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(71) **Applicant**: **ARKEMA INC.** [US/US]; 900 First Avenue, King of Prussia, Pennsylvania 19406 (US).

(72) **Inventors**: **LIU, Lily**; 802 Wakehurst Drive, Cary, North Carolina 27519 (US). **DUPONT, Francois**; 85 rue Deleuvre, F-69004 Lyon (FR).

(74) **Agents**: **MORREALE, Lynn B.** et al.; Arkema Inc., 900 First Avenue, King of Prussia, Pennsylvania 19406 (US).

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(54) **Title**: PAPER COATING COMPOSITION COMPRISING VOID LATEX PARTICLES AND CALCIUM CARBONATE

(57) **Abstract**: The present invention relates to paper coating pigments. More particularly, the present invention relates to a paper coating composition comprising plastic pigments and calcium carbonate, to methods for preparing the composition, to the use of the composition in paper coating, and to coated paper prepared with the said composition.

PAPER COATING COMPOSITION COMPRISING VOID LATEX PARTICLES AND CALCIUM CARBONATE

The present invention relates to paper coating pigments. More particularly, the present invention relates to a paper coating composition comprising plastic pigments and calcium carbonate, to methods for preparing the composition, to the use of the composition in paper coating, and to coated paper prepared with the said composition.

BACKGROUND OF THE INVENTION:

In the present invention, the term "paper" means any kind of paper, but also board, card, paperboard and the like.

Coated paper is used for a large range of products including packaging, art paper, brochures, magazines, catalogues and leaflets. Such paper is coated with an aqueous composition, known as a "coating composition" or sometimes as a “coating color”, so as to impart to said coated paper a number of properties, such as opacity, paper gloss, brightness, whiteness or printability, including print gloss.

The coating compositions are generally made of water and of one or more inorganic pigments, such as kaolin, calcium carbonate, talc and/or titanium dioxide. They also comprise one or more binders, which may be of natural origin, such as starch, casein or carboxymethylcellulose (CMC), and/or of synthetic origin, such as the emulsions of latexes: styrene butadiene, styrene-acrylate copolymers or vinyl copolymers. Finally, they may include various additives such as, for example, dispersants, thickeners, water retention agents and/or optical brighteners.

Productivity, quality, and cost reduction are recurrent goal-related themes in the paper technical field. The paper market is indeed notably driven by a continual need for cost effective innovation, and one of the themes in this view is the increase of the solids contents of the paper coating composition. By doing so, it is then possible to reduce the amount of energy required to dry the wet layer of the paper coating composition on the surface of paper.

The productivity, quality and cost reduction goals greatly influence the composition of the coating composition, the number of layers and the coat weights.

For this reason notably, demands on the light weight coated (LWC) paper and ultra light weight coated (ULWC) paper, also known as light lightweight coated (LLWC) paper, have increased. Such types of paper are indeed produced at low cost, in large quantities, on high speed machines. The coat weights are very low. These materials may be coated once and are then called "single coated". They me be coated twice with a pre-layer followed by a top layer and then they are called "double coated". The coating composition may conveniently be applied by means of blade coaters, or by transfer rolls coaters called Metering Size Press or possibly by a curtain coater.

For precise definitions of LWC and ULWC papers, reference can be made to patent document number US 7,758,690. LWC paper is defined as coated to a coating weight of from about 5 g/m^2 to about 13 g/m^2 on each side, for a total grammage (weight per unit area of the coated paper) in the range of from about 49 g/m^2 to about 65 g/m^2. ULWC paper is defined as coated to a coating weight from 5 g/m^2 to 7 g/m^2 per side, for a grammage in the range of from about 35 g/m^2 to about 48 g/m^2.

Clay, or equivalently referred to as kaolin hereafter, is generally used for preparing coating compositions for the manufacture of LWC and ULWC paper. Reference can be made in this regard to PCT patent application WO 00/59841 which relates to kaolin pigments especially useful for coating LWC and ULWC paper for rotogravure and offset printing. Kaolin clay presents the advantage of providing paper gloss and print gloss.

However, the use of kaolin in paper coating composition has one major drawback: an increase of the coating composition solids content generates very high viscosities under high shear rates, which then leads to too high pressure of the metering devices of the coating machines or uncontrolled coat weights or the formation of coating defects such as splitting, bleeding or streaks.

As explained in document WO 2011/124958, high shear rate viscosity, i.e. viscosity ACAV at 10^6 s^{-1}, is a key factor to determine the metering device pressure to apply

for a targeted coat weight. For example, the greater the high shear rate viscosity, the greater the blade pressure must be to control the deposited coat weight. By measuring the ACAV viscosity of the composition, it is thus possible to determine which pressure to apply.

A simple solution to the technical problem of excessive blade pressure would be to reduce the solids content of the coating composition by diluting the dry extract to reduce viscosity. However, the energy required for then drying the wet layer would be increased and the quality of the coated paper would be significantly affected.

It would therefore be advantageous for the formulator to benefit from an alternative to the use of kaolin mineral pigment in coating composition so as to allow an increase of the solids content of the paper coating composition.

An object of the present invention is thus to provide an alternative to the use of kaolin in pigment compositions of paper coating colors.

Another object of the present invention is to provide a solution to the problem of high viscosity under high shear rate associated with the use of kaolin in paper coating compositions.

It is still another object of the invention to provide a pigment composition for paper coating allowing to the preparation of LWC and ULWC papers, coated for off-set printing.

DESCRIPTION OF THE INVENTION:

It has now been found that a specific combination of one mineral pigment along with one plastic pigment can reach the above-mentioned goals.

More precisely, the specific combination of calcium carbonate particles with hollow sphere latex pigments, used as pigment composition in paper coating composition, allow a significant reduction of composition viscosities under high shear rates, and then allow to increase the solids content of the coating composition while maintaining good operating conditions that remain within the usual limits of adjustment.

The inventors have been able to show that increasing the solids content of the paper coating composition also has the following advantages: first of all, reduction of energy consumption when drying the coated paper; gloss maintained due to increased solids content; and need for binders and additives (including optical brightener) reduced.

The combination of calcium carbonate particles and hollow latex pigments used as pigment composition for paper coating allow to meet the conditions needed for the preparation of LWC and ULWC papers, viz. rheology of the paper coating composition adapted to coating processes and high solids content of the paper coating compositions.

Paper Coating Composition:

The coating composition according to the present invention comprises an aqueous suspension of the defined particulate pigment together with the binder and water, and optionally one or more further additive components, as discussed above.

The coating compositions according to the present invention preferably consist essentially of an aqueous suspension of the defined particulate pigment, the binder and water, and optionally one or more further additive selected from the list of additive types given above, with less than about 10% by weight of other ingredients.

It is thus an object of the present invention to provide a paper coating composition for use in producing a coating on paper and other substrates, the so obtained coated paper or substrate having a coating weight of less than or equal to 13 g/m^2 per side. The paper coating composition according to the present invention comprises an aqueous suspension of pigments together with binder, wherein the pigment composition comprises, consists essentially of or consists of:

a) a first pigment which is hollow latex pigments and

b) a second pigment which is calcium carbonate particles,

with the proviso that the pigment composition does not contain kaolin or does contain substantially no kaolin.

According to an aspect of the invention, the paper coating composition according to the present invention comprises an aqueous suspension of pigments together with binder, wherein the pigment composition consists essentially of:

a) a first pigment which is hollow latex pigments and

b) a second pigment which is calcium carbonate particles,

with the proviso that the pigment composition does not contain kaolin or does contain substantially no kaolin.

The paper coating composition is intended for use to coat paper or substrate at a coating weight of less than or equal to 13 g/m^2 per side, e.g. less than or equal to 12 g/m^2 or less than or equal to 11 g/m^2. This coating rate corresponds to light weight coated (LWC) paper and ultra light weight coated (ULWC) paper, also known as light lightweight coated (LLWC) paper.

According to an aspect of the present invention, paper coating composition is intended for use to coat paper or substrate at a coating weight ranging from 5 g/m^2 to 13 g/m^2 per side.

According to another aspect of the present invention, paper coating composition is intended for use to coat paper or substrate at a coating weight of less than or equal to 11 g/m^2 per side.

The paper coating composition of the invention more particularly allows a decrease of the viscosity of the coating at a high shear rate (ACAV viscosity), while maintaining the viscosity of the coating at low shear rate (Brookfield viscosity) as high as possible. This compromise corresponds to obtaining a paper coating that is both workable (maintaining the low gradient viscosity), and can be used for coating at high speed or with a high solids content (decreasing the high-gradient viscosity, to counterbalance the increase in blade pressure).

This property is particularly advantageous in high-speed coating processes (1 000 to 2 000 m/s) or those implementing high solids-content coatings (greater than 70% of their total weight) or those characterized by a low deposit, or a combination of these processes. Additionally, these results may be obtained by substantially decreasing the

quantities of additives (thickeners, optical brighteners, latex…) in the formulation: as a result, the cost of the formulation is greatly improved.

It is important to have a coating composition that can easily be pumped and filtered into the coating method's supply circuits, and with no tendency to the formation of foam or splatters and to excessively fast sedimentation. This requirement corresponds to maintaining the low shear rate viscosity, or the Brookfield™ viscosity measured at 100 revolutions/minute and at 25°C with the device of the same name, without which the coating slip is too liquid.

Another major rheological characteristic is the high shear rate viscosity, as expressed through a ACAV viscosity value at 25°C measured in a capillary viscosimeter in which the coating may be subjected to high shear rates (10^5 à 3 x 10^6 s^{-1}) of the same order of magnitude as those observed during the coating method when the coating blade scraping off the excess deposited coating slip is applied. High shear rate viscosity is a determining factor in which blade pressure to apply. The greater the high shear rate viscosity, the greater the blade pressure must be to control the deposited coat weight. It is thus important to decrease the high-gradient viscosity, to counterbalance the increase in blade pressure.

The Applicant has been able to identify and demonstrate that the combination of calcium carbonate (mineral pigment) along with hollow latex pigments (plastic pigment, for example Celocor® latexes available from Arkema) in a paper coating is what leads to such a result, even with substantially no kaolin in the composition.

In one embodiment, the pigment composition comprises, consists essentially of or consists of:

from 0.5 to 10 parts of hollow latex pigments and

from 90 to 99.5 parts of calcium carbonate particles,

parts based on 100 parts by weight of total pigments.

In another embodiment, the pigment composition comprises, consists essentially of or consists of:

from 1 to 8 parts of hollow latex pigments and

from 92 to 99 parts of calcium carbonate particles,

parts based on 100 parts by weight of total pigments.

Pigment 1: void latex particles:

The "void latex pigments", or equivalently "hollow latex pigments", of the present invention generally comprise a hollow interior and an outer shell which encloses the hollow interior, although as will be explained subsequently in more detail one or more additional layers may be present between the outer shell and the interior void of each particle. The void latex particles of the present invention may be characterized as being “non-film-forming.” By "non-film-forming" it is meant that the void latex particles will not form a film at ambient temperature or below, or in other words will only form a film at temperatures above ambient temperature. For the purposes of this specification, ambient temperature is taken as being in the range of 15°C to 45°C. Thus, for example, when incorporated into an aqueous coating composition, applied to a substrate temperature and dried or cured at ambient temperature or below, the void latex particles do not form a film.

The void latex particles generally remain as discrete particles in the dried or cured coating. The void latex particles are capable of functioning as opacifiers; that is, when added in sufficient amount to a coating composition that would otherwise be transparent when dried, they render the dried coating composition opaque. The term “opaque” means that the coating composition has a higher refractive index when the void latex particles of the present invention are present in a coating composition compared to the same coating composition not including the void latex particles of the present invention, wherein the refractive index is measured after the coatings are dry to the touch. The term “outer shell polymer” refers to the outer layer of the particle of the present invention after swelling.

Generally speaking, the void latex particles may have a diameter of at least 200 nm, at least 250 nm, at least 300 nm, at least 350 nm, or at least 400 nm and a diameter of not more than 700 nm, not more than 650 nm, not more than 600 nm, not more than 550 nm, or not more than 500 nm. The hollow interior generally has a diameter of at least 100 nm, at least 150 nm, or at least 200 nm, but typically is not more than 600 nm or not more than 500 nm or not more than 400 nm in diameter. The thickness of

the layers surrounding the hollow interior, including the outer shell and also any additional layers which may be present, generally is from 40 to 120 nm. Typically, the void latex particles will be approximately spherical in shape, although oblong, oval, teardrop or other shapes are also possible.

The outer shell is polymeric and may, for example, be comprised of a thermoplastic polymer. The outer shell polymer may have a glass transition temperature (Tg) above ambient temperature, typically at least 60°C, at least 70°C, at least 80°C or at least about 90°C. The Tg of the outer shell polymer may be, for example, from 60°C to 140°C.

The void latex particles of the present invention may be prepared by different methods, including, for example, by processes which utilize multi-stage emulsion polymer particles. The multi-stage emulsion polymer particles may comprise a core comprising a polymer of at least one hydrophilic monoethylenically unsaturated monomer and an outer shell comprising a polymer of at least one hydrophobic monoethylenically unsaturated monomer. The multi-stage emulsion polymer particles may be contacted with a swelling agent, such as a base, which is capable of swelling the core, particularly in the presence of water.

The swollen core causes the outer shell to expand, such that when the polymer particles are subsequently dried and/or re-acidified the outer shell remains enlarged in volume and a void is created within the particle as a result of the shrinkage of the swollen core.

As the swollen core shrinks, it may form a coating on the interior surface of the shell of the particle. The void latex particles may each contain a single void. However, in other embodiments of the invention, the individual void latex particles may contain a plurality of voids (e.g., a void latex particle may contain two or more voids within the particle). The voids may be connected to each other through pores or other passageways. The voids may be substantially spherical in shape, but may adopt other forms such as void channels, interpenetrating networks of void and polymer, or sponge-like structures.

The aforementioned multi-stage emulsion polymer particles may be prepared by sequential emulsion polymerization, using a batch process where the product of one stage is used in the stage that follows. For instance, the product of the core stage may be used to prepare the product of the next stage, be it an outer shell or an intermediate encapsulating polymer stage. Similarly, the shell stage is prepared from the product of the core stage or, when there are one or more encapsulating polymer stages, an intermediate encapsulating polymer stage.

Methods previously described in the art for producing void latex particles may be used in the present invention. Methods for obtaining void latex particles are described, for example, in U.S. Pat. Nos. 4,427,836; 4,468,498; 4,594,363; 4,880,842; 4,920,160; 4,985,469; 5,216,044; 5,229,209; and 5,273,824, each of which is incorporated herein by reference in its entirety for all purposes. For example, particles in accordance with the present invention may be made as described in the following examples: (1) examples 0-14 of U.S. Patent No. 4,427,836, (2) examples 0-12 of U.S. Patent No. 4,468,498, (3) examples 1-4 of U.S. Patent No. 4,594,363, (4) examples I-IX of U.S. Patent No. 4,880,842, (5) examples 1-13 of U.S. Patent No. 4,920,160, (6) examples 1-7 of U.S. Patent No. 4,985,469, (7) examples 1-7 of U.S. Patent No. 5,216,044, (8) examples 1-8 of U.S. Patent No. 5,229,209, and (9) examples 1-50 of U.S. Patent No. 5,273,824.

The weight ratio of the core to the outer shell may generally, for example, be in the range of from 1:5 to 1:20 (e.g., from 1:8 to 1:15). To decrease the dry density of the final void latex particles, the amount of outer shell relative to the amount of core should generally be decreased; however, sufficient outer shell should be present such that the core is still encapsulated. In some embodiments, the particle size of the dry void latex particles may be between 300 and 550 nm, or between 300 and 600nm, with a dry bulk density of between 0.55 to 0.70 g/cc.

According to one aspect of the invention, the heart of the void latex pigments is empty, e.g. filled with air or filled with water. The percentage of hollow pigments can be determined by comparing the volume occupied by the latex pigments after having been compacted from a dilute solution in a centrifuge with the volume of non-empty in the same pigment dispersion composition.

Pigment 2: calcium carbonate particles:

For the purpose of the present invention, the term "calcium carbonate particles" refers to a material that comprises at least 80 wt.-% calcium carbonate, based on the total weight of the calcium carbonate particles.

The term "calcium carbonate" in the meaning of the present invention comprises ground calcium carbonate (GCC) as well as precipitated calcium carbonate (PCC).

"Ground calcium carbonate" (GCC) in the meaning of the present invention is a calcium carbonate obtained from natural sources, such as limestone, marble, calcite or chalk, and processed through a wet and/or dry treatment such as grinding, screening and/or fractionating, for example by a cyclone or classifier.

"Precipitated calcium carbonate" (PCC) in the meaning of the present invention is a synthesized material, generally obtained by precipitation following a reaction of carbon dioxide and calcium hydroxide (hydrated lime) in an aqueous environment or by precipitation of a calcium- and a carbonate source in water. Additionally, precipitated calcium carbonate can also be the product of introducing calcium and carbonate salts, calcium chloride and sodium carbonate for example, in an aqueous environment. PCC may be vaterite, calcite or aragonite.

Throughout the present document, the "particle size" of the calcium carbonate particles is described by its distribution of particle sizes. The value d_x represents the diameter relative to which x % by weight of the particles have diameters less than d_x. This means that the d_{20} value is the particle size at which 20 wt.-% of all particles are smaller, and the d_{75} value is the particle size at which 75 wt.-% of all particles are smaller. The d_{50} value is thus the weight median particle size, i.e. 50 wt.-% of all grains are bigger or smaller than this particle size. For the purpose of the present invention the particle size is specified as weight median particle size d_{50} unless indicated otherwise. For determining the weight median particle size d_{50} value for particles having a d_{50} value between 0.4 and 2 μm, a Sedigraph 5120 device from the company Micromeritics, USA, can be used.

The particles of calcium carbonate may be in slurry or suspension of $CaCO_3$ particles. According to the present invention, the term "slurry" means a water suspension that comprises insoluble solids and optionally at least one additive.

According to an aspect of the invention, the particle size distribution of the calcium carbonate particles is such that at least 60% by weight of the particles have an equivalent spherical diameter of less than 2 μm, for example at least 70 wt. %, at least 80 wt. %, at least 90 wt. % of the particles have an equivalent spherical diameter of less than 2 μm

According to another aspect of the invention, the calcium carbonate particles have a weight median particle size d_{50} from 0.1 to 100 μm, for example from 0.25 to 50 μm, from 0.3 to 5 μm, or from 0.4 to 3.0 μm.

Binder:

The binder of the composition according to the present invention may be selected from binders which are well known in the art. The binder may form from 4 wt. % to 30 wt. %, e.g. from 5 wt. % to 20 wt. %, especially from 5 wt. % to 15 wt. %, of the solids content of the composition (dry/dry). The amount employed will depend upon the composition and the type of binder, which may itself incorporate one or more ingredients.

Examples of suitable binders include starch, a styrene butadiene rubber latex, acrylic polymer latex, polyvinyl acetate latex, or styrene acrylic copolymer latex.

Any of the above binders and binder types may be used alone or in admixture with each other and/or with other binders, if desired.

Solids content:

The solids content of the paper coating composition according to the present invention may be greater than about 63 wt. %, preferably at least about 65 wt. %, preferably as high as possible but still giving a suitably fluid composition which may be used in coating (e.g. up to about 75 wt.%).

According to one aspect of the invention, the coating composition has a solid content greater than 65% by weight, for example a solid content ranging from 65 wt. % and 72 wt. %.

Optional components:

The coating composition according to the present invention may contain one or more optional additional components, if desired.

Such additional components, where present, are suitably selected from known additives for paper coating compositions.

Examples of known classes of optional additive are as follows:

- one or more thickeners and/or one or more water retention agents, e.g. in levels up to about 5% by weight; for example acrylic associative thickeners, polyacrylates, emulsion copolymers, polyvinyl pyrrolidone, CMC (carboxymethyl celluloses, for example sodium carboxymethyl cellulose), acrylic acid copolymers, HMC (hydroxymethyl celluloses), HEC (hydroxyethyl celluloses), PVOH (polyvinyl alcohol), starches, proteins, gums, alginates,
- dispersants, e.g. in levels up to about 5% by weight, for example polyacrylates, acrylic acid copolymers
- one or more defoamers, e.g. in levels up to about 2% by weight,
- one or more optical brightening agents (OBA) and/or fluorescent whitening agents (FWA), e.g. in levels up to about 3% by weight,
- one or more biocides, e.g. in levels up to about 2% by weight,
- one or more additional pigments; indeed, the pigment combination of the present invention, namely the void latex particles and calcium carbonate system, may be used as the sole pigment in the paper coating compositions, or it may be used in conjunction with one or more other known pigments, such as for example, titanium dioxide, calcium sulphate, satin white, talc… When a mixture of pigments is used, the calcium carbonate and void latex particles system is preferably present in the composition in an amount of at least about 80% of the total dry weight of the mixed pigments.

For all of the above additives, the percentages by weight quoted are based on the dry weight of pigment (100%) present in the composition. Where the additive is present in a minimum amount the minimum amount may be about 0.01% by weight based on the dry weight of pigment.

Preparation of the coating composition:

It is prepared by mixing together an aqueous dispersed suspension containing the pigment components, with the binder and any other optional additional constituents, in a manner familiar to those skilled in the art.

Pigments blends:

Another aspect of the invention concerns a pigment blend for paper coating composition. More precisely, the present invention concerns a pigment composition to be used as the pigment component of the paper coating composition for preparing light weight coated paper (LWC) or a ultra light weight coated paper (ULWC).

The pigment blend/composition of the invention comprises, consists essentially of or consists of:

a) a first pigment which is hollow latex pigments and

b) a second pigment which is calcium carbonate particles,

with the proviso that the pigment blend/composition does not contain kaolin.

In a variant, the pigment blend/composition of the invention comprises, consists essentially of or consists of:

a) from 0.05 to 20 wt. % of the total pigment dry weight, of hollow latex pigments and

b) from 80 to 99.95 wt. % of the total pigment dry weight, of calcium carbonate particles,

with the proviso that the pigment blend/composition does not contain kaolin or does contain substantially no kaolin.

In another variant, the pigment blend/composition of the invention comprises, consists essentially of or consists of:

a) from 0.1 to 15 wt. % of the total pigment dry weight, of hollow latex pigments and

b) from 85 to 99.9 wt. % of the total pigment dry weight, of calcium carbonate particles,

with the proviso that the pigment blend/composition does not contain kaolin or does contain substantially no kaolin.

In another variant, the pigment blend/composition of the invention comprises, consists essentially of or consists of:

a) from 0.5 to 10 wt. % of the total pigment dry weight, of hollow latex pigments and

b) from 90 to 99.5 wt. % of the total pigment dry weight, of calcium carbonate particles,

with the proviso that the pigment blend/composition does not contain kaolin or does contain substantially no kaolin.

Method for preparing a coated paper:

In accordance with another aspect of the invention, there is provided a method for preparing a coated paper comprising as a first step the application to the paper of a coating weight of less than or equal to 13 g/m^2 per side, of a coating composition comprising or consisting essentially of or consisting of:

a) a pigment composition comprising hollow latex pigments and calcium carbonate particles, with the proviso that the pigment composition does not contain kaolin,

b) a binder,

c) water, and

d) optionally a rheology-modifying agent and/or an optical brightener,

and, as a second step, the calendering of the paper to form a coating thereon.

Method for decreasing high shear rate viscosity:

Another object of the invention consists of a method for decreasing high shear rate viscosity of a paper coating, wherein the coating comprises water, at least one binder, a pigment composition, and optionally a rheology-modifying agent and/or an optical brightener,

wherein said pigment composition comprises, consists essentially of or consists of hollow latex pigments and calcium carbonate particles, with the proviso that the pigment composition does not contain kaolin.

In one embodiment of the present invention, said paper coating is intended for use to coat paper or substrate at a coating weight of less than or equal to 13 g/m^2 per side, e.g. less than or equal to 12 g/m^2 or less than or equal to 11 g/m^2. This coating rate corresponds to light weight coated (LWC) paper and ultra light weight coated (ULWC) paper, also known as light lightweight coated (LLWC) paper.

In another embodiment, the method is for decreasing high shear rate viscosity of a paper coating, and at the same time, maintaining the low shear rate viscosity of said paper coating.

In another embodiment, the method is for decreasing high shear rate viscosity of a paper coating having a solids content greater than about 63 wt. %, preferably at least about 65 wt. %, preferably as high as possible but still giving a suitably fluid composition which may be used in coating (e.g. up to about 75 wt. %).

In a first variant, the method is for decreasing high shear rate viscosity of a paper coating having a solids content greater than about 65% by weight, for example a solid content ranging from 65 wt. % and 72 wt. %.

In a second variant, the method is for decreasing high shear rate viscosity of a paper coating having a solids content greater than about 66% by weight, for example a solid content ranging from 66 wt. % and 72 wt. %.

Uses for preparing a coating composition to be used at a coating weight of less than or equal to 13 g/m2 per side:

An aspect of the invention relates to the use of a pigment composition comprising hollow latex pigments and calcium carbonate particles, with the proviso that the pigment composition does not contain kaolin, for preparing a coating composition to be used at a coating weight of less than or equal to 13 g/m^2 per side.

Uses for decreasing high shear rate viscosity:

Another object of the invention relates to the use of a pigment composition comprising hollow latex pigments and calcium carbonate particles, with the proviso that the pigment composition does not contain kaolin, for decreasing high shear rate viscosity of a paper coating, wherein the coating comprises, consists essentially of or consists of water, at least one binder, said pigment composition, and optionally a rheology-modifying agent and/or an optical brightener.

Paper coating methods:

The methods of paper coating generally require a means of applying the coating composition to the material to be coated, viz. an applicator; and a means for ensuring that a correct level of coating composition is applied, viz. a metering device.

Examples of known coaters which may be employed include air knife coaters, blade coaters, rod coaters, bar coaters, multi-head coaters, roll coaters, roll/blade coaters, cast coaters, laboratory coaters, gravure coaters, kiss coaters, liquid application systems, reverse roll coaters and extrusion coaters.

Coated Paper:

The present invention also concerns a paper coated with a coating comprising a dry residue of the paper coating composition as described above.

According to one aspect, the paper is a light weight coated paper (LWC) or a ultra light weight coated paper (ULWC).

This paper is intended for use for off-set printing process.

Measurement methods:

Particle size distribution (mass % particles with a diameter < X) and weight median grain diameter (d_{50}) of particulate material:

Weight median grain diameter and grain diameter mass distribution of a particulate material were determined via the sedimentation method, i.e. an analysis of sedimentation behaviour in a gravimetric field. The measurement was made with a Sedigraph™ 5120.The method and the instrument are known to the skilled person and are commonly used to determine grain size of fillers and pigments. The measurement was carried out in an aqueous solution of 0.1 % by weight of $Na_4P_2O_7$. The samples were dispersed using a high speed stirrer and ultrasonic.

Solids content (wt.-%) of a material in slurry:

The weight solids content was determined using a Moisture Analyser MJ 33, Mettler Toledo.

Brookfield viscosity:

The Brookfield viscosity was measured after 1 minute of stirring by the use of a RVT model Brookfield™ viscometer at a temperature of 20°C (±2°C), and a rotation speed of 100 rpm (revolutions per minute) with the appropriate disc spindle from N° 1 to 5.

ACAV viscosity:

The ACAV viscosity was measured with a capillary rheometer (ACA®) at 25°C with the appropriate capillary.

Glass transition temperature (Tg) of latex polymer particles:

The Tg of latex polymer particles was determined using a differential scanning calorimeter (DSC), TA instruments Q2000 with an RCS 90 cooling system.

Embodiments of the present invention will now be described by way of example with reference to the following illustrative Examples.

EXAMPLES:

Example 1:

This example illustrates the preparation of paper coating compositions according to the present invention (INV) or outside of the invention (OI).

Test #1 corresponds to the preparation of a coating composition outside of the invention, said composition comprising 40 parts of kaolin (Capim NP) and 60 parts of calcium carbonate (Hydrocarb® 90, Omya). The coating composition is formulated so as to present a solids content of 63 wt.-%.

Test #2 corresponds to the preparation of a coating composition identical to the one of Test #1, except that the solids content has been increased to 67 wt.-%.

Test #3 corresponds to the preparation of a coating composition identical to the one of Test #2 (solids content: 67 wt.-%.), except that the quantity of thickener (Rheocoat® 93) has been reduced by half.

Test #4 illustrates the preparation of a coating composition according to the invention, said composition comprising 97 parts of calcium carbonate (Hydrocarb® 90, Omya) and 3 parts of hollow latex pigments sold by Arkema under the tradename Celocor®. The coating composition is formulated so as to present a solids content of 67 wt.-%.

Test #5 illustrates the preparation of a coating composition according to the invention, said composition comprising 95 parts of calcium carbonate (Hydrocarb® 90, Omya) and 5 parts of hollow latex pigments sold by Arkema under the tradename Celocor®. The coating composition is formulated so as to present a solids content of 66 wt.-%.

To be noted that in tests #4 and 5 according to the invention, the quantity of thickener (Rheocoat® 93, Coatex) has been reduced by half, and the quantity of optical brightener (Blankophor® PT) and a polyvinyl alcohol (Polyvinylic alcohol BF 4-98) have also been reduced, with the associated advantages, e.g. reduction in cost formulation.

The Brookfield viscosity at 100 rpm (low shear) and the ACAV viscosity at 10^6 s^{-1} (high shear) of each composition are measured and indicated in the Table 1 below.

	Test #1	Test #2	Test #3	Test #4	Test #5
OI : outside invention INV : invention	OI	OI	OI	INV	INV
Hydrocarb® 90	60	60	60	97	95
Capim NP	40	40	40		
Celocor®	0	0	0	3	5
Latex® DL 966	7.5	7.5	7.5	7	7
Stabilys® A030	2	2	2	1	1
Polyvinylic alcohol BF 4-98	0.5	0.5	0.5	0.4	0.4
BLANKOPHOR® PT	1	1	1	0.4	0.4
RHEOCOAT® 93	0.2	0.2	0.1	0.1	0.1
Solids content	63	67	67	67	66
Brookfield viscosity @ 100 tr/mn	1150	2580	1220	1090	1110
High shear viscosity ACAV @ 10^6 s^{-1}	60	140	135	100	97

Table 1

The viscosity values, low shear rate and high shear rate, obtained for test #1 are compatible with the LWC and MWC paper application. However, the solids content of the composition is adjusted to 63 wt.-%, which has the major disadvantage of requiring more energy for drying paper.

Test #2: Increasing the solids content of the composition leads to an increase of the viscosity at low shear rate, as well as at high shear rate, thereby rendering the composition inadapted to LWC paper coating process.

Test #3: Reducing the amount of thickening in the coating composition does not solve the problem of high viscosity at high shear rate of test #2.

Tests #4 and #5: The values of viscosity under high shear rate are all inferior to those of tests #2 and #3 at the same solids content (i.e. 66-67 wt.-%). These values of viscosity are compatible with the LWC coating processes.

It is thus shown that it is possible to prepare a coating for LWC paper or MWC without kaolin, having a high solids content.

The coatings were also used to coat paper, simple application layer (11 g/m^2). Although the results are not shown in Table 1 above, the gloss level of the coated papers thus obtained with a coating according to the tests #4-5 is comparable to the one obtained with Test #1 and despite the absence of kaolin.

Additionally, they have the same levels of whiteness and opacity, despite the fact that the amounts of optical brightener and a polyvinyl alcohol were reduced relative to formulations of Tests #1 to #3.

The use of hollow latex microspheres thus provides an alternative to the use of kaolin in paper coatings for LWC paper without compromising brightness, opacity or whiteness.

CLAIMS

1. Method for preparing a coated paper comprising:

applying to the paper a coating weight of less than or equal to 13 g/m^2 per side, of a coating composition comprising:

a) a pigment composition comprising hollow latex pigments and calcium carbonate particles, with the proviso that the pigment composition does not contain kaolin,

b) a binder, and

c) water,

calendering the paper to form a coating thereon.

2. A paper coating composition for preparing a coated paper having a coating weight of less than or equal to 13 g/m^2 per side, said composition comprising:

a) a pigment composition comprising hollow latex pigments and calcium carbonate particles, with the proviso that the pigment composition does not contain kaolin,

b) a binder, and

c) water.

3. The paper coating composition according to claim 2, wherein the pigment composition consists in:

from 0.5 to 10 parts of hollow latex pigments and

from 90 to 99.5 parts of calcium carbonate particles,

parts based on 100 parts by weight of total pigments.

4. The paper coating composition according to claim 2-3, wherein the pigment composition consists in:

from 1 to 8 parts of hollow latex pigments and

from 92 to 99 parts of calcium carbonate particles,

parts based on 100 parts by weight of total pigments.

5. The paper coating composition according to claims 2-4, wherein said paper coating composition has a solids content greater than 63 % by weight.

6. The paper coating composition according to claims 2-5, wherein said paper coating composition has a solids content greater than 65 % by weight.

7. The paper coating composition according to any one of claims 2-6, wherein said hollow latex pigments have a diameter between 300 and 600 nm and the outer shell has a glass transition temperature above 60°C.

8. The paper coating composition according to any one of claims 2-7, wherein the particle size distribution of the calcium carbonate particles is such that at least 60% by weight of the particles have an equivalent spherical diameter of less than 2 μm.

9. The paper coating composition according to any one of claims 2-8, wherein said calcium carbonate particles have a weight median particle size d_{50} from 0.1 to 100 μm.

10. A paper coated with a coating comprising a dry residue of the paper coating composition of claims 2-9.

11. The paper according to claim 10, which is a light weight coated paper (LWC) or an ultra light weight coated paper (ULWC).

12. Use of a pigment composition for decreasing high shear rate viscosity of a paper coating, wherein the coating comprises water, at least one binder, said pigment composition, and optionally a rheology-modifying agent and/or an optical brightener,

wherein said pigment composition consists of hollow latex pigments and calcium carbonate particles, with the proviso that the pigment composition does not contain kaolin.

13. The use according to claim 12, wherein said pigment composition consists of:

a) from 0.05 to 20 wt. % of the total pigment weight of hollow latex pigments, and

b) from 80 to 99.95 wt. % of the total pigment weight of calcium carbonate particles.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/024815

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - D21H 19/42 (2015.01)
CPC - D21H 19/42 (2015.04)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - D21H 19/00, 19/06, 19/36, 19/38, 19/42 (2015.01)
CPC - D21H 19/00, 19/06, 19/36, 19/38, 19/42 (2015.04) (keyword delimited)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 106/400, 401, 409; 427/331, 355, 356, 358 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Orbit, Google Patents, Google
Search terms used: paper coating hollow shell latex pigment calcium carbonate CaCO3 binder water calendering kaolin g/m2

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94/04603 A1 (THE DOW CHEMICAL COMPANY) 03 March 1994 (03.03.1994) entire document	1-3, 12, 13
Y	WO 98/20201 A1 (SD WARREN COMPANY) 14 May 1998 (14.05.1998) entire document	1-3, 12, 13
Y	US 4,474,860 A (VAN GILDER et al) 02 October 1984 (02.10.1984) entire document	12, 13

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 May 2015	26 JUN 2015

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/024815

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-11
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.