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(54) Title: METHODS TO ENHANCE ALKENYL SUCCINIC ANHYDRIDE SIZING ON PAPER

(57) Abstract: A method to enhance alkenyl succinic anhydride sizing on paper is disclosed there. Methods to make paper products with increased ink penetrations time are provided. Paper products with increased ink penetration time are also disclosed.

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METHODS TO ENHANCE ALKENYL SUCCINIC ANHYDRIDE SIZING ON PAPER

FIELD OF INVENTION

This invention is related to paper manufacture and more specifically to paper sizing. The invention is related to enhancement of paper sizing in neutral or alkaline conditions.

BACKGROUND

Sizing is used during paper manufacture to reduce the paper's tendency to absorb liquid when the paper is dried. The goal of sizing is to allow inks and paints to remain on the surface of the paper and to dry there, rather than be absorbed into the paper. To reach this goal various sizing agents have been developed and commonly used in papermaking. Paper sizing may be conducted at the wet-end of papermaking process or a suitable coating may be applied on dried paper. Wet-end sizing agents may also have other functionalities than increasing resistance to water penetration only. Wet-end sizing agents may also decrease dusting, control spread of inks, improve dewatering, improve paper quality among other functions.

Paper sizing at the wet-end of papermaking process uses internal sizing agents. The internal sizing agents have some basic characteristics such as high hydrophobicity, good retention on fibers, and uniform distribution throughout the fiber surfaces. Internal sizing agents must have characteristics such that they will be strongly bonded with fibers. Rosin is the oldest internal sizer and effective for acidic papermaking conditions, however it loses it efficacy under higher pH-values. Alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) have been specifically developed as internal sizers for basic or neutral papermaking conditions.

ASA shows many advantages over AKD on various paper grades. ASA reacts with cellulose hydroxyl readily and develops an instant on-machine sizing effect. This is especially important for many paper grades with surface sizing or coating. Fast sizing development achieved with ASA ensures that the application of subsequent surface chemicals remain mostly on the surface of the paper web.

AKD, on the other hand reacts relatively slowly with cellulose and the sizing development may take days or weeks after drying. Moreover, paper sized with AKD tends to have a low surface friction coefficient. Low surface friction coefficient may limit usability of the paper for example in printing as the paper may be too slick or slippery for automatic stackers.

Unlike AKD, ASA does not lower paper surface friction coefficient. Structurally, ASA is unsaturated linear hydrocarbon chain having five-membered anhydride ring. The anhydride ring has no fixed position in the chain, and thus ASA is a mixture of isomers. The generally accepted ASA sizing mechanism is that the anhydride group reacts with cellulose hydroxyl groups (esterification) and the long hydrophobic chains protect fiber from water penetration. However, ASA sizing performance is negatively affected by papermaking wet-end conditions due to ASA hydrolysis and loss of sizing efficiency.

Various strategies have been developed to enhance ASA performance under alkaline papermaking conditions. Most paper mills using ASA use cationic starch as emulsifying agent. Cationic starch has been shown to promote ASA sizing efficiency and greater starch dosages will typically lead to higher sizing level. However, starch is often not a desired constituent in papermaking mills because it may lead to excessive biological growth and deposit issues. Alum (aluminum sulfate) has been reported to further enhance the sizing performance of the ASA/cationic starch system. It is believed that alum increases the driving force for the attachment of starch and ASA to fiber.

In papermaking industry usually the ingredients are added into the suspension. However, adding acid into the suspension to lower the pH would require large amounts of acid and would not be economically feasible. In addition, in many cases lowering of pH of the suspension is not possible; for example the process of making paper with high brightness (e. g. white writing paper) needs to have precipitated calcium carbonate (PCC) filler in the slurry and in this case the pH cannot be lowered as PCC does not work at lower pH.

Therefore, there is a need for improving ASA performance specifically in alkaline wet-end conditions. In paper industry one essential parameter is cost and adaptability with the

existing methods and machinery. Any new method should be economic to use and should require only minimal adaptions to the existing systems.

SUMMARY OF INVENTION

This invention provides a new and economic method to improve ASA sizing effect in neutral and alkaline wet-end papermaking process.

In the present invention it was surprisingly found that applying a pH lowering agent directly on surface of paper formed in alkaline or neutral wet-end papermaking process improves ASA sizing efficiency markedly.

It is an object of this invention to provide an economic method to improve ASA sizing efficiency in alkaline or neutral wet-end papermaking process.

The current invention provides a method for enhancement of alkenyl succinic anhydride (ASA) sizing on paper, the method comprising the steps of: a) forming a paper sheet or web from pulp suspension in neutral or alkaline wet-end papermaking process, where ASA is used as an internal sizing agent in the suspension; b) lowering pH of the paper sheet or web by applying lowering agent onto the paper sheet or web, said agent being capable to lower pH of the paper to a range between 4 and 8, preferably to a range between 4.5 and 7.5; and c) allowing the paper sheet or web to dry.

In certain embodiments the pH lowering agent is applied by spraying the paper, i.e. by spraying the paper or board web or by spraying the paper or board sheet.

In certain embodiments the pH lowering agent is selected from the group consisting of a mineral acid, an organic acid, an acrylic acid-containing polymer, a conjugate acid of a weak base, an amine-containing polymer or its salt, and any combinations thereof. In certain embodiments the mineral acid is selected from the group consisting of phosphoric acid, boric acid, sulfuric acid and hydrochloric acid. In certain embodiments the organic acid is selected from the group consisting of formic acid, acetic acid, citric acid, malic acid and lactic acid. In certain embodiments the amine-containing polymer, is polyvinylamine,

polyethylenimine, polyamidoamine, or polyamidoamine epichlorohydrin. In certain preferable embodiments the pH lowering agent is citric acid.

In certain embodiments the pH lowering agent is applied on the paper product in an amount ranging from 0.1 lb/ton of paper to 20 lb/ton of paper, more preferably 1- 10 lb/ton of paper, most preferably 2-6 lb/ ton of paper.

In certain embodiments the ASA internal sizing agent further comprises starch or polyacrylamide.

In certain embodiments the ASA internal sizing agent further comprises starch and ratio of starch to ASA is within a range of 1:5 to 5:1 (w/w), more preferably between 1:1 to 2:1 (w/w).

In certain embodiments a coagulant is present in the suspension. The coagulant may be selected from a group consisting of glyoxylated polyacrylamide, cationic starch, polyaluminum chloride, alum, polyamine, polydiallyldimethylammonium chloride (poly-DADMAC), polyvinylamine, polyamidoamine epichlorohydrin, and polyethylenimine (PEI). In certain embodiments the coagulant is cationic starch having a degree of substitution (DS) in the range of 0.01 to 0.3.

In certain embodiments a flocculant is present in the suspension.

In certain embodiments the suspension contains calcium carbonate, preferably precipitated calcium carbonate (PCC), as filler.

Pulp suspension of cellulosic fibers, suitable for use in the present invention, may be obtained by any known pulping method, such as chemical pulping, mechanical pulping or chemithermomechanical pulping (CTMP), In certain embodiment the pulp suspension comprises softwood pulp, hardwood pulp, recycled pulp or any combination thereof.

In certain embodiments the enhancement of ASA sizing is measured as increased ink penetration time wherein the ink penetration time is increased by at least 25% compared to

ink penetration of similarly treated paper sheet without treatment of the sheet with the pH lowering agent.

Another object of the current invention is to provide a paper product having an enhanced ink penetration time, said enhancement being achieved by a method comprising the steps of: forming a paper sheet from pulp suspension in neutral or alkaline wet-end papermaking process, where ASA is used as an internal sizing agent in the suspension; lowering pH of the paper sheet by applying lowering agent onto the paper sheet, said agent being capable to lower pH of the paper to a range between 4 and 8, preferably to a range between 4.5 and 7.5; and allowing the paper sheet to dry.

In certain embodiments the pH lowering agent is applied by spraying the paper.

In certain embodiments the pH lowering agent is selected from the group consisting of a mineral acid, an organic acid, an acrylic acid-containing polymer, a conjugate acid of a weak base, an amine-containing polymer or its salt, and any combinations thereof. In certain embodiments the mineral acid is selected from the group consisting of phosphoric acid, boric acid, sulfuric acid and hydrochloric acid. In certain embodiments the organic acid is selected from the group consisting of formic acid, acetic acid, citric acid, malic acid and lactic acid. In certain embodiments the amine-containing polymer, is polyvinylamine, polyethylenimine, polyamidoamine prepared by reacting adipic acid with diethylenetriamine, or polyamidoamine epichlorohydrin. In certain the pH lowering agent is citric acid.

In certain embodiments the pH lowering agent is applied on the paper product in an amount ranging from 0.1-20 lb/ton of paper, more preferably 1-10 lb/ton of paper, most preferably 2-6 lb/ton of paper.

In certain embodiments the ASA internal sizing agent further comprises starch or polyacrylamide. In certain embodiments the ASA internal sizing agent further comprises starch and ratio of starch to ASA in step is within a range of 1:5 to 5:1 (w/w), more preferably between 1:1 to 2:1 (w/w).

In certain embodiments a coagulant is present in the suspension. In certain embodiments the coagulant is selected from a group consisting of glyoxylated polyacrylamide, cationic starch, polyaluminium chloride, alum, polyamine, poly-DADMAC, polyvinylamine, polyamidoamine epichlorohydrin, and PEI. In certain embodiments the coagulant is cationic starch having a degree of substitution (DS) in the range of 0.01 to 0.3.

In certain embodiments a flocculant is present in the suspension. In certain embodiments the suspension contains precipitated calcium carbonate (PCC) as filler. In certain embodiment the pulp suspension comprises softwood pulp, hardwood pulp, recycled pulp or any combination thereof. In certain embodiments the paper product is a carton board, a liner board, a writing paper, an office paper, a publishing book, a paper bag and sack, a gypsum board liner or a wrapping paper. In certain embodiments the ink penetration time is increased by at least 25% compared to compared to ink penetration of similarly treated paper sheet without treatment of the sheet with the pH lowering agent.

The invention according to this disclosure provides clear advantages over the known art. The efficiency of ASA sizing can be increased markedly with the method of this invention. The method provides means to limit the amount of starch used and thus decreases risk of biological growth in the mills. Application of pH lowering agent can easily be combined in existing papermaking processes and machines. The amounts of pH lowering agent are low and the agents used are inexpensive.

Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating specific embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

By “paper” as used in this disclosure, is meant both paper and board, even if not always explicitly stated so. Furthermore “paper sheet”, as used in this disclosure, encompasses and is synonymous with paper webs and board webs as well as board sheets.

By “sizing”, or “paper sizing” as used in this disclosure, it is meant a fibrous substrate's ability to resist wetting or penetration of a liquid into a paper sheet.

By “sizing efficiency” as used in this disclosure, it is meant the ability of the sized paper to resist wetting or penetration of liquid into paper sheet and is measured by ink penetrating time.

By “neutral or alkaline wet-end papermaking process” as used in this disclosure, it is meant a papermaking process, where the paper sheets are formed from fiber slurries having pH generally in the range of 7.0-8.5. Depending on multiple factors, such as the type of pulp used, the type of paper produced, the process includes adding various chemicals in various stages of the process. Such chemicals may for example act as wet strength additives, dry strength additives, binding agents, fillers, retention agents, and so on. The invention described in this disclosure is applicable to any neutral or alkaline wet-end papermaking process.

By ‘coagulant’ it is meant various high charge cationic additives including but not limited to glyoxylated polyacrylamide, cationic starch, polyaluminum chloride (PAC), poly-dimethylamine-epichlorohydrin (a polyamine), poly-ethyleneimine (PEI) and poly-diallyldimethylammonium chloride (DADMAC).

The starch may be any type of starch, e.g. cationic starch, non-ionic starch, degraded, non-degraded starch, oxidized starch, or slightly anionic oxidized starch. Starch may be potato, rice, corn, waxy corn, wheat, barley, maize or tapioca starch. Typically the amylopectin content of the cationic starch is in the range of 65 – 90 %, preferably 70 – 85 %. In certain embodiments at least 70 weight-% of the starch units of the cationic starch have an average molecular weight (MW) over 20 000 000 g/mol, preferably 50 000 000 g/mol, more preferably 100 000 000 g/mol. Cationic starch derivatives include primary, secondary, tertiary, or quaternary amine starch derivatives and other cationic nitrogen substituted

starch derivatives, as well as cationic sulfonium and phosphonium starch derivatives. Starch may be cationized by any suitable method. Starch may be cationized by using 2,3-epoxypropyltrimethylammonium chloride or 3-chloro-2-hydroxypropyl-trimethyl-ammonium chloride. It is also possible to cationize starch by using cationic acrylamide derivatives, such as (3-acrylamidopropyl)-trimethylammonium chloride. Cationic starch has usually a degree of substitution (DS), which indicates the number of cationic groups in the starch on average per glucose unit, in the range of 0.01 – 0.5, preferably 0.02 – 0.3, more preferably 0.035 – 0.2, even more preferably 0.05 – 0.18, sometimes even preferably 0.05 – 0.15.

By 'flocculant' it is meant polymeric additives that are used to improve retention, drainage and sheet or web formation in the papermaking process. The flocculants can be cationic, anionic, nonionic, or amphoteric. A cationic flocculant is a polymer containing one or more cationically charged groups originating from monomers selected from dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate or their quaternary ammonium salts, diallylcyclohexylamine hydrochloride, diallyldimethylammonium halide, methacrylamidopropyltrimethylammonium halide, allyl amine. The cationic flocculant can also be selected from reaction derivatized polyacrylamides, cationized starch or guar gum, said polymers having a molecular weight of greater than 1,000,000 daltons. An anionic flocculant is a polymer containing one or more anionically charged groups originating from monomers selected from acrylic acid, 2-acrylamido-2-methylpropane sulfonate, maleic acid, itaconic acid, vinyl sulfonic acid and 2-hydroxy-3-acrylamide propane sulfonate, or their water-soluble alkali metal salts. The anionic flocculant may be prepared by hydrolyzing acrylamide polymers, said polymers having a molecular weight of greater than 1,000,000 daltons. An amphoteric flocculant contains both one or more cationically charged groups and one or more anionically charged groups. A nonionic flocculant can be selected from the group consisting of polyethylene oxide and poly(meth)acrylamide.

The use of the word "a" or "an" when used in conjunction with the term "comprising" in the claims and/or the specification may mean "one," but it is also consistent with the meaning of "one or more," "at least one," and "one or more than one."

Throughout this document, the term "about" is used to indicate that a value includes the standard deviation of error for the device or method being employed to determine the value.

The use of the term "or" in the claims is used to mean "and/or" unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and "and/or."

As used in this disclosure, the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

Aqueous dispersions of alkenylsuccinic anhydride (ASA) cellulose-reactive sizing agent have been widely used in the paper and board making industry for many years as internal sizers for basic or neutral papermaking conditions, for sizing a wide variety of grades which include printing and writing grades and bleached and unbleached board grades. However, ASA sizing performance is negatively affected by papermaking wet-end conditions due to ASA hydrolysis and loss of sizing efficiency. The present invention provides a method to improve ASA sizing efficiency in alkaline or neutral papermaking process by applying a pH lowering agent on the surface of formed paper web. The pH lowering agent increases the ASA sizing efficiency by lowering the pH of the paper and/or by increasing bonding interaction between the acid and cellulose fibers and/or ASA and the cellulose fibers. The method provided in this disclosure is generally applicable to any neutral or alkaline wet-end papermaking process irrespective of various additives and chemicals added during the process into the slurry.

In one embodiment of the invention, a pH lowering agent is applied on a surface of a formed paper or board web. The pH lowering agent may be applied on upper side of the paper web or on lower side of the paper web, or on both sides. In one preferred embodiment the pH lowering agent is sprayed on the paper surface(s).

In one embodiment of the invention, the pH lowering agent is an agent that is capable of lowering the pH of the paper surface to pH 4-8, more preferably to pH 4.5-7.5. The pH may be measured from wet paper surface or from water extracted from the paper.

According to one embodiment of the invention the pH lowering agent is selected from the group consisting of: a mineral acid, an organic acid, an acrylic acid-containing polymer, a conjugate acid of a weak base, an amine-containing polymer or its salt, and any combinations thereof.

According to one exemplary embodiment, the pH lowering agent comprises a mineral acid selected from the group consisting of phosphoric acid, boric acid, sulfuric acid, hydrochloric acid, and combinations thereof.

According to one exemplary embodiment, the pH lowering agent comprises an organic acid selected from the group consisting of formic acid, acetic acid, citric acid, malic acid, lactic acid, and combinations thereof.

According to one exemplary embodiment, the pH lowering agent comprises an acrylic acid containing polymer selected from the group consisting of polyvinylamine, polyethylenimine, polyamidoamine, polyamidoamine epichlorohydrin, and any combinations thereof. In one further embodiment the polyamidoamine is prepared by reacting adipic acid with diethylenetriamine.

According to one exemplary embodiment, the pH lowering agent comprises ammonium chloride.

According to one exemplary embodiment, the pH lowering agent is sprayed on the paper in an amount of ranging from 0.1-20 lb/ton of paper, more preferably 1-10 lb/ton of paper, most preferably 2-6 lb/ton of paper.

According to one exemplary embodiment the pH lowering agent is citric acid. According to one embodiment citric acid is sprayed in an amount ranging from 0.1-20 lb/ton of paper, more preferably 1-10lb/ton of paper, most preferably 2-6 lb/ton of paper.

The efficacy of the ASA sizing is generally measured as ink penetrating time. In the invention according to this disclosure it was surprisingly found that applying a pH lowering agent on paper web in neutral or alkaline wet-end papermaking process, the ink penetration time of the paper increased at least by 25% as compared to similarly treated paper without the application of the pH lowering agent.

The efficacy of ASA sizing was increased by application of pH lowering agent on paper web irrespective of the coagulant used in the papermaking process. Exemplary coagulants are glyoxylated polyacrylamide, cationic starch, polyaluminium chloride, alum, polyamine, poly-DADMAC, polyvinylamine, polyamidoamine epichlorohydrin, PEI.

The efficacy of ASA sizing was increased by application of pH lowering agent on paper web irrespective of the flocculants used in the papermaking process.

The efficacy of ASA sizing increased by application of pH lowering agent on paper web irrespective of presence or absence of alum.

The efficacy of ASA sizing increased by application of pH lowering agent on paper web irrespective of the starch/ASA ratio in the slurry. Starch/ASA ratio according to certain embodiments is 1:5 to 5:1 (w/w), more preferably 1:1 to 2:1 (w/w).

The following examples are included to demonstrate certain embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

Materials and methods used in the examples

Coagulant A (FB3300 sold by Kemira Chemicals) used in some of the below examples is a commercial glyoxylated polyacrylamide sample prepared by cross-linking reaction

between a poly(acrylamide-co-dimethyldiallyammonioum chloride) based polymer and glyoxal.

Coagulant B (Fennocel 5137 sold by Kemira Chemicals) used in some of the examples is a cationic starch sample with a degree of substitution (DS) of 0.15.

ASA emulsifier was a cationic starch sample with DS of 0.05 (Fennobond 1000, sold by Kemira Chemicals).

APAM A (Kemira Chemicals) is a commercial dry polyacrylamide sample prepared by copolymerization of acrylamide and sodium acrylate. The weight average molecular weight of the product was around 20 million Daltons.

Anhydrous citric acid (>99.5%), sodium bicarbonate (>99%), sodium sulfate ((>99%), and anhydrous calcium chloride (>96%) were purchased from Sigma Aldrich.

Hydores AS 2300 is a commercial ASA sample (sold by Kemira Chemicals).

ASA emulsion preparation

Hydores AS 2300, Fennbond 1000 and water were first added to a high speed blender. The solid content of ASA was 1% while the weight ratio of ASA to starch was adjusted as shown in the examples below. The mixture was emulsified under high speed blending for two minutes. Finally the produced emulsion was stored at 4°C and used 3 hours after emulsification.

Handsheet preparation

Handsheets were prepared using a pulse mixture (2.5 wt%) of virgin bleached hardwood (50%) and virgin bleached softwood (50%). The Canadian Standard Freeness as a measure of drainage rate of diluted pulp was 450 mL. In the following steps, pulp dilutions were carried out using a specially formulated water to simulate papermaking mill white water. This formulated water contained 150 ppm of sodium sulfate, 35 ppm of calcium chloride, and 200 ppm alkalinity (adjusted by sodium bicarbonate.) The final pH was adjusted to 7.8 using dilute hydrochloric acid and sodium hydroxide. During handsheet making, the pulp

suspension was first diluted to 0.5 wt%. Next ASA emulsion, coagulant and APAM A were introduced to the diluted pulp suspension sequentially with a time interval of 30 seconds. The dosages of ASA, coagulant, and APAM were 3 lb/ton, 4 lb/ton, and 0.3 lb/ton, respectively. The pulp suspension was agitated with an overhead mixer during chemical addition to ensure proper mixing. Then, four 3-g sheet of paper were formed using a standard 82 x8" Nobel & Woods handset mold, to target a basis weight of 52 lb/3470 ft^2. The handsheets were pressed between felt in the nip of a pneumatic roll press at about 15 psig and dried on a rotary dryer at 110 °C. Last, the handsheets were conditioned in the standard TAPPI control room overnight before paper testing.

Size test by ink resistance

The sizing performance of handsheet was evaluated based on TAPPI Standard Test Method T530- Size Test for Paper by Ink Resistance. This method measures the resistance of paper to permeation of an aqueous acidic dye (naphtol green B with 15 N formic acid) and is useful general purpose test for degree of sizing. In a typical test, a piece of handsheet contacts the dye either with the top side or the bottom side. Sizing level was evaluated as the time required reaching 80% reflectance endpoint. The top side refers to the side of handsheet in contact with dryer surface, while the bottom side refers to the side of handsheet in contact with felt.

Examples 1 and 2 Glyoxylated polyacrylamide as coagulant

Table 1. Citric acid spray considerably improves poor ASA sizing when the coagulant is glyoxylated polyacrylamide.

Example no.	*Alum dose lb/ton*	*4lb/ton dry strength resin*	*Starch/ASA ratio*	*3lb/ton citric acid spray*	*side contact ink*	*ink penetrating time (seconds)*
1	0	Fennobond 3300	1:1	no	bottom	4
					top	6
2	0	Fennobond 3300	1:1	yes	bottom	576
					top	869

In examples 1 and 2 (Table 1) glyoxylated polyacrylamide was used as a coagulant. Starch/ASA ratio in the ASA emulsion was 1:1. In example 1 the handsheet was not treated with citric acid spray while in example 2, the sheet was sprayed with 3 lb/ton citric acid. The results shown in Table 1, shows that glyoxylated polyacrylamide as a coagulant

did not provide any sizing improvement under the test conditions of 200 ppm alkalinity at pH 7.8. Example 2 shows that citric acid spraying considerably increased the ink penetration time thus proving that citric acid spraying improved poor ASA sizing when the coagulant is glyoxylated polyacrylamide.

Examples 3 and 4 cationic starch as coagulant

Table 2. Spraying organic acid enhances ASA sizing when coagulant is cationic starch

Example no.	*Alum dose lb/ton*	*4lb/ton dry strength resin*	*Starch/ASA ratio*	*3lb/ton citric acid spray*	*side contact ink*	*ink penetrating time (seconds)*
3	0	Fennocel 5137	1:1	no	bottom	756
					top	925
4	0	Fennocel 5137	1:1	yes	bottom	1563
					top	1870

In examples 3 and 4 (table 2) the coagulant used was a cationic starch. Starch/ASA ratio in the ASA-emulsion was 1:1 (w/w), similarly as in examples 1 and 2 (table 1). In example 3 the sheet was not treated with citric acid, while in example 4 the sheet was sprayed with 3 lb/ton citric acid. Without citric acid spray (example 3) the ink penetration time of the paper was clearly longer than in example 1 (table 1), showing that cationic starch improves the ASA sizing better than GPAM coagulant. Example 4 shows that citric acid spraying roughly doubled the penetration time as compared to example 3, proving the efficiency of organic acid spraying to enhance ASA sizing when coagulant is cationic starch.

Examples 5 and 6 glyoxylated polyacrylamide as coagulant with alum

Table 3. Organic acid spray increases penetration time, but alum does not enhance the ASA sizing when glyoxylated polyacrylamide was used as coagulant

Example no.	*Alum dose lb/ton*	*4lb/ton dry strength resin*	*Starch/ASA ratio*	*3lb/ton citric acid spray*	*side contact ink*	*ink penetrating time (seconds)*
5	6	Fennobond 3300	1:1	no	bottom	26
					top	30
6	6	Fennobond 3300	1:1	yes	bottom	563
					top	663

In examples 5 and 6 (table 3) the effect of alum was tested in combination with glyoxylated polyacrylamide. Starch/ASA ratio in the ASA emulsion was 1:1 (w/w). The results show that there was only minimal positive effect of alum (compare example 1 and example 5). Citric acid spray increased the penetration time, but the results were similar as without alum (compare example 2 and 6). Thus alum did not enhance the ASA sizing when glyoxylated polyacrylamide was used as coagulant.

Examples 7 and 8 glyoxylated polyacrylamide as coagulant in presence of alum and high starch/ASA ratio

Table 4. Citric acid spray increases the penetration time, but starch/ASA ratio does not affect the ink penetration.

Example no.	*Alum dose lb/ton*	*4lb/ton dry strength resin*	*Starch/ASA ratio*	*3lb/ton citric acid spray*	*side contact ink*	*ink penetrating time (seconds)*
7	6	Fennobond 3300	2:1	no	bottom	31
					top	44
8	6	Fennobond 3300	2:1	yes	bottom	634
					top	1084

In examples 7 and 8 (table 4) the effect of alum was tested in combination with glyoxylated polyacrylamide as coagulant and 2:1(w/w) starch/ASA ratio in ASA emulsion. The ink penetration in example 7 shows that increase of the starch/ASA ratio does not

affect the ink penetration (compare example 5, table 3 and example 7, table 4). Spraying with citric acid again increased the penetration time.

Examples 9 and 10 cationic starch as coagulant in presence of alum

Table 5. Citric acid increased markedly the penetration time when starch was coagulant in presence of alum.

Example no.	*Alum dose lb/ton*	*4lb/ton dry strength resin*	*Starch/ASA ratio*	*3lb/ton citric acid spray*	*side contact ink*	*ink penetrating time (seconds)*
9	6	Fennocel 5137	1:1	no	bottom	381
					top	601
10	6	Fennocel 5137	1:1	yes	bottom	1195
					top	1010

In examples 9 and 10 (table 5) the effect of alum was tested in presence of cationic starch as coagulant. Starch/ASA ratio in ASA emulsion was 1:1(w/w). Alum did not seem to have an effect on the sizing (compare example 3, table 2 and example 9, table 5). Again spraying citric acid increased markedly the penetration time (Compare example 9 and 10).

Example 11 and 12 cationic starch as coagulant in presence of alum and high starch /ASA ratio

Table 6. Starch/ASA -ratio improves sizing effect slightly (compare example 9 and 11), but major improvement was achieved by spraying citric acid on the paper

Example no.	*Alum dose lb/ton*	*4lb/ton dry strength resin*	*Starch/ASA ratio*	*3lb/ton citric acid spray*	*side contact ink*	*ink penetrating time (seconds)*
11	6	Fennocel 5137	2:1	no	bottom	701
					top	701
12	6	Fennocel 5137	2:1	yes	bottom	1421
					top	1700

In examples 11 and 12 (table 6) the effect of high starch/ASA ratio in presence of cationic starch coagulant and alum was tested. The starch/ASA ratio was 2:1(w/w). The starch/ASA -ratio alone seemed to improve the sizing effect slightly (compare example 9,

table 5 and 11, table 6), but the major improvement was achieved by spraying citric acid on the paper. The improvement in ink penetration time was over 100% as compared to same treatment without citric acid (compare example 11 to example 12).

The examples described above and results shown below in tables 1-6, clearly show that citric acid spraying improves the ASA sizing as measured by ink penetrating time both when a cationic starch coagulant or a glyoxylated polyacrylamide coagulant is used.

Overall the results demonstrate clearly that application of a pH lowering agent, here exemplary wise citric acid, on handsheet surface enhanced ASA sizing performance considerably. First, citric acid alone increased ink penetration time without starch dry strength resins. Furthermore, surface citric acid and wet-end starch displayed synergistic effect on sizing. Finally, addition of alum or increasing emulsification starch dosage did not change the trend and surface citric acid application increased ink penetration time under any testing conditions.

CLAIMS

1. A method for enhancement of alkenyl succinic anhydride (ASA) sizing on paper, board or the like, said method comprising the steps of:
   a) forming a paper or board sheet or web from pulp suspension of cellulosic fibers in neutral or alkaline wet-end papermaking process, where ASA is used as an internal sizing agent in the suspension;
   b) lowering pH of the paper or board sheet or web by applying a pH lowering agent onto the paper or board sheet or web, wherein the pH of the paper or board is lowered to a range between 4 and 8, preferably to a range between 4.5 and 7.5; and
   c) allowing the paper or board sheet or web to dry.

2. The method of claim 1, wherein the enhancement of ASA sizing is measured as increased ink penetration time.

3. The method according to claim 2, wherein the ink penetration time is increased by at least 25% when compared to ink penetration time of a paper or board sheet or web otherwise similarly treated but without applying the pH lowering agent onto the paper or board sheet or web.

4. The method of any one of claims 1-3, wherein in step b) the pH lowering agent is applied on a surface of the formed paper or board sheet or web.

5. The method of any one of claims 1-4, wherein in step b) the pH lowering agent is applied by spraying the paper or board sheet or web.

6. The method of any one of claims 1-5, wherein in step b) the pH of the paper or board surface to pH 4-8, more preferably to pH 4.5-7.5.

7. The method of any one of the claims 1 to 6, wherein the pH lowering agent is selected from the group consisting of a mineral acid, an organic acid, an acrylic acid-containing polymer, a conjugate acid of a weak base, an amine-containing polymer or its salt, and any combinations thereof.

8. The method of claim 7, wherein the mineral acid is selected from the group consisting of phosphoric acid, boric acid, sulfuric acid and hydrochloric acid.

9. The method of claim 7, wherein the organic acid is selected from the group consisting of formic acid, acetic acid, citric acid, malic acid and lactic acid, preferably citric acid.

10. The method of claim 7, wherein the amine-containing polymer is polyvinylamine, polyethylenimine, polyamidoamine, or polyamidoamine epichlorohydrin.

11. The method of any one of claims 1-10, wherein the pH lowering agent is applied on the paper or board sheet or web in an amount ranging from 0.1-20 lb/ton of paper/board, more preferably 1-10 lb/ton of paper/board, most preferably 2-6 lb/ton of paper/board.

12. The method of any one of claims 1-11, wherein the ASA internal sizing agent further comprises starch or polyacrylamide.

13. The method of claim 12, wherein the ASA internal sizing agent comprises starch, and ratio of starch to ASA in step a) is within a range of 1:5 to 5:1 (w/w), more preferably between 1:1 to 2:1 (w/w).

14. The method of any one of claims 1-13, wherein a coagulant is present in the suspension of cellulosic fibers.

15. The method of claim 14, wherein the coagulant is selected from a group consisting of glyoxylated polyacrylamide, cationic starch, polyaluminium chloride, alum, polyamine, poly-diallyldimethylammonium chloride (poly-DADMAC), polyvinylamine, polyamidoamine epichlorohydrin, and polyethylenimine (PEI).

16. The method of claim 15, wherein the coagulant is cationic starch having a degree of substitution (DS) in the range of 0.01 to 0.3.

17. The method of any one of claims 1 to 16, wherein a flocculant is present in the suspension of cellulosic fibers.

18. The method of claim 1 to 17, wherein the pulp suspension of cellulosic fibers contains calcium carbonate, preferably precipitated calcium carbonate (PCC), as a filler.

19. The method according to any one of the claim 1-18, wherein the pulp suspension comprises softwood pulp, hardwood pulp, recycled pulp or any combination thereof.

20. A paper or board product having an enhanced ink penetration time, said enhancement being achieved by a method of anyone of the claims 1-19.

21. The paper or board product of claim 20, wherein the paper or board product is carton board, liner board, writing paper, office paper, publishing book, paper bag and sack, gypsum board liner, wrapping paper.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2018/050506

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H17/15 D21H17/16 D21H17/65 D21H21/16
ADD.

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)
D21H

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/022956 A1 (RODRIGUEZ AUGUSTO [US] ET AL) 3 February 2005 (2005-02-03) paragraphs [0002], [0047], [0053] paragraph [0019] - paragraph [0022] paragraph [0045] - paragraph [0046] examples 1-4; tables 1-4 claims 1-24 -----	1-7, 9-11, 13-21
X	US 2008/124499 A1 (SUNDVALL HELEN [SE] ET AL) 29 May 2008 (2008-05-29) paragraphs [0005], [0020] paragraph [0047] - paragraph [0062] paragraphs [0033], [0034] claims 1-21 ----- -/--	1-7, 10-16, 18-21

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

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/298478 A1 (NAGOSHI MASANORI [JP]) 22 October 2015 (2015-10-22) paragraph [0055] - paragraph [0057] paragraph [0089] - paragraph [0094] claims 1-10	1,8,9, 20,21
X	US 2006/051529 A1 (OGINO TAKASHI [JP] ET AL) 9 March 2006 (2006-03-09) examples 1-14; table 1A paragraph [0031] paragraph [0076] - paragraph [0079]	1,7,9, 12-16,20
X	JP H04 257394 A (MITSUBISHI PAPER MILLS LTD) 11 September 1992 (1992-09-11) paragraph [0002] - paragraph [0009] claims 1-3	1,7,10, 12,20

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FI2018/050506

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005022956 A1	03-02-2005	BR PI0413006 A	26-09-2006
		CN 1849425 A	18-10-2006
		EP 1649105 A1	26-04-2006
		JP 2007500800 A	18-01-2007
		US 2005022956 A1	03-02-2005
		US 2006260774 A1	23-11-2006
		WO 2005012639 A1	10-02-2005
US 2008124499 A1	29-05-2008	CN 101087694 A	12-12-2007
		EP 1855891 A1	21-11-2007
		FI 20041664 A	24-06-2006
		US 2008124499 A1	29-05-2008
		WO 2006067273 A1	29-06-2006
US 2015298478 A1	22-10-2015	CN 104582977 A	29-04-2015
		DE 112013004041 T5	07-05-2015
		JP 6049546 B2	21-12-2016
		JP 2014054832 A	27-03-2014
		US 2015298478 A1	22-10-2015
		WO 2014027614 A1	20-02-2014
US 2006051529 A1	09-03-2006	CN 1830679 A	13-09-2006
		JP 4543841 B2	15-09-2010
		JP 2006077356 A	23-03-2006
		US 2006051529 A1	09-03-2006
JP H04257394 A	11-09-1992	NONE	