The present invention relates to a coating composition that comprises a composite structure with a body of polysaccharide, into which carbonate has been precipitated. The invention also relates to a coated paper or board product, onto which the said composition has been spread on one or both sides into one or more layers; as well as to paint that is formed of the coating composition according to the invention, or that contains the said composition.
Fig. 1

Fig. 1A
LIGHT AND SMOOTH COATING FOR PAPER OR BOARD, OR A PAINT COATING, FORMED USING A COMPOSITE STRUCTURE

CROSS REFERENCE TO RELATED APPLICATIONS


TECHNICAL FIELD

The present invention relates to a coating that employs a composite structure, the body of which consists of polysaccharide, into which carbonate is precipitated. In particular, the invention relates to the use of such a carbonate polysaccharide structure in the coating layer of paper or board, in the coating of paints, or in materials similar to paints (for example in varnishes). Said structure improves the smoothness, thickness, mottling, strength, opacity, and brightness of the coating layer of the finished paper or board or the paint coating, as well as the optical density of the ink, and the stiffness and sizing ability of the coated paper or board.

BACKGROUND

The most common coating pigments, which are used in the manufacture of paper and board, are kaolins, talcs, gypsum, ground calcium carbonate (GCC), and precipitated calcium carbonate (PCC). Additionally, there are more expensive special pigments, such as precipitated aluminium silicates, satin white, and titanium dioxide. In the manufacture of paper and board, coating pigments are preferably used, as they improve the optical properties of the paper and board and the setting of printing ink (the printability), and make it possible to reduce the basis weight of the paper body stock, board or coating layer; in particular, if the coverage of the coating is good. A good coverage appears as the lack of mottling to the human eye.

Paints employ the same coating pigments mentioned above. Titanium is used in considerably larger amounts than in the coating of paper or board, however. Another great difference, compared with the coating of paper and board, is that in latex paints, in particular, latex is used considerably more frequently as a binder than pigments. Regarding paints, the purpose is to form, on the surface that is to be painted, a wear-resistant film coat that is as solid as possible and has a good opacity. Additionally, various additives that improve the formation of a film are used in paints, softening the latex particles and helping to form a solid paint film.

In both coating applications, i.e., in the coating of paper and board and in paints, the purpose of the binder is to attach the pigments to the base, which is to be coated, and to the coating. In paints, a solid coating is formed, while in the coating of paper and board, the purpose of the use of binders is to ensure that the pigments of the coating and the actual coating remain attached to the paper or board during the printing, in particular. In the coatings of paper and board, there is no solid film surface, due to the smaller amount of binder. The purpose of a porous surface, among others, is to provide a suitable setting velocity of ink for each printing method (e.g., offset, gravure printing, flexographic printing, inkjet).

The aim is to make the surface of the base paper or board as even as possible, so as to obtain as good a coverage as possible, by using as small an amount of coating as possible. For that reason, the base paper or board is, typically, first pre-calendered before the coating. In a machine calender, there are metal rollers on both sides of the paper or board; this keeps the thickness standard, but the density varies. In a soft calender, the paper or board travels between a hard and rubber-coated roller. One advantage thereof is that the density variation is minor. In both types of calender, generally, one metal roller is heated. There are also supercalenders and multi-roll calenders, which comprise more than ten rollers, between which the paper or board travels. In the pre-calendering, there are often two rollers and, in the finishing calendering (super and multi-roll calendering), more than ten rollers. In the calendering, the upper and lower surfaces of the paper or board are mechanically pressed against each other. The finishing calendering is carried out, among others, to provide an improved pre-coating or a printable front coat. The greatest disadvantage of calendering is that it decreases the thickness of the coated paper or board, i.e., it increases the density of the product. Other disadvantages include the weakening of stiffness levels, strength properties, and optical properties.

The poor smoothness of the coated paper or board appears as poorer coverage and a need of a larger amount of coating to fill the holes on the surface that is to be coated. When a coated surface is printed, the poor coverage of the coating is often seen as an uneven print quality, i.e., so-called mottling. The poor smoothness of the coating or the resulting poor coverage can also cause gloss mottling or unevenness of the gloss in glossy coated paper and board grades. This is also referred to as the opacity and brightness mottling of the coating. Regarding the mottling of the print, among others, the following types of mottling can be distinguished: back trup, hydrophobic, single-colour, density, and dry mottling. It is believed that the mottling is caused by the differences in micro porosity of the coating structure or an uneven distribution of binder in the coating. The mottling of the print is caused, when more or less ink is absorbed in the mottled area of the paper or board than in the surrounding area.

In addition to the calendering, efforts have been made to respond to the unevenness of the rough base paper or board by adding plastic pigments to the slip. The purpose of the use thereof is, among others, to increase the ability of the coating to react to the irregularities of the base, in order to maintain the light structure of the coated paper or board by smaller calender loads in the calendering. Generally, the light structure is also visible as an improved opacity, brightness, and optical density of the print. Ideally, after the calendering, the coating would have a good coverage, i.e., as little mottling as possible, it would be light, i.e., its thickness would be high, its smoothness good, and the other qualities of paper or board, such as gloss, would be at the target level and the mottling would be minor. The nip pressure of the calendering can be decreased, if some coating provides the desired level of smoothness easier than another. In that case, a lighter, stiffer, and stronger coating is obtained, which still has the desired level of smoothness, and we would be closer to the ideal that is mentioned above.
With paints, there is no calendaring, but also in this coating application, an improved coverage of the surface that is to be painted is obtained by means of a smoother coat of paint. This means that a sufficient coverage can be obtained with a smaller amount of paint, whereby expensive titanium can be saved, in particular.

The picking of the coating of paper and board, i.e., the peeling of the fibres, pigments, or the surface of the coating itself is a very harmful defect in quality, in the printing, in particular. In the printing machines, the material that has peeled off the coating accumulates, on the printing surfaces and in the dampening fluid of the first printing unit (in multi-colour printing), in particular. In printed paper or board, this is visible as mottles, missing spots, the peeling of the coating, and other quality problems. Most generally, the picking of the coating surface causes the peeling of single fibres and fibre bundles; at its worst, the delamination of part of the coating can take place. The picking in the printing is caused by that, for the splitting of the ink in the printing nip, the force that is perpendicular to the coating surface exceeds the local strength of the coating surface at the outlet of the printing nip. Binders are used in an attempt to prevent these quality problems. An example of these comprises starch.

The ability of starch to form the bonding strength of the coating is caused by its large number of hydroxyl groups, which increase its ability to form hydrogen bonds. In plants, starch is found in small (2–150 μm) granules that are separated during the manufacturing process. All plants contain starch. Starch is commercially produced from potato, tapioca, barley, wheat, rice, and corn, however, and to some extent, from tuberous roots, leguminous plants, fruit, and hybrids.

Generally, starch is not soluble in cold water. This is due to the fact that starch polymers are in a well-organized form, bound by hydrogen bonds in the starch granules. When an aqueous starch solution is heated, the starch granules first swell, whereby single starch polymers are released from each other.

Starch is often treated to make the starch cationic; the stability of the solution is increased and/or its rheological properties are improved at higher dry matter contents. Being a polyol, the chemical forming products of starch are, generally, ethers or esters. These treatment alternatives include hydroxy-alkylation, cationization, carboxymethylation, acetylation, thermo-mechanical treatment, enzyme treatment, hydrogen peroxide treatment, sodium hypochlorite treatment, and acid treatment. Starches that dissolve in cold water, i.e., so-called cold-soluble starches, are also provided by treating the starch.

Native (untreated) starch is anionic; therefore, its attachment to the fibre, during the paper and board manufacturing process, without a cationic treatment is poor. At present, cationic starches are ethers that are manufactured using an epoxy chemical that contains a quaternary ammonium group. Cationized starch is the treated starch that is used the most.

Typically, the starch polymers inside the starch granules should be released either by adding to hot water or cooking the aqueous starch solution. The cold-soluble starches mentioned above constitute an exception to this. Typically, the purpose of the coating slip that is used in the coating of paper or board is to provide as high a dry matter content as possible. Generally, an improved water retention, runnability, and quality properties are then achieved. When starch is used, therefore, efforts are made to minimize the amount of water needed in the manufacturing process of starch.

In addition to starch, other strength-improving additives have also been used. Guar gum is a vegetable gum that is used most frequently. Guar gum and locust bean gum are seed gums and consist of galactomannan. Karaya gum has a more complex structure; it is a branched polysaccharide. The use of vegetable gums has been limited by their price that is higher than starch. They have also been more difficult to treat than starch.

Cellulose and nanocellulose also belong to polysaccharides. Nanocellulose or microfibrillated cellulose can be manufactured from all materials that contain cellulose, such as wood. The structure of nanocellulose is considerably smaller than that of a normal cellulose polymer; therefore, it contains a considerably larger number of hydroxyl groups that form hydrogen bonds. Nanocellulose is also called microfibrillated cellulose, nanofibrillated cellulose, nanofibres, and microfibres.

Accordingly, there is a need for a lighter coating of paper or board, or a paint coating, which provides a good coverage and improves the essential quality properties. The light, smooth coating gives the manufacturer of paper or board a possibility to achieve a smooth finish that provides high-quality printing results and reduces the required coating material costs. A coating that has a good coverage can also decrease the basis weight of the base paper or board, to some extent. Additionally, in the pigmentation of paper and board, in particular, an improved pre-coating can be achieved, compared to the known solution.

SUMMARY

An object of the present invention is to provide a new coating pigment that is suitable for paper and board products and paints, improving their smoothness, strength, mottling, coverage, opacity, brightness, the optical density of the print, and their sizing ability.

The purpose of the invention, in particular, is to provide a coating pigment that contains a carbonate polysaccharide composite in its coating structure.

The purpose of the coating pigment in question is to provide an improved smoothness and thickness, while keeping the brightness and opacity of the paper or board product and the paint, in particular, on a good level. The increase in thickness provides a lighter coating structure.

Thus, the present invention relates to a coating composition for the coating, pigmenting, or surface sizing of the paper or board product, containing the said composite structure. This composition is suitable to be used, among others, as the coating pigment of the applications mentioned above.

To be more precise, the coating composition, according to the present invention, containing a composite structure with a polysaccharide body, into which carbonate has been precipitated; its use as a paint; and the application of the said paint wherein on the surface to be painted is such that the coating composition is mixed with optional additives and binders, whereby the composition is spread onto the surface in wet form with a roller or by spraying or in dry form by powder painting, whereby the coat of paint is dried.

Correspondingly, the coated paper or board product, according to the invention, is characterized by on one or both surfaces thereof, is spread into one or more layers, and the method of manufacturing the same is characterized by the
coating composition is spread on one or both sides of the uncoated paper or board product into one or more layers.  

[0025] The present invention is multifunctional and improves various properties. The composite structure, according to the invention, provides, among others, an improvement in the smoothness properties of the products of various applications and a decrease in the motting thereof, as well as an improvement in the evenness of the coating.  

[0026] In the case of fibre products, their important properties, such as brightness, opacity, and printability can also be kept on a good level, while part of the raw materials of the coating can be replaced with the coating pigment, according to the invention, due to its lighter structure. The light structure and smoothness that are caused by the use of the composite, according to the invention, enable a decrease in the calender pressures in the nip, whereby the compaction of the paper or board can be reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] The present invention and its advantages will now be described in further details with reference to the accompanying drawings where:

[0028] FIGS. 1A and 1B show SEM images of the coatings, wherein the carbonate starch composite, according to the invention, is applied on the surface of LWC base paper (FIG. 1A), and a reference coating that uses GCC (FIG. 1B).

DETAILED DESCRIPTION

[0029] The present invention relates to a coating composition that comprises a composite structure, the body of which consists of polysaccharide, on which carbonate is precipitated.  

[0030] The invention also relates to a coated paper or board product, on one or both surfaces of which, the said composition is spread into one or more layers.

[0031] Another application, according to the invention, comprises paints, which are certain kinds of coatings and, correspondingly, can consist of the coating composition, according to the invention, or contain the composition.

[0032] The polysaccharide is preferably selected from starch, carboxy-methyl cellulose, guar gum, pectin, citosine, dextrons, galactomannan, alginites or nanocellulose or a mixture of any of the above, more preferably from starch or nanocellulose, most suitably from starch or cold-soluble starch.

[0033] In the case of starch, its particles can be treated before using it in the said composite structure, so that the particle is expanded, or even fully or partly broken. Generally, this is carried out by heating which, in the case of the present invention, can be carried out, for example, in a solution that contains carbonate ions and other states of carbonate in the prevailing pH (i.e., in a so-called carbonate ion solution).

[0034] Calcium and/or magnesium carbonate is precipitated into cold-soluble starch, nanocellulose or a mixture thereof from the carbonate ion solution by means of low pressure, heating, mixing, the dosing of an additive that contains alkaline, or a mixture of any of the above.

[0035] The carbonate that is included in the composite structure and precipitated into the polysaccharide is preferably calcium or magnesium carbonate or a mixture thereof, whereby the carbonate ion solution also contains calcium or magnesium ions of a mixture thereof.

[0036] Regarding their crystal structure, precipitated calcium carbonates are typically calcite, aragonite, or vaterite. Typically, calcite is found as flaky and cubic crystal forms. Scalenohedral, rhombohedral, acicular, spherical, and prismatic crystal forms are also possible to obtain by changing the precipitation conditions, such as the concentration of slaked lime and the reaction temperature.

[0037] The manufacture of the composite structure according to the invention is described in Finnish patent application Serial No. 20125569, and the invention of this application relates to the use of the composite structure according to the above-mentioned application in the coating of paper or board, or in paints.

[0038] “Carbonate ion solution” refers to a carbonate system that can contain carbonate ions (CO₃²⁻), bicarbonate ions (HCO₃⁻), carbonic acid (H₂CO₃), and even carbon dioxide (CO₂), but this content and the mutual ratios of these states vary according to the pH of the solution.

[0039] The carbonate system, thus, refers to the change of different carbonate states, according to the pH. The main states are as follows:

[0040] H₂CO₃ ↔ HCO₃⁻ ↔ CO₃²⁻

At an acidic pH, soluble carbon dioxide (CO₂) and, to a minor extent, carbonic acid (H₂CO₃), are the main states of carbonate. In the neutral (on both sides of a pH of 7) and alkaline ranges, bicarbonate or hydrocarbonate (HCO₃⁻) is the main state of carbonate up to a pH of about 10. In a highly alkaline range (pH=10), carbonate (CO₃²⁻) is the main state. The alkalinity of carbonates refers to the content of strong acid, with which the aqueous solution can be titrated to the end point of phenolphthalain. At that time, all of the CO₃²⁻ has been converted into the ion state HCO₃⁻. This takes place at a pH of about 8.3. In the most important pH range of the paper and board manufacturing process, the pH of 6-8, bicarbonate (HCO₃⁻) is the most predominant state. Furthermore, reasonably well dissolved carbon dioxide and some carbonic acid and colloidal carbonate have come to this pH range from the acidic range of the pH range. The solution in the acidic pH range is herein called the acidic carbonate ion solution.

[0041] By increasing the pH or temperature, the bicarbonate ions can be made change into carbonate particles from the carbonate ion solution. Correspondingly, when the temperature is raised, carbon dioxide is released and the carbonate reacts with free calcium or magnesium ions, according to the following reaction equations:

Ca²⁺ + 2HCO₃⁻ → CaCO₃↓ + CO₂↑ + H₂O.

[0042] The reaction above also works, when a sufficiently warm carbonate ion solution is subjected to low pressure or centrifugal force, so that the carbon dioxide is released from the solution in the air.

[0043] When the pH is increased with an alkali, for example with NaOH or Ca(OH)₂, the carbonate particles can be precipitated according to the following reaction equations:

Ca²⁺ + 2HCO₃⁻ + 2NaOH → CaCO₃↓ + Na₂CO₃ + 2H₂O.

Ca²⁺ + 2HCO₃⁻ + Ca(OH)₂ → 2CaCO₃↓ + 2H₂O.

[0044] The bicarbonate in the acidic carbonate ion solution is assumed to help the generated carbonate filler to attach to the polysaccharide polymer. The bicarbonate ion, as such, includes a possibility for the formation of hydrogen bonds, which is important for the attachment of polysaccharides to the fibre, among others. It could be considered that bicarbon-
ate controls the attachment to the hydroxyl groups of polysaccharides before precipitating into carbonate.

When a polysaccharide that is treated with cationization is used, in the invention, it is probable that the cationic groups help the generated carbonate polysaccharide structure attach to the other components of the coating. Due to these reasons, the composite pigment is capable of enhancing the strength bonds of the binders of the coating to the pigments that are used.

As mentioned above, for example, starch, carboxymethyl cellulose, guar gum or nanocellulose or a mixture of any of the above, more preferably starch or nanocellulose, most suitably starch can be used as the polysaccharide.

Amphoteric starches function in a wider pH range than cationic starches. Hence, they are advantageous polysaccharides to be used in the present invention. Other forming alternatives of starch include hydroxy-alkylated, cationization, carboxymethylation, acetylation, thermo-mechanical treatment, enzyme treatment, hydrogen peroxide treatment, sodium hypochlorite treatment, and acid treatment.

Vegetable gums are more difficult to treat than starch. Correspondingly, polyacrylamide (PAM), nanocellulose, and carboxymethylcellulose (CMC) do not need to be treated, as PAM is already found in either cationic or anionic form, and the others already contain a sufficient number of hydroxyl groups that form the hydrogen bonds. Consequently, in their untreated form, they are well suited to be used as polysaccharides in the invention.

The applications of the above mentioned composite structure according to the invention can include the coating of paper, coating of board, and paints. Generally, the composite structure then functions as a coating pigment in the end product.

In paper or board coatings or paint coatings, the composite structure can be used together with other coating pigments or as a single coating pigment.

The composite structure is most suitably dosed into the paint or coating slip in as high a dry matter content as possible.

The fibre product to be manufactured can be coated, surface-sized or pigmented printing paper, packing board, kraft paper or another paper grade that uses mechanical pulp or chemical pulp fibre or both.

The Finnish patent application Serial No. 20125569 shows that, by raising the pH of the carbonate ion solution, which is at an acidic pH, to the neutral range, when the polysaccharide in the acidic carbonate ion solution (pH 1-6.5), by means of heating, the dosing of an additive that contains alkaline additives, low pressure, mixing or a combination of any or all of the above, the carbonate can be precipitated on the polysaccharide. Additionally, it is possible to use any known additives, such as acids that influence the crystal and structure of the precipitated carbonate. The method of precipitating carbonate on polysaccharide, which is described in the said patent application and, particularly, its claims, can thus also be implemented in connection with the formation of the coating composition of the present invention. In the manufacture of paper or board, in addition to the opacity, brightness, and printability (an improvement in the absorption properties of ink), this composite structure of precipitated carbonate and polysaccharide gives the surface-sized, pigmented or coated end product or the latex paints a decrease in mottling and an improvement of smoothness, above all.

Typically, the carbonate polysaccharide composite, according to the invention, is used in the coating, surface sizing or pigmentation of paper or board, and in paints, according to the following alternatives (A-D). The coating, surface sizing or pigmentation can be carried out on one or both sides, one or more times, alternatively, using one or more on-machine or off-machine coating units. When the coating is carried out several times, drying can be carried out between the coating layers, or a new coating layer can be applied directly on top of the wet coating. The coating layer herein refers to a coating layer that is provided on the base paper or board by coating, pigmenting or surface sizing. The base paper or board can be precalendered or uncalendered.

A) The composite according to the invention is mixed with a coating slip together with other pigments, binders, and other additives that are used in the slip, so that the dry matter content of the slip is at least 55%. The paper or board is coated with this slip at least once. Thereafter, the dried and coated paper or board can be calendered to a desired target smoothness and thickness. Other possible layers of coating or pigmentation do not necessarily contain the composite, according to the invention, in the slip. When the paper or board is coated with more than one layers of coating, the previous coating layer can be dried and/or calendered before the new coating layer is spread on top of the previous one. Alternatively, the new coating layer can also be spread directly on top of the previous layer without drying and/or calendering.

B) The composite according to the invention is mixed with a pigmentation paste together with other pigments, binders, and other additives, which are used in the paste, so that the dry matter content of the paste is at least 20%. The paper or board is pigmented with this paste at least once. Thereafter, the dried and pigmented paper or board can be calendered to a desired target smoothness and thickness. The base paper or board, which is pigmented one or more times, can be coated with one or more coating layers, according to alternative A, or with one or more coating layers, which do not contain the said composite. When the paper or board is coated with more than one layer of coating, the previous coating layer can be dried and/or calendered before a new coating layer is spread on top of the previous layer. Alternatively, the new coating layer can also be spread directly on top of the previous layer without drying and/or calendering.

C) In surface sizing, the composite according to the invention is used, whereby the picking problem of the surface can be kept under control, and a coating is obtained, which improves the brightness, opacity, and the optical density of the print. When the composite according to the invention is used in surface sizing, other pigments, binders, and additives can possibly also be used in the surface-sizing paste. The surface sizing can be used as the first coating on the base paper or board before the pigmenting of alternative B and/or the coating of alternative A, or before the spreading of pigmentation or coating layers that contain no composite. When the paper or board is coated with more than one layer of coating, the previous coating layer can be dried and/or calendered before the new coating layer is spread on top of the previous one. Alternatively, the new coating layer can also be spread directly on top of the previous layer without drying and/or calendering.

Consequently, one or more layers of pigmentation, or one or more layers of coating, or one or more layers of surface
size contain the composite according to the invention, whereas the other layers can either contain the said composite or not.

D) The use of the composite according to the invention in paints; particularly, to reduce the required amount of paint, due to an improved coverage, without weakening the picking strength, opacity or wear resistance of the paint layer.

The other additives mentioned above include other pigments, binders, and additives, such as latexes, polyvinyl alcohol, CMC, starches, proteins, caseins, or dispersing agents, anti-foam agents, foam removers, pH regulators, hardening agents, regulators of water retention and rheology, synthetic thickeners, lubricants, optical clarification agents, colouring agents, and microbiocides.

Latex is a binder that is used the most frequently both in the paper or board applications and paint applications. Typically, latexes are combinations of styrene butadiene, polyvinyl acetate, and acrylate latexes or the combinations of their different copolymers. In both of the applications above, efforts have been made to reduce the portion of latex in the coating slip or paint to decrease the costs.

The amount of latex varies according to the printing method. In offset printing, the surface of the paper is moistened by water, whereby the picking strength (wet strength, in particular) is of importance and, generally, 10-15 parts of latex are needed. In gravure printing, no dampening solution is used, but the smoothness of the paper is an important property. In that case, the amount of latex is generally 4-5 parts of latex.

The most common of the other binders are starch, carboxy-methyl cellulose (CMC), polyvinyl alcohol, protein, and casein. Polyvinyl alcohol and CMC yield the best bonding strength, but being more expensive than latex, they are not used to a great extent.

Regarding the other additives that are used in coating slips include dispersing agents, anti-foam agents, foam removers, pH regulators, hardening agents, regulators of water retention and rheology, synthetic thickeners, lubricants, optical clarification agents, colouring agents, and microbiocides.

The base paper or board that is coated with the composite structure mentioned above, particularly, contains chemical pulp fibre and/or wood fibre and/or synthetic fibre. In the present invention, the fibres can be any natural fibres and/or synthetic fibres. In particular, the fibres can comprise chemical pulp or mechanical pulp or a mixture thereof. For example, sulphate and sulphite cellulose fibres, dissolving pulp, nanocellulose, chemi-mechanical (CTMP), thermo-mechanical (TMP) pressure groundwood (PWG), ground pulp, recycled fibre or the fibres of de-inked pulp, can comprise the solid matter. Typically, sulphate and sulphite celluloses are called chemical pulps, and thermo-mechanical pulp, pressure groundwood, and groundwood pulp are called mechanical pulps.

In addition to the coated, surface-sized or pigmented printing papers and packing materials, different special paper grades (e.g., wall paper base and kraft paper), and different paints constitute good applications, since in these products, the smoothness and motting of the coating layer are of great importance. In these applications, particularly, the surface sizing and pigmentation are essential.

The present invention also relates to a method of manufacturing the coated paper or board product, wherein the coating composition mentioned above is spread on one or both sides of an uncoated paper or board product to form one or more layers.

The method of coating, i.e., the method of spreading the composition, can employ methods that contact the paper or board during the coating, or non-contacting coating methods. The most important non-contacting methods are the curtain coating and spray coating. Blade coating, rod coating, air brush coating and film transfer coating are the most important contact methods of coating. The blade coating can be further divided into long dwell time, short dwell time, and jet application. In these methods mentioned above, the coating slip is prepared in an aqueous solution, which is dried after the coating. In the coating of paper and board, the drying is generally carried out with hot air or infrared lamps. Generally, the paints dry by air-drying. There are also waterless or powder coating methods, which are meant to make charged dry pigments attach to the surface to be coated. These methods may also employ the use of binders. The coating can be applied directly on the surface of the manufactured paper or board without a separate intermediate rolling of ink (on-machine coating) or after an intermediate rolling of ink at a separate coating head (off-machine coating). Both sides of the paper or board can be coated simultaneously or at different stages. The coating can be carried out one or more times, whereby drying can be carried out between the different runs of coating. Typically, the dry matter content of the coating slips is about 60% or more, and the amount of coating is 10-30 g/m²/side. In addition, surface sizing and pigmentation are carried out, wherein the composition of the pastes is simpler, and the dry matter contents and desired amounts of coat are lower.

In the surface sizing, the picking strength and stiffness of the paper or board is enhanced, and any partly loose fibres and other components can be bound to the surface.

This also improves the smoothness, porosity, gloss, and the absorption of ink. The surface sizing can also constitute a pre-treatment for the paper and board that is to be coated. Starch, as such, can be used in the surface sizing pastes in a dry matter content of about 10%. In the surface sizing, the amount of surface size on the surface of the base paper or board is, generally, 0.5 . . . 3 g/m²/side. A pond size press or sym-sizer film coater is conventionally used in the surface sizing.

A light coating, i.e., pigmentation, improves the properties and printability of the surface of the paper/board. The paste often contains a pigment that is added to the starch solution, often calcium carbonate, and possible additives. The dry matter contents in the pigments are about 20-55%. The amount of coating is 1 . . . 10 g/m²/side, depending on the paper and board grade and the purpose of use.

Regarding the coverage of the coating, the blade coating provides a surface with a poorer coverage on a rough base paper or board than, for example, the air brush coating, film transfer coating, and the non-contacting coating methods. This is due to the incapability of the blade coating to follow the irregularities of the surface that is coated.

The following non-limiting examples illustrate the invention and its advantages.

EXAMPLES

Example 1

A carbonate ion solution was prepared, so that 170 g of burnt lime (CaO) was mixed with 1000 g of water at 55°C.
The Ca(OH)$_2$—slurry that was thus generated was allowed to react, in the mixture, with the carbon dioxide that was conducted thereto, so that the final pH was 6.2. This solution was allowed to sediment for 48 hours, whereafter the clear solution was separated from the sedimented ingredient. The dry matter content of this solution was 42%. The carbonate ion solution that was thus prepared was used as raw material in the cooking of the coating starch in the tests described below.

Example 2

[0075] The carbonate ion solution that was prepared, according to the previous example, was used as the cooking water of starch in this example. In test point A, 20 parts of starch were cooked (95°C, 30 minutes, mixing) together with the carbonate ion solution of Example 1, so that the final dry matter content of the paste was 50%. The starch that was used was potato starch (coating quality) from Chemigate Oy. In test point B, the same starch was used as in test point A. In test point B, starch was first cooked (95°C, 30 minutes, mixing), and ground calcium carbonate (Hydrocarb 90, Omya) was added thereto by gently mixing, so that the proportion of starch is 20 parts and the final dry matter content is 50%.

[0076] Three different rods were used to coat an uncoated copying paper of 80 g/m$^2$ to three different coat weights. The coating was carried out by a laboratory coater (RK K303 Multicenter), using a velocity of 6. Thereafter, the sheets were dried in a conditioning room for 48 hours, at 23°C, and a relative humidity of 50%. Thereafter, their weight coats were verified and they were soft-calendered in the following conditions:

<table>
<thead>
<tr>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
</tr>
<tr>
<td>two nips</td>
</tr>
<tr>
<td>pressure of 200 kN/m</td>
</tr>
</tbody>
</table>

[0077] The following properties were determined from the calendered samples:

<table>
<thead>
<tr>
<th>Test point</th>
<th>Brightness %</th>
<th>Opacity %</th>
<th>Thickness μm</th>
<th>Picking strength</th>
<th>Smoothness PPS-10 (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>86.5</td>
<td>89.7</td>
<td>149</td>
<td>18</td>
<td>1.4</td>
</tr>
<tr>
<td>B</td>
<td>83.1</td>
<td>85.4</td>
<td>135</td>
<td>14</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The results are shown in Table 1. All of the results are normalized to a coat weight of 8 g/m$^2$.

Table 1 shows that, when the structure of the coating can be kept light (high thickness) and the surface of the coating smooth, excellent brightness and opacity properties are also achieved. If the coated samples of both of these test points had been calendered to the same level of smoothness, the properties of the coating according to the invention (test point A) would even have been better, because the calendering could have been carried out at a lower nip pressure.

Example 3

[0088] The carbonate ion solutions that were prepared, according to Example 1, were used as the cooking water of the cooking of starch in this example. The potato starch that was used in the tests was from Chemigate Oy (Raisamyl).

[0089] In test point A, 35 parts of starch were cooked (95°C, 30 minutes, mixing) together with the carbonate ion solution of Example 1, so that the final dry matter content of the paste was 40%. In test point B, the same starch was used as in test point A. In test point B, starch was first cooked (95°C, 30 minutes, mixing), and ground calcium carbonate (Hydrocarb 90, Omya) was added thereto by gently mixing, so that the proportion of starch is 35 parts and the final dry matter content is 40%.

[0090] Three different amounts of coating were run by the CLC coating machine (CLC 6000) on an LWC base paper of 40 g/m$^2$. A blade coating unit and a velocity of 800 m/min were used in the coating. The target amounts of coating were within 3-9 g/m$^2$. Thereafter, the sheets were conditioned for 48 hours at 23°C, and a relative humidity of 50%, before measurements. Thereafter, the amounts of coating thereof were verified and they were calendered in the same conditions as in the previous Example 2. The following properties were determined from the calendered samples:

[0091] ISO brightness (Minolta Spectrophotometer 3610d), ISO 2470
[0092] Opacity (Minolta Spectrophotometer 3610d), ISO 2471
[0093] Thickness (L&W Thickness tester SE51), ISO 534
[0094] IGT pick (AIC2-5), 4 m/s, medium viscous oil, ISO 3783
[0095] Smoothness (Parker print surface), ISO 8791-4

[0096] The mottling was assessed as follows. The samples were printed at a four-colour Heatset-offset line frequency of 60 l/cm, using round dots. The C70 and B70 frames on the “mottling” areas on both sides of the samples were measured, so that some paper around them was also included in the image. Herein, the clustering method was used, wherein the mottles (0.5-10 mm) are searched by the threshold method, and grouped according to the size and contrast. As the measuring instrument, the Hewlett-Packard ScanJet 7400C desktop scanner was used, with which the version 3.02 of the Hewlett-Packard Precision Scan Pro system software was used. In the measurement, the settings of the system software were according to Table 2.

**TABLE 2**

| Settings of the Precision Scan Pro software for determining the mottling. |
|-----------------------------|-----------------|
| Resolution                  | 1200 dpi         |
| Exposure time “Highlights”  | 235              |
| Exposure time “Shadows”     | 0                |
| Exposure time “Midtones”    | 2.2              |
| Creasing                    | None             |
| Noise removal               | None             |

[0097] The results are shown in Table 3. All of the results are normalized to a coat weight of 8 g/m$^2$. 

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**TABLE 1**

<table>
<thead>
<tr>
<th>Test point</th>
<th>Brightness %</th>
<th>Opacity %</th>
<th>Thickness μm</th>
<th>Picking strength</th>
<th>Smoothness PPS-10 (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>86.5</td>
<td>89.7</td>
<td>149</td>
<td>18</td>
<td>1.4</td>
</tr>
<tr>
<td>B</td>
<td>83.1</td>
<td>85.4</td>
<td>135</td>
<td>14</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Table 3 shows that, when the structure of the coating can be kept light (high thickness) and the surface of the coating smooth, the mottling index is also improved (a lower value). The mottling index is an index that emphasizes the size and contrast of the mottles by the number. If the coated samples of both of these test points had been calendared to the same level of smoothness, the properties of the coating according to the invention (test point A) would even have been better, because the calendared could have been carried out at a lower nip pressure.

The selection of base paper has obviously influenced the levels of brightness. Any other selection would also have provided improved brightness results.

The SEM images of FIG. 1 show that the composite of the invention (test point A) provides a surface that consists of small granules (FIG. 1A). The coating that contains ground calcium carbonate (test point B) obviously constitutes a denser and coarser surface (FIG. 1B) than the test point A, according to the invention (FIG. 1A). The enlargement of the figures is considerably smaller than the resolution of the human eye. When examined visually, the smaller granule provides an improved coverage, due to its homogeneous and small granules.

While the present invention has been illustrated and described with respect to a particular embodiment thereof, it should be appreciated by those of ordinary skill in the art that various modifications to this invention may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. A coating composition for the coating, pigmentation, or surface sizing of a paper or board product, comprising containing a composite structure with a polysaccharide body, into which carbonate has been precipitated.

2. The coating composition according to claim 1, wherein the polysaccharide is starch, cold-soluble starch, carboxymethyl cellulose, guar gum or nanocellulose or a mixture of any of the above, preferably starch or nanocellulose, most preferably cold-soluble starch, whereby the shape of the polysaccharide body is preferably swollen or partly or fully broken.

3. The coating composition according to claim 1, wherein the precipitated carbonate is calcium or magnesium carbonate or a combination thereof, and at least part of the carbonate is preferably precipitated from the solution directly into the polysaccharide body.

4. The coating composition according to claim 3, wherein part of the carbonate is added carbonate, which is preferably calcium carbonate, such as precipitated calcium carbonate (PCC) or ground calcium carbonate (GCC) or a mixture thereof.

5. The coating composition according to claim 1, further comprising other pigments, binders, and additives, such as latex, polyvinyl alcohol, CMC, starch, kaolin, calcined kaolin, talc, titanium dioxide, composite pigments, granule pigments, protein, casein, dispersing agents, anti-foam agents, foam removers, pH regulators, hardening agents, lubricants, regulators of water retention and rheology, synthetic thickeners, lubricants, optical clarification agents, colouring agents, and/or microcicides.

6. The coating composition according to claim 1, wherein a coating slip is having a dry matter content of at least 55%.

7. The coating composition according to claim 1, wherein a pigmentation paste is having a dry matter content of at least 20%.

8. The coating composition according to claim 1, wherein a surface sizing paste is having a dry matter content of at least 2%.

9. Use of the coating composition according to claim 1 as paint.

10. A coated paper or board product, wherein, on one or both surfaces thereof, the composition according to claim 1 is spread into one or more layers.

11. The coated paper or board product according to claim 10, wherein also one or more layers of other coating, pigmentation or surface sizing pastes are spread on one or both surfaces thereof.

12. The coated paper or board product according to claim 10, wherein the coating composition, which has been spread on its surface, has formed after the drying one or more layers of coating, pigmenting, or surface sizing, the basis weight of which is at least 0.05 g/m².

13. The coated paper or board product according to claim 10, wherein it is a surface-sized or pigmented printing paper or packing material, or a special paper grade, such as a wallpaper base or kraft paper.

14. A method of manufacturing the coated paper or board product according to claim 10, wherein a coating composition containing a composite structure with a polysaccharide body, into which carbonate has been precipitated, is spread on one or both sides of the uncoated paper or board product into one or more layers.

15. The method according to claim 14, wherein a contacting or non-contacting coating method is used for the spreading of the coating composition, whereby the contacting methods are selected from the group of curtain and spray coating, electric-field-assisted coating, and dry powder coating; and the contacting methods are selected from a group of blade, rod, and air brush coating, and film transfer coating.

16. The method according to claim 14, wherein the coating composition is prepared in an aqueous solution, and after spreading onto the paper or board product, excess water is removed by drying, preferably with hot air or infrared lamps.

17. The method according to claim 14, wherein the coating is made without a separate intermediary rolling.

18. The method according to claim 14, wherein the coating is made at a separate coating station after intermediary rolling.

19. A method of spreading paint on a surface to be painted, wherein the coating composition according claim 1 is mixed with optional additives and binders, whereby the composition is spread onto the surface in wet form with a roller or by spraying or in dry form by powder painting, whereas the paint of paint is dried.