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(54) Sizing process.

(57) A method of sizing cellulosic fibres materials for the formation of sheet products, e.g. paper, is carried out at a pH of 6-10 using a sizing agent and a cationic material, which is a powdered aluminium compound (preferably the hydroxide) on whose surface is a substance which is cationic at pH 6-10. The invention allows the use of rosin-based sizes at neutral-alkaline pHs and results in a paper with better aging and ink acceptance properties.

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This invention relates to a process of sizing of cellulosic fibrous material which is to be formed into sheet products, and more particularly to such a process in which the size used is based on rosin.

Cellulosic fibrous material which is to be formed into sheet products such as paper, cardboard, paperboard and the like is generally sized such that the final sheet has stiffness and can readily accept printing inks. Conventional sizing processes have generally used sizes based on rosin. In a typical process, a size which is based on a rosin acid emulsion or soap is added at the paper machine wet-end. In addition, there is added a cationic substance. This is usually an aluminium salt (the sulphate and the chloride are the most commonly used). This, it is believed, precipitates the rosin acids on to the cellulosic fibres and there forms with them a rosinate complex.

This process suffers from a number of disadvantages. The favoured aluminium salts are cationic only at acidic pHs (typically 4-6). The resulting paper is not stable to aging. A further disadvantage is that the preferred filler for the final material is chalk, favoured because of its cheapness and whiteness, but this reacts in an acid environment to generate carbon dioxide and cause foaming. As a result, more expensive (and less satisfactory) clays must be used as fillers.

Attempts have been made to operate this process at pHs above 6, but it has been found that the sizing becomes erratic and very difficult to control, especially when chalk is used. This is believed to arise at least partially as a result of the diminution of the cationic character of the aluminium at the higher pHs. A proposed solution has been the use of non-rosin-based sizing materials, such as those based on alkyl ketene dimers. These have the double disadvantage in comparison with rosin-based sizes of being considerably more expensive and of not functioning so well - they do not develop their sizing properties immediately on the paper machine but require a certain "cure" time.

There therefore exists in the art a need for a cheap sizing process which can be carried out in the neutral-alkaline pH range (that is, pH 6 and above).

It has now been discovered that it is possible to provide such a process. There is therefore provided, according to the present invention, a process of sizing at a pH of 6-10 a cellulosic fibrous material adapted to be used in the formation of a sheet, comprising the addition to the material at the wet-end stage of a sizing material and a cationic material which cationic material is a powdered water-insoluble aluminium compound on the surface of which is present a substance which is cationic at pH 6-10.

By "powdered" is meant that the aluminium compound has initially the form of particles of a fine, free-flowing powder. The use of such powders is important to the invention. It has been proposed that dispersions of very fine gelatinous precipitates of aluminium hydroxide be prepared in situ. Such dispersions are not suitable for use in this invention for a number of reasons, including the following:

(a) the starting compound is an aluminium salt, generally the sulphate, and this introduces undesirable ions into the system;

(b) the dispersion of gelatinous material has residual acidity which poses problems for any proposed use of calcium carbonate; and

(c) the particles have a layer of electrolyte on their gelatinous sufaces, which makes it very difficult to deposit cationic substance thereon, as hereinunder described.

The aluminium compounds useful in the working of this invention are water-insoluble or at most sparingly water-soluble. Suitable compounds include the oxide, hydroxide, diacetate, carbonate and oxalate, the preferred material being the hydroxide ($Al(OH)_3$). It is permissible to use two or more such compounds. All of the compounds are available as free-flowing powders.

The aluminium compound to be used preferably has a particle size in the range of from 0.5-10μm, preferably 1-10μm, more preferably 1-5μm, most preferably 1-2μm. With some exceptions, commercially-available powders are coarser than this, but the appropriate size can readily be achieved by use of conventional wet grinding apparatus such as bead mills.

The cationic substance which is present on the surface of the aluminium compound particles may be selected from any suitable substances which are cationic at pH 6-10, more preferably 6-9 and most preferably 7-8, and which may be attached to the surface of the aluminium compound particles. Again, two or more such substances may be used. Any known method of attaching a cationic substance to an aluminium compound particle may be used. One method of attachment is simple adsorption, and many cationic substances will adsorb on to the particles when cationic substance and particles are blended. Alternatively, there may be used intermediate compounds which attach particle and cationic substances to each other. This, however, is relatively expensive and adds a further stage in the preparation, and adsorption is preferred both for its simplicity and for the superior results achieved with adsorbed cationic materials. The preferred cationic substances are polymeric and may be based on a number of chemistries, which include cationic polyacrylamides, polyethyleneimines, polydialkyl dimethylammonium chloride, polyamides and amine/epichlorhydrin and dicyandiamide/formaldehyde condensates. The most preferred cationic substances are polytertiary amine and polyquaternary ammonium compounds. Typical examples of suitable cationic materials may be found in the "Cartafix" (trade mark) range of Sandoz Ltd., for example "Cartafix" TE and "Cartafix" DPR.

Preferably in a process according to the invention, the ratio of insoluble aluminium compound to cationic substance is from 1:0.001 to 1:0.2 (based on the dry weights of both materials), more preferably 1:0.00 1 to 1:0.1.

The sizing materials for use in this invention may be selected from any known sizing materials, be they natural or synthetic. Suitable sizing materials include colophony, animal size, casein, starch, waxes, fatty acids and tall resins. Of the synthetic sizes, especially suitable products are those based on ketene dimers, polyvinyl alcohols or polyvinyl acetates. There can also be used modified resin sizes such as are obtained, for example, by reacting colophony with dienophilic acids, a typical example of such a product being commercially available under the trade name "RLE 30" (Roe Lee Paper Chemicals). However, one of the great advantages of the present invention is that it permits the use of rosin-based sizes in neutral or alkaline environments and these are the preferred sizes. All rosin-based sizing materials known tothe art may be used, for example, rosinate soaps, rosin acid emulsions and cationic and nonionic rosin preparations.

In use in a paper-making process, the sizing material and the cationic material are added at a suitable stage in the wet-end. In this regard, the process of the invention is no different from the known art and any suitable stage may be chosen. The cationic material is added as an aqueous dispersion of particles and is dispersed therein. The invention encompasses both the solid and aqueous dispersion forms of the cationic compound as novel compositions of matter. The preferred ratio of cationic material to sizing material is from 1:0.1 to 1:10.0, preferably 1:0.1 to 1:5.0, based on the weight of the dry aluminium compound and the weight of dry sizing material. However, there are circumstances when it is possible to work well outside this ratio range and these are further described hereinunder. The actual quantities used depend very much on such factors as the nature of the fibrous cellulosic material, and the type and quantity of other components present, but as a general indication, the sizing material is added at a rate of from 0.1 - 2.0%, preferably from 0.2-0.5% by weight of dry cellulosic fibre.

The sizing material and the cationic material may be added in any order, but the preferred order is sizing material first, followed by cationic material.

Other materials commonly used in the art may also be used in art-recognized quantities. One very important category of such materials is that of pigments and fillers. All fillers and pigments conventionally used in the manufacture of paper can be used in the process according to the present invention, for example, kaolin, aluminium silicate, calcium silicates, oxyhydrates of aluminium, talcum, satin white, gypsum, barium sulphate, calcium carbonate, magnesite, zinc oxide, titanium dioxide. However, calcium carbonate, which may be natural calcium carbonate in finely divided form or precipitated calcium carbonate, is preferred because its degree of whiteness is superior, for example, to that of kaolin, and its favourable flow behaviour permits the achievement of especially high degrees of filling in the paper. In this way, the properties of the paper are also positively influenced; the opacity is increased, the degree of whiteness is improved, the resistance to aging is increased and the mechanical properties are improved.

One interesting and unexpected aspect of this invention is the ability of the cationic material to neutralize the adverse effects of anionic species which may be present in the wet-end-in the terminology of the art, it can act as a "trash quencher". It has this effect when used in conjunction with a sizing material according to the invention or when used alone. In the former case, it is permissible to exceed the preferred ratio of cationic material to sizing material given hereinabove, the excess cationic material acting as a "trash quencher". The invention therefore provides a method of neutralizing the adverse effects of undesirable anionic species present in a cellulosic fibre pulp, comprising the addition thereto of a quantity of an aqueous slurry of a cationic material as hereinabove described sufficient to effect said neutralization.

The process of the invention has several advantages. It permits the use of the well-known and cheap rosin-based sizes and chalk filler, yet it is a process conducted at neutral or mildly alkaline pHs. The result is a paper which is of better appearance and printability and which lasts much longer. The invention therefore provides a sized sheet of cellulosic fibrous material, produced by a process as hereinabove described. The process has the additional advantage of being able to work with pulps containing high levels of undesirable anionic species. The cationic compounds for use in the process of this invention are readily made from inexpensive materials.

The invention is further described with reference to the following examples in which all parts are expressed by weight.

Example 1

(a) Preparation of cationic material

243 parts of deionized water are mixed with 12 parts of "Cartafix" TE (trademark) a commercially-available 20% active cationic polyquaternary amine polymer based on amine/epichlorhydrin chemistry. 45 parts of powdered aluminium hydroxide (dried gel, 50-57.5% as Al_2O_3) is stirred into this mixture. The resulting slurry, containing 15% aluminium hydroxide powder, is transferred to a bead mill having a glass grinding bead size of 1 mm. The slurry is milled at a speed of 3000 rpm for 20 minutes, after which time the mean particle size is 2 to 5 μm and the viscosity 560 mPa (Brookfield viscometer, spindle 3, speed 100 rpm). The yield is 300 parts.

(b) Use according to the invention

A bleached cellulose pulp comprising 50% sulphate softwood and 50% sulphate hardwood is refined at 4% consistency to a freeness of 35°SR and then diluted with water to 2% (dry weight). To 3 parts (dry weight) aliquots of this pulp slurry are added various levels of rosin acid (RLE 30), followed 60 sec. later by different amounts of the cationic material whose preparation is described hereinabove. The pH of the slurry is adjusted to 7.5 with dilute sodium hydroxide.

After 5 minutes stirring, sheets of paper are made from the treated pulp on a Rapid-Köthen sheet former. After pressing and then drying in a Schröter dryer for 5 min. at 90°C, the sheets are conditioned and the degree of sizing then determined using the Cobb test (60 seconds) according to the German Industrial Standard DIN 53133.

As a control, several sheets are made using alum instead of the cationic compound of the invention.

The results are set out in Table 1.

TABLE 1

Sheet No.	Rosin Size solids/fibre Wt. %	Wt.% of Cationic Material (as $Al(OH_3)$ on fibre)	Alum solids/fibre Wt. %	Cobb (60 s) gsm
1	0.3	0.2	--	40.4
2	0.3	0.3	--	27.2
3	0.3	0.4	--	26.2
4	0.3	0.5	--	24.3
5	0.5	0.1	--	68.1
6	0.5	0.2	--	26.7
7	0.5	0.3	--	22.8
8	0.5	0.4	--	21.7
9	0.5	0.5	--	24.4
10	0.5	--	0.4	58.2
11	0.5	--	0.5	46.9
12	0.5	--	1.0	45.8
13	--	--	--	186.8

The results clearly illustrate the benefits of the invention. The lower the Cobb value, the better, 20-25 being regarded as very good. It can be seen that compositions according to the invention can achieve this. The sheet nos. 10-12, on which are used typical compositions according to the art, show much higher Cobb values.

EXAMPLE 2

A cationic material is prepared by the following method:

186 parts of deionised water is mixed with 24 parts "Cartafix" TE, and 90 parts of a commercially-available fine particle size aluminium trihydroxide (average particle size = 1 micron) is stirred into the solution to make a free-flowing slurry. The yield of the slurry is 300 parts.

Hand sheets are made according to the method of Example 1(b), using varying proportions of the resin size of that Example and the slurry whose preparation is described hereinabove. The Cobb values obtained are as follows:

Rosin Size (solids/fibre)	Cationic slurry (solids/fibre)	Cobb (60 s)
0.3%	0.2%	26.3
0.3%	0.3%	23.7
0.5%	0.3%	21.4
0.5%	0.4%	20.2

The Cobb values are nearly all in the "very good" category.

EXAMPLE 3

138 parts of deionised water is mixed with 72 parts "Cartafix" DPR, a commerically available 20% active amine/epichlorohydrin-based cationic poyltertiary amine polymer. 90 parts of the aluminium trihydroxide used in Example 2 is then mixed in to give a yield of 300 parts.

Hand sheets are made as described in Example 1 (b), keeping the level of size constant at 0.2% and varying the amount of cationic compound. The Cobb values obtained are as follows.

Rosin Size (%) (solids/fibre)	Cationic Slurry (%) (solids/fibre)	Cobb (60) (g/m^2)
0.2	0.05	22.7
0.2	0.10	15.2
0.2	0.30	14.9
0.2	0.50	15.9
0.2	1.00	16.0

Claims

1. A process of sizing at a pH of 6-10 a cellulosic fibrous material adapted to be used in the formation of a sheet, comprising the addition to the material at the wet-end stage of a sizing material and a cationic material, which cationic material is a powdered water-insoluble aluminium compound, on the surface of which is present a substance which is cationic at pH 6-10.

2. A process according to claim 1, wherein the substance is cationic at pH6-9.

3. A process according to claim 1 or claim 2, wherein the particle size of the powdered aluminium compound is from 0.5-10μm, more preferably 1-10μm, still more preferably 1-5μm and most preferably 1-2μm.

4. A process according to any one of claims 1-3, wherein the aluminium compound is aluminium hydroxide.

5. A process according to any one of claims 1-4, wherein the cationic substance is polymeric.

6. A process according to any one of claims 1-5, wherein the cationic substance has a chemistry selected from cationic polyacrylamides, polyethyleneimines, polydialkyl dimethylammonium chloride, polyamides and dicyandiamide/formaldehyde and amine/epichlorhydrin condensates, and is preferably selected from polytertiary amines and polyquaternary ammonium compounds.

7. A process according to any one of claims 1-6, wherein the weight ratio of aluminium compound to cationic substance is from 1:0.001 to 1:0.2, preferably 1:0.001 to 1:0.1, based on the dry weight of both materials.

8. A cationic material, being a powdered, water-insoluble aluminium compound on the surface of which is present a substance which is cationic in the pH range 6-10, preferably 6-9, more preferably 7-8.

9. An aqueous dispersion of the cationic material of claim 8.

10. A method of neutralizing the adverse effect of undesirable anionic species present in a cellulosic fibre pulp, comprising the addition thereto of a quantity of an aqueous slurry of a cationic material according to claim 8 sufficient to effect said neutralization.

11. A sized sheet of cellulosic fibrous material, prepared by means of a process according to claim 1.

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EUROPEAN SEARCH REPORT

Application Number
EP 92 81 0722

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY,vol.52,nØ4,Oct 1981,page 468,abstract nØ4276,Appleton,Wisconsin,USA &JP-A-56026959(SHOWA)16-03-1981 -----	1-11	D21H17/67 D21H17/69 D21H17/33 D21H17/45 D21H17/46

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 JANUARY 1993	FOUQUIER J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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