anionic, nonionic, catlonic and amphoteric surfactants is incorporated into the paper sizing composition.

18. A pre-blended paper sizing composition comprising a rosin-based or resin-based paper sizing agent and at least one aluminium compound, characterised in that the composition is suitable for use in the manufacture of sized paper on or immediately after its formulation by combination of the paper sizing agent and the aluminium compound and that the composition is effective to size paper-making stock or to surface-size paper under conditions including a neutral or alkaline pH.

19. Sized paper, when made by a method according to any of claims 1 to 17.

20. Sized paper, when made using a sizing composition as defined in claim 18.