(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 625 337 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
**17.07.2019 Bulletin 2019/29**

(21) Application number: **11831005.1**

(22) Date of filing: **04.10.2011**

(51) Int Cl.:
***D21H 19/54*** *(2006.01)* ***D21H 17/28*** *(2006.01)*
***D21H 17/66*** *(2006.01)* ***D21H 21/16*** *(2006.01)*
***D21H 21/54*** *(2006.01)* ***B41M 5/00*** *(2006.01)*
***B41M 5/52*** *(2006.01)*

(86) International application number:
**PCT/SE2011/051182**

(87) International publication number:
**WO 2012/047162 (12.04.2012 Gazette 2012/15)**

(54) **SURFACE TREATMENT COMPOSITION AND PAPER OR PAPERBOARD COMPRISING A SURFACE TREATMENT COMPOSITION**

OBERFLÄCHENBEHANDLUNGSZUSAMMENSETZUNG SOWIE PAPIER ODER PAPPE MIT DER OBERFLÄCHENBEHANDLUNGSZUSAMMENSETZUNG

COMPOSITION POUR TRAITEMENT DE SURFACE ET PAPIER OU CARTON COMPORTANT UNE COMPOSITION POUR TRAITEMENT DE SURFACE

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

(30) Priority: **08.10.2010 SE 1051056**

(43) Date of publication of application:
**14.08.2013 Bulletin 2013/33**

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Printed by Jouve, 75001 PARIS (FR)

## Description

### TECHNICAL FIELD

**[0001]** The present invention relates to a surface treatment composition comprising starch particles, intended for the coating or surface sizing of paper, paperboard or other fibrous webs. The invention also relates a paper or paperboard comprising said composition.

### BACKGROUND OF THE INVENTION

**[0002]** The predominant part of all paper and paperboard that is to be used in copying machines, laser printers, inkjet printers and other different printing methods such as offset printing and flexoprinting, is surface treated with some sort of composition in order to improve printability as well as other properties of the paper or paperboard. The composition is often either a surface sizing composition or a coating color.

**[0003]** If the composition mainly comprises starch in a dissolved form, the surface treatment composition is called a surface sizing. If the composition contains some sort of pigment in the form of solid particles, the composition is called a pigmentation composition or a coating color.

**[0004]** Surface sizing compositions mainly consists of modified starches or other hydrocolloids or surface sizing agents. Furthermore, surface sizing improves the surface strength and printability of the paper or paperboard surface.

**[0005]** Compositions containing pigments, i.e. pigmentation compositions or coating colors, are most often used to improve the printability of the paper. Moreover, the smoothness of the surface of the paper or board is improvement and the control of printing ink absorption can be improved. The colorant of the ink should mainly be absorbed on the surface of the paper and the solvent of the ink should be penetrated into the paper. To these advantages may be added that the paper exhibits an improved "feeling".

**[0006]** A conventional coating color usually contains an inorganic pigment that most often consists of calcium carbonate and/or clay. Other pigments exist too, such as e.g. silicon dioxide and in rare occasions, organic pigments such as plastic pigments. Besides plastic pigments, the paste also contains a binding agent that can consist of dissolved starch and/or a synthetic binding agent. Examples of common synthetic binding agents are styrene butadiene latex and acrylate latex.

**[0007]** Inkjet printing, puts high demands on a printing paper, since the ink must be quickly dried on the substrate and yet provide a high print quality with, e.g. a high optical print density, minimized feathering and bleeding and low strike-through. In recent years it has been found that when multivalent salts, such as calcium chloride, are added to the surface size, the applied ink will precipitate fast on the surface of the paper and give rise to a significant improvement in print quality. This is especially advantageous in inkjet printing. US6207258 discloses a composition useful for surface treating a sheet substrate for inkjet printing, the composition comprising a salt of a divalent metal.

**[0008]** Multivalent cations, e.g. calcium, are sometimes added to sizing or coating compositions in the form of lubricants, e.g. calcium stearate. However, the concentration of calcium, in e.g. calcium stearate is not high enough to give rise to the desired effects on the print quality. Therefore, the calcium amounts needs to be higher than traditionally used in such products.

**[0009]** One problem with the addition multivalent salts to coating and/or sizing compositions is that the high concentration of salt needed in order to achieve the desired effects oftentimes causes rheology problems and undesired precipitations. This is especially a problem when high amounts, such as 1-5 parts of salt, is added to anionically charged sizing, pigmentation or coating compositions. Multivalent cations interact strongly with typical anionic-charged polymers or minerals, or additives which are used in papermaking. Improvement in calcium stability of anionically charged particles can e.g. be improved by providing steric or electrosteric stability. However, high amounts of electrolytes may cause colloidal flocculation and precipitation.

**[0010]** Ink-jet printing can be done with different types of inks, either dye-based inks, pigment based inks or inks based on the combination of pigment and dye. Starch, especially cross-linked starch, improves the printing properties of a paper or paperboard when printed with dye-based inks. Cross-linked starch used as a surface treating composition is described in for example WO03021039. The printing properties for pigment based inks improves by the presence of metal salts.

**[0011]** US2006254738, US3368987, JP20000127610 and US2007246179 describes compositions used for treatments of paper or paperboard.

**[0012]** It is an object of the present invention to find a solution to the problem of adding additives, such as salts of multivalent metals, to surface sizing and/or coating or pigmentation compositions without disturbing the rheological profile of the composition at the same time as it improves the printing properties of both dye-based and pigment based inks.

### SUMMARY OF THE INVENTION

**[0013]** The above object, and other advantages, is achieved by the surface treatment composition of the present invention.

**[0014]** The present invention relates to a surface treatment composition for paper, paperboard or other fibrous webs wherein the composition comprises starch particles that comprise at least one salt.

**[0015]** The at least one salt is incorporated in the starch particle. In this way it is possible to increase the amount of salt added to a surface treatment composition and also

to the surface of a paper or paperboard.

**[0016]** The at least one salt is a salt of a multivalent metal, such as a divalent or trivalent metal. The salt is preferably a calcium, magnesium or aluminum salt, preferably calcium chloride or polyaluminum chloride.

**[0017]** The starch is preferably cross-linked starch. By using cross-linked starch in a surface treatment composition it is possible to subject the composition and/or the starch to elevated temperature without dissolving the entire amount of starch particles. In this way the starch particles tend to stay on the surface of a treated paper or paperboard and thus not being absorbed into the paper or paperboard. This improves the printing properties of the paper or paperboard. Another advantage with the cross-linked starch is that the absorption of the printed ink is improved. It is important that the colorant of the ink is absorbed and mainly kept on the surface of the paper and that the solvent, i.e. water or ink solvent, is quickly released by the composition and absorbed by the paper. Due to the improved absorption of the composition it is also possible increase the amount of ink added to the paper or paperboard. The paper or paperboard is thus not as sensitive to large amount of ink, which makes it possible to improve the printing quality of prints demanding high amounts of ink, such as pictures. Also, some solvent of inks demands cross-linked polymers in order to work properly.

**[0018]** The starch is preferably cross-linked by one or more compounds chosen from the group that consists of methylamine compounds, polyvalent acids, polyvalent acid esters, polyvalent acid halides, polyvalent acid anhydrides, polyaldehydes, polyepoxides, polyisocyanates, divinyl compounds, phosphoryl chloride, polyamine polyepoxide resin, 1,4-butane diolglycidyl ether, epichlorohydrin, trimetaphosphates, mixtures of anhydrides of acetic acid and two and three protonic acids, sodium hypochlorite, or mixtures thereof.

**[0019]** The composition comprises starch particles in an amount of more than 65% by weight, and at least 10% by weight of the starch in the composition consists of starch particles in the entire temperature range of 20-50°C. Both bulk and stiffness of the treated paper or paperboard is improved when starch in the form of particles is present in the composition.

**[0020]** The ratio between the salt and starch of the composition is between 1:50 to 1:5. There is an optimal amount of both starch and salt in the composition. More or less starch respectively salt will deteriorate ink-jet printing properties of the paper or paperboard.

**[0021]** The composition preferably comprises dissolved starch. The dissolved starch will work as a binder of the composition.

**[0022]** The composition may also comprise an additive, preferably an anionic or amphoteric additive which will modify the starch particles. In this way it is possible to alter the charge of the particles making them more stable or more compatible to other additives or to the fibers.

**[0023]** The invention also relates to a paper or paperboard product comprising a surface layer of a surface treatment composition as described herein.

## DETAILED DESCRIPTION OF THE INVENTION

**[0024]** The surface-treatment composition of the present invention comprises starch particles encapsulating at least one salt. The salt can be said to be trapped in the starch particle. The use of such particles in a surface treatment composition increases the printing properties of both dye based and pigment based inks. Also, such composition decreases rheology and viscosity problems that are connected with prior art compositions comprising as high concentrations of salt as the inventive composition. Consequently, higher concentrations of the salts in a surface treatment composition may be used without causing rheology or viscosity problems.

**[0025]** By addition of the surface treatment composition according to the invention to a surface of a paper or paperboard, it is possible to increase the amount of salt on the surface of the paper or paperboard at the same time as the amount of salt, seeing to the entire paper or paperboard, is decreased compared to prior art solutions. This is due to that the surface treatment composition and thus also the salt of the composition is, to a larger extent, retained on the surface of the paper or paperboard. The added salt is thus not absorbed into the paper or paperboard making it possible to decrease the amount of salt added in order to achieve the desired amount of salt on the surface and thus also good printing properties.

**[0026]** Another advantage with the present surface treatment composition is that it improves the printing properties of a paper or boards since the colorant of the ink which is printed is absorbed on the surface and thus not absorbed by the treated paper or paperboard. The cross-linked starch will absorb the ink and since the starch is added and retained on the surface of a paper or paperboard the ink is thus also retained on the surface and not absorbed further into the paper or paperboard. Furthermore, the ink will also come in contact with the incorporated salt since the starch particle will absorb the ink and the ink will thus get in contact with the salt within the starch particle. This also improves the printability since the ink is absorbed on the surface of the paper or paperboard. In this way the surface treatment composition is suitable for both dye based and pigment based inks.

**[0027]** The composition preferably also comprises dissolved starch. The dissolved starch will work as a binder. As a consequence of the dissolved starch, the composition will also comprise dissolved salt that is released when the starch is dissolved. The dissolved salt will improve the printing properties of a treated paper or paperboard in the same way as metal salts used in prior art, i.e. when salt is added as a separate component to a paper or paperboard surface. Furthermore, the dissolved salt will also decrease the viscosity of the composition

which makes it possible to increase the dry content of the composition.

**[0028]** The surface treatment composition can be seen as both a surface sizing composition and a coating color. The surface treatment composition according to the invention preferably comprises both dissolved starch as well as starch particles. Consequently, the composition gives both sizing and coating properties to the treated paper or paperboard.

**[0029]** The salt is a salt of a multivalent metal, such as a divalent or trivalent metal salt, for example calcium, magnesium or aluminum salt, which is added. It is preferred to use calcium chloride or polyaluminium chloride. Use of particles comprising multivalent metals salts according to the invention, render it possible to dose a higher concentration of multivalent metals salt to a sizing or a coating composition without effecting the rheology of the composition negatively. In this way, the printability of the sized or coated paper or board can be improved. Moreover, use of the particles according to the invention also reduces the concentration of the free anion of the multivalent salt, e.g. a chloride ion, in the composition whereby the risk of corrosion is reduced.

**[0030]** The starch particle is preferably cross-linked. The dry starch particles is preferably of a size of between 1-1000 μm, even more preferably between 1-100 pm. It is preferred that the starch particle is a cross-linked starch gel. At none or a very low degree of cross-linking, the starch dissolves if a starch slurry is heated. At an increased degree of cross-linking the amount of the starch that dissolves decreases. The starch used in the invention may have very different degrees of cross-linking. From a relatively low degree of cross-linking, in which about 10 % by weight (by total weight of the composition) of the starch exist as solid particles at a temperature of about 20 to 50 °C, and the rest of the starch constitutes a binder in dissolved form, to a high degree of cross-linking, where about 100 % of the starch exist as solid particles in the temperature interval given above. It is preferred that at least 15 %, preferably at least 20 % by weight (by total weight of the composition) of the starch content of the composition at about 20 to 50 °C is constituted by starch particles according to the invention. It should be noted that what has just been stated is not contradictory to the limitation that more than 65 % by weight (by total weight of the composition) of the solids content should be starch particles, given that the solid pigments of the composition are essentially only composed of these starch particles or only at very small amounts comprise other types of pigments. Independent of the cross-linking degree, the composition may also contain other types of soluble starch or some synthetic polymer, in order to obtain an adequate amount of binder and further improved printability properties. Examples of such polymers are styrene-acrylate, styrene maleic acid anhydride, polyvinylalcohol, polyvinylpyrrolidon, polyvinylformamide.

**[0031]** The starch may also be cross-linked fragmented starch.

**[0032]** The starch is preferably based on potato, maize, wheat, waxy maize, rice or tapioca. The starch may be non-ionic or ionic for example anionic, cationic or amphoteric.

**[0033]** In order to further improve the paper properties that have been mentioned above, e.g. printability, the starch may be additionally modified. The starch may be modified to act as cation active, anion active, amphoteric or hydrophobic. Cationic cross-linked starch may react better with dye-based inks which is anionic.

**[0034]** Preferably, the starch exhibits a degree of substitution of 0.01 - 0.30 and even more preferred 0.02 - 0.20. Uncharged starch too may however work according to the invention.

**[0035]** According to one aspect of the invention, the surface treatment composition may also comprise a minor amount of other pigments in the form of solid particles. Such pigments may e.g. be constituted by calcium carbonate, clay, silicon dioxide and/or aluminum oxide. It is however also conceivable, and in many cases preferable, that the solid content of the composition is essentially only constituted by the inventive starch particles. The composition may also comprise surfactants.

**[0036]** The composition may also comprise an additive, preferably a charged additive which makes it possible to alter the charge of the starch particle in a desired way. The additive may preferably be anionic or amphoteric. By the addition of the additive to the composition comprising starch particles the particles will be modified. It is thus possible to modify the starch particles in order to make them more stable, make them more compatible with the fibers or with other components normally used in papermaking. The additive may preferably be carboxymethyl cellulose (CMC), polyvinyl alcohol, anionic galactoglucomannan, anionic starch, polyphosphoric acid, alginate polyacrylic acid, protein, anionic polyacryl amide, anionic silica, papermakers alum and polymethacrylic acid.

**[0037]** Furthermore, the composition according to the invention also improves brightness, opacity, bulk, surface smoothness and air resistance of a sized or coated paper or paperboard. One reason to this is that the starch particles of the surface treatment composition are amorphous and that they thereby have a much larger specific surface than conventional pigments. The high specific surface of the composition is probably also the reason for the improved printing properties of the paper when inkjet printers are used as the absorption of ink into the paper is improved due to an increased number capillaries having a smaller radius. This large surface also advantageously absorbs printing ink in offset printing. Furthermore, it has been observed that the starch particles, even if being non gelatinised, exhibit an advantageously sticky surface.

**[0038]** The invention further relates to a paper or paperboard product comprising the surface treatment composition described above. The paper or paperboard is

especially suitable for printing with flexographic or digital printing techniques, such as inkjet, electrophotography, liquid toner or electrostatic printing. An big advantage with the composition according to the invention is that it can be used for both dye-based and pigment based inks. For example, it is suitable for hybrid printed products, in which one of the printing methods is based on pigmented water based inkjet inks. Moreover, the invention is also applicable for hybrid inks, which here relates to inks containing both dye and pigment particles.

**[0039]** The addition of the surface treatment composition to a surface of a paper or paperboard may take place in any conventional way. It is for example possible to transfer the composition to the surface by rod coating, blade coating, fountain coating, spray coating or other known coating techniques.

**[0040]** The salt may be incorporated in the starch particle in several different ways. The salt may be incorporated in the starch particles before or after the cross-linking of the starch. If cross-linked fragmented starch is used, the salt may be incorporated before or after the fragmentation of the starch.

**[0041]** It is possible that cross-linked starch particles alternatively cross-linked fragmented starch may be added to a solution comprising dissolved salt. The starch particle will swell in the solution and dissolved salt is thus absorbed and thus incorporated by the starch particles forming the particles according to the invention.

**[0042]** Another possibility for production of starch particles is during the production of cross-linked starch, the salt can thus be added in liquid or solid state just before the extruder which is used for the production of cross-linked starch. If necessary, the pressure and/or temperature is raised during the extrusion.

**[0043]** A third way to incorporate the salt in the starch particles, is to add the salt to a starch slurry and treated in a jet cooker. In a jet cooker, the temperature and pressure is raised by adding direct steam into the cooker. In this way starch particles comprising salt is formed.

**[0044]** The invention may beneficially be used for papers of different types, such as paper for inkjet printers, envelope paper, copying paper, paper for laser printers or other types of paper or paperboard. It is also possible to add the composition to a non-fibrous material, such as a biopolymer film preferably located on the surface of a fibrous material.

**[0045]** The invention is not limited to the described embodiments, but may be varied within the scope of the claims.

## Claims

1. A surface treatment composition for paper, paperboard or other fibrous webs, **characterized in that** the composition comprises starch particles in an amount of more than 65% by weight, and at least 10% by weight of the starch in the composition consists of starch particles in the entire temperature range of 20-50°C and wherein the starch particles comprise at least one salt of a multivalent metal and wherein the ratio between salt and starch of the composition is between 1:50 to 1:5 and the salt is incorporated in the starch particle.

2. The composition according to claim 1, **characterized in that** the salt is a calcium, magnesium or aluminum salt, preferably calcium chloride or polyaluminum chloride.

3. The composition according to any of the preceding claims **characterized in that** the starch is cross-linked starch.

4. The composition according to claim 3, **characterized in that** the starch is cross-linked by one or more compounds chosen from the group that consists of methylamine compounds, polyvalent acids, polyvalent acid esters, polyvalent acid halides, polyvalent acid anhydrides, polyaldehydes, polyepoxides, polyisocyanates, divinyl compounds, phosphoryl chloride, polyamine polyepoxide resin, 1,4-butane diolglycidyl ether, epichlorohydrin, trimetaphosphates, mixtures of anhydrides of acetic acid and two and three protonic acids, sodium hypochlorite, or mixtures thereof.

5. The composition according to any of the preceding claims **characterized in that** the composition comprises dissolved starch.

6. The composition according to any of the preceding claims **characterized in that** the composition comprises an additive, preferably an anionic or amphoteric additive.

7. Paper or paperboard, **characterized in that** it comprises a surface layer comprising the surface treatment composition according to any one of claims 1-6.

## Patentansprüche

1. Zusammensetzung zur Behandlung von Oberflächen für Papier, Karton oder sonstige fibröse Netze, **dadurch gekennzeichnet, dass** die Zusammensetzung Stärkepartikel in einer Menge von mehr als 65 Gew.-% umfasst und zumindest 10 Gew.-% der Stärke in der Zusammensetzung aus Stärkepartikeln im gesamten Temperaturbereich von 20 - 50 °C bestehen und wobei die Stärkepartikel zumindest ein Salz eines multivalenten Metalls umfassen und wobei das Verhältnis zwischen Salz und Stärke der Zusammensetzung zwischen 1:50 und 1:5 liegt und das Salz im Stärkepartikel aufgenommen ist.

2. Zusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** das Salz ein Kalzium-, Magnesium- oder Aluminiumsalz, bevorzugt Kalziumchlorid oder Polyaluminiumchlorid ist.

3. Zusammensetzung nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Stärke vernetzte Stärke ist.

4. Zusammensetzung nach Anspruch 3, **dadurch gekennzeichnet, dass** die Stärke durch eine oder mehr Verbindungen vernetzt ist, die aus der Gruppe ausgewählt werden, die aus Methylaminverbindungen, polyvalenten Säuren, polyvalenten Säureestern, polyvalenten Säurehalogeniden, polyvalenten Säureanhydriden, Polyaldehyden, Polyepoxiden, Polyisocyanaten, Divinylverbindungen, Phosphorylchlorid, Polyaminpolyepoxidharz, 1,4-Butandiglycidether, Epichlorhydrin, Trimetaphosphaten, Mischungen aus Anhydriden der Essigsäure und Protonensäuren mit zwei und drei Protonen, Natriumhypochlorit, oder Mischungen daraus besteht.

5. Zusammensetzung nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Zusammensetzung gelöste Stärke umfasst.

6. Zusammensetzung nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Zusammensetzung ein Additiv, bevorzugt ein anionisches oder amphoteres Additiv umfasst.

7. Papier oder Karton, **dadurch gekennzeichnet, dass** es/er eine Oberflächenschicht umfasst, die eine Zusammensetzung zur Behandlung von Oberflächen nach einem der Ansprüche 1 bis 6 umfasst.

**Revendications**

1. Composition destinée au traitement de surface de papier, de carton ou d'autres nappes fibreuses, **caractérisée en ce que** la composition comprend des particules d'amidon en une quantité supérieure à 65 % en poids, et au moins 10 % en poids de l'amidon dans la composition est constitué de particules d'amidon dans toute la plage de températures de 20 à 50 °C et où les particules d'amidon comprenant au moins un sel de métal polyvalent et où le rapport entre le sel et l'amidon dans la composition est compris entre 1:50 et 1:5 et le sel est incorporé dans les particules d'amidon.

2. Composition selon la revendication 1, **caractérisée en ce que** le sel est un sel de calcium, de magnésium ou d'aluminium, de préférence du chlorure de calcium ou du chlorure de polyaluminium.

3. Composition selon l'une quelconque des revendications précédentes, **caractérisée en ce que** l'amidon est de l'amidon réticulé.

4. Composition selon la revendication 3, **caractérisée en ce que** l'amidon est réticulé par un ou plusieurs composés choisis dans le groupe constitué par les composés de méthylamine, les acides polyvalents, les esters d'acides polyvalents, les halogénures d'acides polyvalents, les anhydrides d'acides polyvalents et les polyaldéhydes, les polyépoxydes, les polyisocyanates, les composés divinyliques, le chlorure de phosphoryle, la résine polyépoxyde de polyamine, l'éther diglycidylique de 1,4-butanediol, l'épichlorhydrine, les trimétaphosphates, les mélanges d'anhydrides d'acide acétique et deux ou trois acides protoniques, le hypochlorite de sodium ou leurs mélanges.

5. Composition selon l'une quelconque des revendications précédentes **caractérisée en ce que** la composition comprend de l'amidon dissous.

6. Composition selon l'une quelconque des revendications précédentes **caractérisée en ce que** la composition comprend un additif, de préférence un additif anionique ou amphotère.

7. Papier ou carton, **caractérisé en ce qu'**il comprend une couche de surface comprenant la composition de traitement de surface selon l'une quelconque des revendications 1 à 6.

## REFERENCES CITED IN THE DESCRIPTION

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