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(54) **A PROCESS FOR THE PRODUCTION OF A SUBSTRATE COMPRISING SILICA PIGMENTS WHICH IS FORMED ON THE SURFACE OF THE SUBSTRATE**

VERFAHREN ZUR HERSTELLUNG EINES AUF DER OBERFLÄCHE EINES ANDEREN SUBSTRATS GEFORMTEN SUBSTRATS AUS SILICIUMPIGMENTEN

PROCÉDÉ DE PRODUCTION D'UN SUBSTRAT COMPRENANT DES PIGMENTS DE SILICE FORMÉS SUR LA SURFACE DU SUBSTRAT

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Description

Field of the invention

[0001] The present invention relates to a process for the production of a substrate comprising silica pigments which is formed on the surface of the substrate.

Background

[0002] Silica is often used as a pigment during manufacturing of printing paper, especially paper for ink-jet printers or presses. The silica pigments can also be used generally in digital printing techniques, such as electrophotography, liquid toner or thermal inks, but also in impact printing techniques such as offset of flexography. Besides the increased printing properties, silica also improves the optical properties of a paper or paperboard.

[0003] Silica pigments can be produced in a number of different ways. One way is to treat sodium silicate (waterglass) with a pH reducing medium which will result in the formation of silica pigments. Other methods can for example be dialysis, electrodialysis, peptization, acid neutralization and ion-exchange.

[0004] Silica pigments, used in paper applications, often have high surface area either because of small particle size or high porosity. One effect of high surface area of such pigments is that they are able to bind a lot of water. Compared with conventional pigments, such as calcium carbonate, kaolin or talcum, high surface area silica pigment dispersions therefore requires special attention in order to achieve high solid content coating or surface treatment dispersions. Increasing the dry content of a dispersion comprising silica pigments through the addition of stabilizers and/or thickening agents will partly provide steric or electrosteric stability to the dispersion, but the final dry content is still significantly lower than what is obtained for standard pigment coating formulations. Furthermore, in order for the silica pigments to bind to a paper, addition of high amounts of binders are also often necessary. The binders secures that the pigments binds to each other and to the fibers, which hence improves surface strength and e.g. decrease problems with dusting. However, problems with rheology can occur during the transfer process of the mixture of stabilizer, binder and silica pigments to a surface of the paper. In order to avoid these problems the dry content of the composition need to be decreased and the dry content of compositions comprising silica pigments is thus quite low which reduces the production rate and increases the water content applied to the paper. As a consequent, the paper must be exposed to immense heat treatment in order for the paper to dry.

[0005] During production of printing paper for ink-jet printing it is often advantageous to add cationic polymers to the solution comprising silica pigments, which thereafter is added to the paper surface. Cationic polymers prevent, for example so called bleeding of the print if it is exposed to water or feathering or wicking which might occur along the fibers. However, when the cationic polymers are mixed with anionic silica pigments problems with high viscosity and precipitations often occur.

[0006] Furthermore, a disadvantage with the usage of silica pigments of today is its current cost structure. It is normally very expensive to buy produced silica pigments since the manufacturing process and drying of the pigments in order to make them usable in the paper mills are very energy demanding. Also, it is quite complicated to store and handle the produced silica pigments at the paper mills. Since silica pigments are porous their volume is often quite big and they thus take up a lot of room. As an alternative, the silica pigments can be transported as a solution to the mills but this is also expensive since the dry content of a silica solution, need to be quite low in order for the solution to be stable, i.e. a lot of water also needs to be transported.

[0007] US 25 688 50 discloses a fire resistive vapour barrier paper which comprises a flexible paper sheet coated on at least one surface thereof with coating having a base which consists of bitumen and water-soluble alkali metal silicate.

[0008] US 30 85 861 discloses a method of preparing finely divided precipitated siliceous pigment from a water-soluble alkali mebal salt.

[0009] There is thus a need for an improved process for the production of a substrate comprising silica pigments.

Description of the Invention

[0010] It is an object of the invention to produce a substrate comprising silica pigments in an improved way.

[0011] Another object of the invention is to produce a substrate comprising silica pigments in a cost effective way.

[0012] These, as well as other objects, are achieved by the present invention, which describes a process for the production of a substrate wherein the process comprises; providing a substrate comprising cellulosic fibers, applying a solution comprising water soluble silicate to the surface of the substrate and treating the substrate so that the water soluble silicate is polymerized forming silica pigments on the surface of the substrate and finally drying the substrate with the formed silica pigments on the surface.

[0013] The water soluble silicate is preferable an alkali metal silicate or a silicic acid.

[0014] The polymerization and/or precipitation of the water soluble silicate may occur by addition of a pH altering medium or by the aid of ion-exchange. Other known methods for the polymerization and formation of silica pigments to occur, such as dialysis or electrodialys, may also be used. It is important that the polymerization and formation of silica pigment occur on the surface of the substrate. Therefore, the treatment of the water soluble silicate much be done so that that the silica pigments

are polymerized and formed on the surface.

[0015] The substrate may be treated by addition of a pH altering medium to the surface of the substrate in order for the silica pigments to polymerize and form on the surface of the substrate. The pH altering medium may be a pH reducing or pH increasing medium. The reaction in which silica pigments are formed is a well know reaction of water soluble silicate, preferable alkali metal silicate or silicic acid, at a reduced or increased pH. It is preferred that the solution comprises alkali metal silicate and that a pH reducing medium is added to the surface of the substrate so that silica pigments are formed on the surface of the substrate. It is also possible that the reaction in which silica pigments are formed is a reaction of silicic acid at an increased or reduced pH.

[0016] By separately adding a solution comprising water soluble silicate and a pH altering medium to a surface of a substrate, it is possible to produce silica pigments directly on the surface of the substrate and thus to avoid the disadvantages mentioned above with the production, such as compatibility and runnability, transportation and storage of the silica pigments.

[0017] By separately adding a solution comprising water soluble silicate and a pH altering medium to the surface of the substrate, a reaction in which silica pigments are formed will occur. The reaction will either occur during the addition of the pH altering medium and the solution comprising water soluble silicate to the surface or after the addition of the pH altering medium and the solution comprising water soluble silicate to the surface of the substrate.

[0018] The pH reducing medium may be an inorganic or organic acid such as sulfuric acid, hydrochloride acid or acetic acid, acid salts, pigments or gases. Other examples of pH reducing mediums are sodium orthoborate (borax), sodium bisulfite, sodium bicarbonate, sodium dihydrogen phosphate, carbon dioxide or a combination of two or more of these substances. Acid salts of weak bases and strong acids such as ammonium sulfate, aluminum sulfate, polyaluminum chloride (PAC), polyaluminum nitrate (PAN) and the like may also be used alone or in combination with any of the substances mentioned above.

[0019] The pH increasing medium may be an alkaline solution such as sodium hydroxide or calcium hydroxide.

[0020] Many different types of silica pigments, such as silica gel, precipitated silica and colloidal silica, may be formed during a reaction of water soluble silicate at a reduced or increased pH. The type of silica pigment formed depends on the pH during the reaction. Thus, the specific type of silica formed on the surface of the substrate may be controlled by the amount and concentration of the pH altering medium added. The pH during the reaction in which silica is formed may be basic, neutral or even acid. If a pH reducing medium is added, the reaction will occur when the pH is reduced but it is not always necessary to neutralize the pH of the solution comprising water soluble silicate or to make it acid, even though it sometimes is preferred. Depending on the pH altering medium used, different type of silica pigments are formed. If for example polyaluminum chloride is used, an aluminum silicate is produced.

[0021] Any water soluble silicate can be used in the present process, alkali metal silicates, such as sodium silicate (waterglass), or silicic acid being preferred.

[0022] The solution comprising water soluble silicate may first be added to the surface of the substrate followed by the pH altering medium. It is also possible to first add the pH altering medium to the surface of the substrate followed by the solution comprising water soluble silicate. The reaction in which silica is formed will thus occur after the addition of the solutions to the surface of the substrate.

[0023] It is also possible that the pH altering medium and the solution comprising water soluble silicate are mixed directly before addition to the surface of the substrate. The reaction in which silica is formed will thus occur during the addition, directly before addition or after the addition of the solutions to the surface of the substrate. It is possible that the reaction in which silica pigments is formed are delayed, so even if the solutions are mixed before addition, the reaction can occur on the surface of the substrate.

[0024] It is preferred that the major part of the silica pigments is formed on the surface of the substrate in order to achieve the advantages mentioned here, especially in order to achieve the increased bonding of the pigments to the fibers.

[0025] One or several binders may be added to the pH altering medium and/or to the solution comprising water soluble silicate in order to provide surface or internal strength alternatively wet strength to the substrate. It is also possible to add the binder separately, i.e. without mixing it with the pH altering medium or the solution comprising water soluble silicate. Possible binders are starch, sodium carboxymethyl cellulose, hydroxyethyl cellulose, resins, nanocellulose or microfibrillated cellulose, protein, polyvinylalcohol-polyvinyl acetate, acrylate based polymers, guar gum, polyvinyl alcohol (PVOH), polyvinyl acetate (PVA), styrene acrylate, styrene butadiene or mixtures of these substances. Other binders or rheology modifying agents can also be used.

[0026] Other additives can also be added either to the pH altering medium and/or to the solution comprising water soluble silicate. Example of such additives are optical brightening agents (OBA), calcium chloride, cationic polymers, organic or inorganic pigments, crosslinkers, humidfiers, fibers, primers, hydrophobic agents, biocides or lubricants.

[0027] The application of the solution comprising water soluble silicate and the pH altering medium to the surface of the substrate can be done in a number of different ways. Examples of possible methods are; by the aid of rolls in combination of one or several film presses, with the aid of spray nozzles positioned in one or several lines across the substrate, with spray nozzles adapted for dos-

age of at least two components, with the aid of curtain coaters or with a combination of any of these methods. If a curtain coater is used, it is possible that two or more curtains origin from the same coater if both a solution comprising water soluble silicate and a pH altering medium is added, so that the solution comprising water soluble silicate is added through one curtain and the pH altering medium through another.

[0028] The application of the solution comprising water soluble silicate and the pH altering medium can further be made by use of a sheet or web-fed printing or converting machine. An offset, flexographic or an inkjet printing press can for instance first print the solution comprising water soluble silicate and then transfer the pH altering medium to the surface and thus create wet on wet application step before either applying a third layer without or with intermediate drying.

[0029] It could also be possible to use an in-situ spray system to dose the solution comprising water soluble silicate and the pH altering medium to the surface of the substrate. The treatment could then be followed by drying or alternatively impact or non-impact printing.

[0030] If the pH altering medium and the solution comprising water soluble silicate are mixed directly before the addition to the surface of the substrate it is preferred that the mixing is done in a spray nozzle or on a roll which then transfers the formed silica to the substrate.

[0031] It is preferred to treat both sides of the substrate with the pH altering medium and/or the solution comprising water soluble silicate, but it is also possible to only treat one side of the substrate.

[0032] It is preferred to add an amount of 0,1-20 g/m2 silica pigments per side of the substrate. However, the amount of silica pigments of the substrate depends on the end use of the final product produced. If the final product is a fine paper used for printing, the silica content may preferable be between 0,1-10 g/m2 per side. However, if it is a medium to high quality ink-jet printing paper the silica content is preferable higher. The concentration of water soluble silicate in the solution which is added to the substrate is regulated in such a way that the amount of silica on the surface of the substrate is within the desired range, i.e. the concentration of the water soluble silicate in the solution and the amount of solution added is regulated so that the amount of silica on the surface is within the desired range. The concentration of the pH altering medium might also be regulated in order to adjust and improve certain functional properties of the paper such as static electricity, ink setting mechanisms or deinkability.

[0033] An advantage with the present invention is that the dry content of the added solution can be increased compared to if silica pigments were directly added to the surface of the substrate as described in prior art. Since the solution comprising water soluble silicate and the pH altering medium is separately added to the surface of the substrate the problems as previously described with a solution comprising silica pigments are avoided and it is thus possible to increase the total dry content of the added solutions. Consequently, less water is added to the substrate and the drying demands are decreased.

[0034] Since it is preferred that the formation of silica pigments occur on the surface of the substrate, the silica pigments will bond stronger to the fibers and the amount of binders can possible be reduced without decreasing the quality of the substrate. Since the solution comprising water soluble silicate is added directly to the surface of the substrate the solution will partly be absorbed by the fibers on the surface of the substrate and the formed silica pigment will thus partly be incorporated into the fiber structure of the surface of the substrate which increases the bond between the silica pigments and the substrate.

[0035] Furthermore, during the reaction of water soluble silicate and a pH altering medium different salts are formed. In the art, these are normally washed away during the production of silica pigments which are to be used in a paper mill. However, during reaction of water soluble silicate on the surface of the substrate according to the invention, the formed salts are not washed away. It has been shown that the presence of these salts, improves the properties of the substrate since it can be used for example in order to regulate the electric properties of the substrate. Which type of salts formed depends on the chemicals used but the salts may for example be sodium, aluminum or calcium salts.

[0036] It is also possible to produce a substrate comprising more than one layer of silica pigments on the surface. This can for example be done by addition of a second solution comprising water soluble silicate and a second pH altering medium. It is also possible to produce more than two layers of silica, such as three, four, five or more in the same manner.

[0037] An additional advantage with the process according to the invention is that it is also possible to add a cationic polymer to the surface of the substrate without the disadvantages mentioned above. Since the formation of the anionic silica particles occur on the surface of the substrate there is no mixing of the anionic silica particles and the cationic polymers before addition of the components to the surface of the substrate. Consequently, the anionic silica particles and the cationic polymers will thus not be able to react and form the mentioned precipitations.

[0038] The most useful of cationic polymers are cationic starches, cationic guars and cationic polyacrylamides, the application of which to papermaking have all been described in the prior art. Other cationic polymers may also be used in combination with the silica pigments, either alone or in addition to the cationic starches, cationic guars and cationic polyacrylamides. Examples of such cationic polymers are polyethyleneimine, polydiallyldimethylammonium chloride, copolymers of acrylamide with 2-methylacryloxyethyltrimethyl ammonium chloride, amine-epichlorohydrin condensation products and cationic wet strength resins obtained by condensing

polyamines with dicarboxylic acids and then further reacting the prepolymer with epichlorohydrin. Cationic starches are particularly useful in that they have the advantages of low cost and of imparting dry strength to the paper. The cationic starch used may be derived from any of the common starch producing materials such as corn starch, potato starch, wheat starch and tapioca starch although the potato starches usually yield the most desirable cationized products.

[0039] By using the process according to the invention, the disadvantages mention above can be avoided and the production cost for a substrate, especially an ink-jet printing paper, is strongly reduced. The energy demand for the production of a substrate comprising silica pigments according to the invention is reduced since there is no need for drying or pretreatment of the silica pigments in order for them to be stable enough to transportation to the site of usage (often from the producer to the customer's mill). Furthermore, the energy demand for the production of a substrate according to the invention is decreased since it is possible to increase the dry content of the solutions added to the surface.

[0040] The substrate is dried after the addition of the pH altering medium and/or the solution comprising water soluble silicate in order for a dried substrate to form. All known processes for drying cellulosic substrates may be used. Since the temperature especially of the surface of the substrate is increased during drying, the reaction in which silica pigments is formed may be accelerated during the drying of the substrate. Thus, the silica pigments may be formed during the drying of the substrate.

[0041] The substrate according to the invention will show improved bond between the fibers and the formed silica pigments. Furthermore, the substrate comprises salts which are formed during the production of silica pigments. It is preferred that the substrate is a printing substrate of paper or paperboard which will be printed in a subsequent printing process.

[0042] In terms of this invention, substrate means to also include but not being limited to a paper or paperboard comprising cellulosic fibers. Other materials suitable for printing are also included, such as plastics, polymer coated paper or paperboard, textiles etc. It may also be possible to provide substrates which will be used as flame retardants with silica pigments, i.e. flame retardant substrates.

[0043] The substrate comprises cellulosic fibers and by this, not only cellulosic fibers but all components which origins from cellulosic fibers are included. Examples of such components are microfibrillated cellulose (nanocellulose) or regenerated cellulose. The cellulosic fibers may be softwood and/or hardwood fibers.

Claims

1. A process for the production of a substrate wherein the process comprises the steps of;
   - providing a substrate comprising cellulosic fibers,
   - applying a solution comprising water soluble silicate to the surface of the substrate,
   - treating the substrate so that the water soluble silicate is polymerized forming silica pigments on the surface of the substrate,
   - drying the substrate.
2. The process according to claim 1 wherein the water soluble silicate is alkali metal silicate or silicic acid.
3. The process according to any of the preceding claims wherein the substrate is treated by addition of a pH altering medium to the surface of the substrate.
4. The process according to claim 3 wherein the pH altering medium is a pH reducing medium.
5. The process according to claim 4 wherein the pH reducing medium is, an inorganic or organic acid, an acid metal salt or a gas or a combination of two or more of these substances.
6. The process according to any of claims 3-5 wherein the solution comprising water soluble silicate is added to the surface of the substrate followed by the addition of the pH altering medium.
7. The process according to any of the preceding claims wherein a cationic polymer further is added to the surface of the substrate.
8. A substrate produced according to the process described in any of claims 1-7.
9. A substrate according to claim 8 wherein the substrate is a printing substrate.

Patentansprüche

1. Verfahren zur Herstellung eines Substrats, wobei das Verfahren die folgenden Schritte umfasst:
   - bereitstellen eines Substrats umfassend Zellulosefasern,
   - aufbringen einer wasserlösliches Substrat umfassenden Lösung auf die Oberfläche des Substrats,
   - behandlung des Substrats auf solche Weise, dass das wasserlösliche Silikat polymerisiert wird, wobei sich auf der Oberfläche des Substrats Silikapigmente bilden,
   - trocknen des Substrats.
2. Verfahren nach Anspruch 1, wobei es sich bei dem

wasserlöslichen Silikat um Alkalimetallsilikat oder Kieselsäure handelt.

3. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Substrat durch Zugabe eines pH-Wert-verändernden Mediums auf die Oberfläche des Substrats behandelt wird.

4. Verfahren nach Anspruch 3, wobei das pH-Wert-verändernde Medium ein pH-Wert-reduzierendes Medium ist.

5. Verfahren nach Anspruch 4, wobei das pH-Wert-reduzierende Medium eine anorganische oder organische Säure, ein saures Metallsalz oder ein Gas oder eine Kombination von zwei oder mehreren dieser Substanzen ist.

6. Verfahren nach einem der Ansprüche 3-5, wobei die wasserlösliches Silikat umfassende Lösung auf die Oberfläche des Substrats aufgebracht wird, gefolgt von der Zugabe des pH-Wert-verändernden Mediums.

7. Verfahren nach einem der vorherigen Ansprüche, wobei ein kationisches Polymer zusätzlich auf die Oberfläche des Substrats aufgebracht wird.

8. Substrat, das in einem Verfahren nach einem der Ansprüche 1-7 hergestellt wurde.

9. Substrat nach Anspruch 8, wobei das Substrat ein Drucksubstrat ist.

Revendications

1. Procédé pour la production d'un substrat, dans lequel le procédé comprend les étapes consistant à :

   - fournir un substrat comprenant des fibres cellulosiques,
   - appliquer une solution comprenant du silicate hydrosoluble sur la surface du substrat,
   - traiter le substrat de manière que le silicate hydrosoluble soit polymérisé, formant des pigments de silice sur la surface du substrat,
   - sécher le substrat.

2. Procédé selon la revendication 1, dans lequel le silicate hydrosoluble est un silicate de métal alcalin ou de l'acide silicique.

3. Procédé selon l'une quelconque des revendications précédentes, dans lequel le substrat est traité par ajout, à la surface du substrat, d'un agent de modification du pH.

4. Procédé selon la revendication 3, dans lequel l'agent de modification du pH est un agent réducteur de pH.

5. Procédé selon la revendication 4, dans lequel l'agent réducteur de pH est un acide inorganique ou organique, un sel de métal acide ou un gaz ou une association d'au moins deux de ces substances.

6. Procédé selon l'une quelconque des revendications 3 à 5, dans lequel la solution comprenant du silicate hydrosoluble est ajoutée à la surface du substrat avant l'ajout de l'agent de modification du pH.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel un polymère cationique est en outre ajouté à la surface du substrat.

8. Substrat produit selon le procédé décrit dans l'une quelconque des revendications 1 à 7.

9. Substrat selon la revendication 8, dans lequel le substrat est un substrat d'impression.

REFERENCES CITED IN THE DESCRIPTION

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