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(54) Title: COMPOSITIONS COMPRISING KAOLIN TREATED WITH A STYRENE-BASED POLYMER AND RELATED METHODS

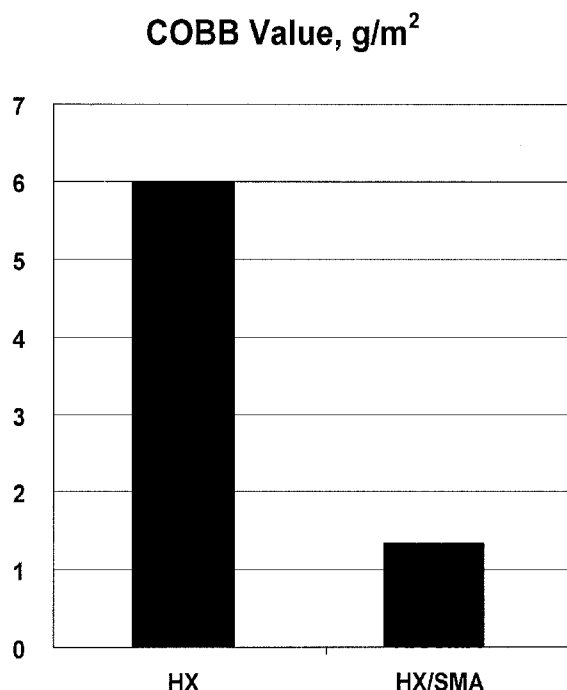


FIG. 1

(57) Abstract: Disclosed are mineral compositions and related methods. A mineral composition may include a mineral treated with a styrene-based polymer. The mineral treated with a styrene-based polymer may be used for a coating on a paper product having a first Cobb value that is less than a second Cobb value of the paper product with the coating devoid of the mineral composition.



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**COMPOSITIONS COMPRISING KAOLIN TREATED WITH A
STYRENE-BASED POLYMER AND RELATED METHODS**

CLAIM OF PRIORITY

[001] This PCT International Application claims the benefit of priority of U.S. Provisional Patent Application No. 61/535,241, filed September 15, 2011, the subject matter of which is incorporated herein by reference in its entirety.

FIELD OF THE DISCLOSURE

[002] The present disclosure relates to compositions comprising minerals suitable for use in coatings for paper products. In particular, the present disclosure relates to compositions comprising minerals treated with a styrene-based polymer for coating paper products, such as paperboard for packaging having water barrier properties, and methods related to minerals treated with a styrene-based polymer.

BACKGROUND OF THE DISCLOSURE

[003] Minerals may be used in pigments in paper coating and filling compositions. For example, kaolinite, the principal constituent of kaolin clay (or kaolinitic clay), is a white clay mineral that imparts brightness, gloss, smoothness, printability, and/or other desirable properties to the surface of coated paper, paperboard, super-calendared paper, and other paper-related products. Minerals may also be used, for instance, in barrier coatings on paper to impart to paper resistance to moisture, moisture vapor, grease, oil, and air, for example. Such coatings are described in, for example, U.S. Patent Nos. 7,208,039, 7,214,264, and 7,226,005, which are all hereby incorporated by reference in their entirety.

[004] Typical wax coatings on corrugating paper products offer water barrier properties that may surpass other protective coatings used for corrugated containers. However, wax is derived from petroleum distillation by-products, which are becoming less

available and more costly. In addition, the inability to easily recycle these one-time-use wax products may be undesirable.

[005] Re-usable plastic containers might be used in place of corrugated paper products for non-durable food packaging. However, recyclable corrugated containers offer economic advantages as compared to re-usable plastic containers due to their ability to be recycled. For example, the used old corrugated containers may be sold for recycling for favorable prices.

[006] In some instances, latex coating used as a wax coating replacement satisfies the sustainability requirements of retailers for recyclable packaging. Latex coatings can impede liquid water absorption and water vapor transmission. However, the application of latex onto paper products requires additional production costs such as off-line or on-line coating, followed by elevated-temperature-drying by air impingement, irradiation, or other drying processes, or a combination thereof. In addition, the cost of latex is substantially greater than wax and thus a disadvantage.

[007] Accordingly, it would be desirable to provide compositions for coating paper-related products that result in improved barrier performance. For example, it would be desirable to provide coating compositions for coating paper, paperboard, or corrugated linerboard, to provide structural integrity and strength under a number of conditions, for instance, under wet or refrigerated conditions.

SUMMARY OF THE DISCLOSURE

[008] In the following description, certain aspects and embodiments will become evident. It should be understood that the aspects and embodiments, in their broadest sense, could be practiced without having one or more features of these aspects and

embodiments. It should be understood that these aspects and embodiments are merely exemplary.

[009] According to one aspect, a mineral composition for use in a coating on a paper product may include a mineral treated with a styrene-based polymer. The paper product may have a first Cobb value less than a second Cobb value of the paper product with the coating being devoid of the mineral composition.

[010] According to a second aspect, a method for making a mineral slurry may include dispersing a mineral treated with a styrene-based polymer in an aqueous composition.

[011] According to another aspect, a method for making a coating for a paper product may include providing a mineral slurry in the coating, wherein the paper product has a first Cobb value less than a second Cobb value of the paper product with the coating devoid of the mineral.

[012] The minerals may include, for example, calcium carbonate (synthetic, precipitated, or ground from naturally occurring material), calcined kaolin, hydrous kaolin, talc, mica, dolomite, silica, zeolite, gypsum, satin white, titania, calcium sulphate, and/or plastic pigment.

[013] Possible advantages of the disclosed embodiments will be set forth in part in the description which follows, or may be learned by practice of the embodiments.

[014] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

BRIEF DESCRIPTION OF THE DRAWING

[015] Fig. 1 is a bar graph showing the Cobb values of paper coated with untreated kaolin and kaolin treated with styrene maleic anhydride in accordance with an exemplary embodiment of the present invention.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

[016] Reference will now be made in detail to exemplary embodiments of the invention.

[017] According to some embodiments, a mineral composition for use in a coating on a paper product may include a mineral treated with a styrene-based polymer. For example, the mineral may include calcium carbonate (synthetic, precipitated, or ground from naturally occurring material), calcined kaolin, hydrous kaolin, talc, mica, dolomite, silica, zeolite, gypsum, satin white, titania, calcium sulphate, and/or plastic pigment. The paper product may have a first Cobb value less than a second Cobb value of the paper product with the coating being devoid of the mineral composition. For instance, in one embodiment the first Cobb value ranges from about 0 g/m² to about 100 g/m². In another embodiment, the first Cobb value ranges from about 1 g/m² to about 75 g/m². In another embodiment, the first Cobb value ranges from about 20 g/m² to about 60 g/m². In still another embodiment, the first Cobb value ranges from about 1 g/m² to about 25 g/m². In yet another embodiment, the first Cobb value ranges from about 1 g/m² to about 10 g/m². In one embodiment, the paper product having a coating including a mineral treated with a styrene-based polymer has a first Cobb value less than a second Cobb value of the paper product with the coating including untreated mineral.

[018] "Cobb value" as used herein is defined as the water absorption (in weight of water per unit area) of a sample. The procedure for determining the "Cobb value" is: 1)

weigh the sample; 2) place the sample in a holder with the appropriate ring; 3) fill the ring with water; 4) wait 30 minutes; 5) pour off water; and 6) weigh the sample. The Cobb value is calculated by subtracting the initial weight of the sample from the final weight of the sample and then dividing by the area of the sample covered by the water.

[019] In certain embodiments, the styrene-based polymer comprises styrene maleic anhydride, styrene butadiene, styrene acrylic, or a combination thereof. Styrene-maleic anhydride may be prepared by the polymerization of styrene or a styrenic monomer and maleic anhydride or derivatives thereof. For example, styrene maleic anhydride may be a copolymer of styrene and maleic anhydride with the ratio of styrene to maleic anhydride varying from 1:1 to 2:1 and greater.

[020] In some embodiments, the mineral (e.g., kaolin) is treated with styrene maleic anhydride in an amount ranging from about 5 to about 400 pounds of styrene maleic anhydride per dry ton of mineral. In other embodiments, the mineral is treated with a styrene-based polymer in an amount ranging from about 25 to about 100 pounds of styrene-based polymer per dry ton of mineral. In another embodiment, the mineral is treated with styrene-based polymer in an amount ranging from about 30 to about 50 pounds of styrene-based polymer per dry ton of mineral. As used herein, "treated" or "treating" may include contacting, coating, and/or dispersing the styrene-based polymer onto or with the mineral, or similar processes.

[021] In some embodiments, the mineral (e.g., kaolin) comprises a filter cake, an evaporator product, or a makedown slurry. In certain embodiments, the mineral comprises a mineral filter cake having a solids content ranging from about 45% to about 60% by weight. In particular embodiments, the mineral filter cake has a conductivity less than about 12,000 μS . In other embodiments, the mineral filter cake has a conductivity less than

about 600 μS . In another embodiment, the mineral filter cake has a conductivity less than about 200 μS . For instance, the mineral may be a mineral filter cake having a particular conductivity prior to the time it is treated with a styrene-based polymer.

[022] According to one aspect, the shape factor of the mineral (e.g., kaolin) treated with a styrene-based polymer may be at least about 10, at least about 20, at least about 30, at least about 40, at least about 50, at least about 60, at least about 70, or at least about 80. In particular embodiments, a high shape factor mineral (e.g., at least about 45) treated with a styrene-based polymer such as styrene maleic anhydride provides a surprising improvement in the water barrier properties of a coating containing such a mineral composition.

[023] "Shape factor," as used herein, is a measure of the ratio of particle diameter to particle thickness for a population of particles of varying size and shape as measured using the electrical conductivity methods, apparatuses, and equations described in U.S. Patent No. 5,576,617, which is incorporated herein by reference. As the technique for determining shape factor is further described in the '617 patent, the electrical conductivity of a composition of an aqueous suspension of orientated particles under test is measured as the composition flows through a vessel. Measurements of the electrical conductivity are taken along one direction of the vessel and along another direction of the vessel transverse to the first direction. Using the difference between the two conductivity measurements, the shape factor of the particulate material under test is determined.

[024] In certain embodiments, the mineral composition (e.g., a kaolin composition) further comprises an aqueous solution substantially devoid of, or devoid of, sodium. In some embodiments, the mineral composition further comprises a pH adjuster. In one embodiment, the pH adjuster comprises ammonium hydroxide. In other embodiments, the

pH adjuster may comprise potassium and/or ammonium hydroxides or carbonates, or combinations thereof. Without being bound by a particular theory, it is believed that pH adjusters such as ammonium flash-off or vaporize during processing (e.g., spray drying) before addition to a coating composition, and thus, do not affect the water barrier properties of the resultant coating.

[025] In some embodiments, the pH of the mineral composition is adjusted to a pH ranging from about 6.0 to about 9.0, or a pH ranging from about 6.5 to about 8.5.

[026] In particular embodiments, the mineral composition (e.g., a kaolin composition) further comprises a dispersant selected from the group consisting of a phosphate, a silicate, and a (poly)acrylate, wherein the dispersant is devoid of sodium. In some embodiments, the mineral composition further comprises carboxymethyl cellulose, used as a thickener, for instance.

[027] In certain embodiments, the mineral composition (e.g., a kaolin composition) further comprises a mineral selected from the group consisting of mica, talc, gypsum, diatomaceous earth, calcium carbonate, attapulgite, bentonite, montmorillonite, and other natural clays (e.g., anhydrous or calcined kaolin clays) or synthetic clays. For example, the mineral composition may include mica in an amount ranging from greater than about 0 to about 5 wt %.

[028] In certain embodiments, the coating including the mineral (e.g., kaolin) treated with a styrene-based polymer is printable.

[029] In another aspect, the invention comprises a method for making a mineral slurry (e.g., a kaolin slurry) comprising dispersing a mineral treated with a styrene-based polymer in an aqueous composition. It has been surprisingly determined that adding styrene-based polymer to the mineral filter cake and/or to the beneficiated mineral slurry

(e.g., makedown slurry) for later transport or spray drying before making a coating including the mineral treated with a styrene-based polymer, results in an improved coating barrier performance. In some embodiments, the mineral treated with a styrene-based polymer is dispersed using a makedown process, wherein a mixer is used to disperse the mineral and styrene-based polymer in an aqueous solution.

[030] In some embodiments, the method further comprises adding a pH adjuster to the aqueous composition. For example, the pH adjuster may comprise potassium and/or ammonium hydroxides or carbonates, or combinations thereof.

[031] In certain embodiments, the aqueous solution is substantially devoid of sodium. Without being bound by a particular theory, it is believed that the substantial absence, or absence of, sodium in the mineral slurry (e.g., a kaolin slurry) provides improved water barrier properties in resultant coating compositions including the mineral treated with a styrene-based polymer. In particular, improved water performance is achieved due to the lack of sodium (such as from typical dispersants), which is hydrophobic and absorbs water, and the use of a styrene-based polymer to disperse a mineral and, in combination with the mineral (e.g., kaolin), provide water barrier properties. In other words, though typical sodium-containing dispersants are not used, the mineral slurry imparting water barrier properties in a coating may still be dispersed at a high solids level due to the styrene-based polymer treatment. In certain embodiments, the mineral slurry has a solids content ranging from about 40% to about 60% by weight, or from about 47% to about 53% by weight. In some embodiments, the dispersing step can be carried out at a temperature ranging from about 75°F to about 150°F.

[032] According to another aspect, the mineral slurry may be in the form of a transportable kaolin slurry or a kaolin slurry to be spray-dried. The method may further

include transporting the mineral slurry or the spray-dried mineral. In some embodiments, the mineral slurry may include water in an amount of at least about 20% by weight of the mineral slurry.

[033] As used herein, “transportable mineral slurry” refers a mineral slurry, which includes fully beneficiated mineral, which is substantially resistant to settling or segregation for a period sufficient for transport from a first location to a second remote location. The pour test can be used as an indicator of the long-term stability of, for example, kaolin slurries. In the pour test, a number of samples of the slurry are placed into beakers and weighed. At selected time intervals, one of the beakers is upended, and the sample is allowed to pour out for a period of one minute. The beaker is then re-weighed, and the percentage of sample that is successfully poured from the beaker is determined as a percentage of the total initial sample weight. Generally, the higher the pour-test percentage, the more stable the slurry is against settling. The stability test may include monitoring the viscosity of the slurry over a 28-day period using a T-bar spindle. After twenty-eight days, the weight percent of the slurry that poured out of the jar in one minute is measured and is designated as the first pour. The sample is returned to the jar and shaken for a few seconds and again poured out for one minute to obtain the weight percent of the slurry for the second pour. For instance, a transportable kaolin slurry may have a 28-day pour test result of at least about 85% poured. The final slurry sample obtained after the 28-day stability tests (before the first pour-off) and obtained from the second pour-off can also be analyzed for the low-shear Brookfield viscosity at 20 to 100 rpm using an appropriate spindle (typically #1 or #2 spindle) and high-shear viscosity using a Hercules viscometer. Brookfield and Hercules viscosity measurements on the aged slurries could be used as an indicator/predictor of slurry rheology properties during transportation and storage.

[034] According to a further aspect, a substrate, such as a paper product, may be coated with a coating composition including a mineral (e.g., kaolin) treated with a styrene-based polymer. For example, the base substrate may include, paper, paperboard, or corrugated linerboard.

[035] According to yet a further aspect, a coating composition may include a mineral (e.g., kaolin) treated with a styrene-based polymer and binder. For example, the binder may include at least one of wheat, corn, potato, and tapioca. According to a further aspect, the binder may include at least one of acrylic latex, vinyl acetate latex, casein, polyvinyl alcohol, and polyvinyl acetate.

[036] According to a further aspect, the binder may comprise from about 3% to about 30% by weight of the coating composition. For example, the binder may comprise from about 3% to about 50% by weight of the coating composition. According to further aspects, the binder may comprise from about 10% to about 40% by weight of the coating composition. By including a mineral (e.g., kaolin) treated with a styrene-based polymer in a coating composition, it may be possible to reduce the amount of binder needed to achieve the same coating properties as a coating devoid of such a mineral composition. In certain embodiments, the coating composition may include about 20% to about 70% solids by weight, wherein 70% by weight of the solids is mineral treated with a styrene-based polymer.

[037] According to some embodiments, mineral compositions (e.g., kaolin compositions) may have one or more of the following characteristics:

- A. Particle size distribution: d_{50} ranging from about 0.2 micron to about 1.5 microns, d_{90} ranging from about 1 micron to about 10 microns, about 10% to

about 99% less than 2 microns, and about 20% to about 80% less than 0.25 micron;

- B. GE Brightness: at least about 89.0, advantageously at least about 90.0, and at least about 92.0;
- C. Brookfield viscosity, measured at 20 rpm and at less than or equal to about 65% solids: about 50 to about 700 centipoise, and in certain embodiments, about 200 to about 500 centipoise; and
- D. Hercules viscosity, measured at 18 dynes and at less than or equal to about 65% solids: about 200 rpm to about 3500 rpm, and in certain embodiments, about 500 rpm to about 2000 rpm, and about 700 rpm to about 1000 rpm.

[038] The mineral compositions (e.g., kaolin compositions) according to some embodiments may also optionally exhibit a steepness ($d_{30}/d_{70} \times 100$) of at least about 30, the value of which changes with embodiments to at least about 35, at least about 40, at least about 45, and at least about 50.

[039] "GE Brightness," as expressed herein, is defined in TAPPI Standard T452 and refers to the percentage reflectance to light of a 457 nm wavelength according to methods well known to those of ordinary skill in the art.

[040] "Viscosity," as used herein, is a measure of the rheological properties of a mineral (e.g., a kaolin clay). In particular, viscosity is a measure of resistance of the mineral to changes in flow. Those having ordinary skill in the art are familiar with typical ways of measuring viscosity, which include Brookfield viscosity and Hercules viscosity.

[041] Brookfield viscometers provide a measure of a low shear viscosity of a mineral slurry, expressed in units of centipoise. One centipoise is equal to one centimeter-gram-second unit. (One centipoise is one one-hundredth (1×10^{-2}) of a poise.) Thus, all

other things being equal, a 100 centipoise sample has a lower viscosity than a 500 centipoise sample.

[042] Hercules viscometers provide a measure of a high shear viscosity of a mineral slurry (e.g., a kaolin slurry). Hercules viscosity is typically measured by placing a cylinder (bob) of appropriate diameter and length (typically the A-bob) into a sample mineral slurry. Hercules viscosities of various samples can be compared by holding constant the percent solids concentration of the sample, the bob size, and the applied force. The Hercules viscometer applies a force to the bob, which causes it to spin at a controlled acceleration rate. As the viscometer increases the bob spin rate, the viscous drag on the cup increases. Mineral slurries (e.g., clay slurries) with poor high shear rheology will exert the maximum measurable force on the cup at a lower bob rpm than mineral slurries with “good” high shear rheology. Hercules viscosity is therefore typically expressed in terms of bob spin rates, or revolutions per minute (rpm). A “dyne endpoint” is an indication of very low Hercules viscosity. A dyne endpoint is reached when the bob reaches its maximum rpm before the maximum measurable force is exerted on the cup.

[043] “Particle size,” as used herein, for example, in the context of particle size distribution (psd), is measured in terms of equivalent spherical diameter (esd). Sometimes referred to as the “ d_{50} ” value, median particle size and other particle size properties referred to in the present application may be measured in a well known manner, for example, by sedimentation of the particle material in a fully-dispersed condition in an aqueous medium using a SEDIGRAPH 5100 machine, as supplied by Micromeritics Corporation. Such a machine may provide measurements and a plot of the cumulative percentage by weight of particles having a size, referred to in the art as “equivalent spherical diameter” (esd), less than the given esd values. The mean particle size d_{50} is the value that may be determined

in this way of the particle esd at which there are 50% by weight of the particles that have an esd less than that d_{50} value.

[044] “Steepness: $(d_{30}/d_{70} \times 100)$,” as used herein, refers to the steepness (or narrowness) of the particle size distribution (psd). This, in turn, refers to the slope of the psd curve of the particulate kaolin according to the present disclosure. “Steepness,” as used herein, may be measured as 100 times the ratio of the d_{30} to d_{70} , where “ d_{30} ” is the value of the particle esd less than which there are 30% of the particles, and “ d_{70} ” is the value of the particle esd less than which there are 70% of the particles, both of which may be obtained from the Sedigraph measurement described above.

[045] According to exemplary embodiments disclosed herein, coating compositions may comprise a particulate mineral (e.g., a particulate kaolin clay) that is processed material derived from a natural source, such as, for example, raw natural kaolin clay mineral. For example, a processed kaolin clay may typically contain at least about 50% by weight kaolinite. For example, most commercially-important processed kaolin clays contain greater than about 75% by weight kaolinite and may contain greater than about 90%, in some cases greater than about 95% by weight, of kaolinite. The kaolin compositions according to the exemplary disclosed embodiments may be prepared according to the exemplary process described below.

[046] For example, a crude feed kaolin clay may first be blunged. Any suitable kaolin feed capable of providing a product having the desired properties may serve as the crude feed. Any suitable kaolin crude feed may serve as the feed, however.

[047] According to some embodiments, blunging mixes the crude feed clay (or other mineral) with water in a high-energy mixer, known by those skilled in the art as a “blunger.” A sufficient amount of water may be added during blunging to form an aqueous

suspension of the crude. Typically, the blunged suspension will contain from about 60% to about 70% solids. However, the blunging may be carried out at solids as low as about 20% according to some embodiments.

[048] Initially and during blunging, the pH of the slurry will typically be in the range of from about 4.0 to about 9.5, or from about 6.5 to about 8.0. The pH of the suspension may be adjusted during blunging, typically to within about 0.5 pH units of neutral to help deflocculate the suspension. The pH may be adjusted by the addition of any known or after-discovered chemicals, gases, or other agents capable of bringing the pH to suitable levels. For example, pH adjusting chemicals include, but are not limited to, sodium, potassium, and/or ammonium hydroxides or carbonates, for example, sodium hydroxide or sodium carbonate. Appropriate amounts of the pH adjusting agent may be added as desired to achieve the target pH, typically in the range of from about 0.5 to about 5.0 pounds per ton.

[049] According to some embodiments, dispersing agents may also be added during blunging to aid in forming the aqueous suspension. Suitable dispersing agents include any known or after-discovered dispersing agents capable of aiding deflocculation. For example, dispersing agents may include ammonium or potassium salts of hexametaphosphate, polyphosphate, silicates, polyacrylate, and/or polyacrlamide/acylate copolymers. Dispersing agents are typically added in a dose range of about 2 to about 10 lbs. per ton of kaolin on a dry basis. According to some embodiments, the dose range may be from about 3 to about 6 lbs. per ton.

[050] After blunging, the crude suspension may be fractionated as desired into fine and coarse fractions. Fractionation (or classification) may be performed using any known or after-discovered method. Exemplary methods include gravity sedimentation or

elutriation, use of any type of hydrocyclone apparatus or a solid bowl decanter centrifuge, disc nozzle centrifuge, or the like.

[051] The separated coarse fraction, sometimes referred to as the “b-fraction,” typically has a psd, such that the percentage of particles having an esd less than 2 μm is from about 20% to about 40%. The b-fraction may be diluted such that the esd less than 2 μm ranges from about 10% to about 60%, with certain embodiments ranging from about 30% to about 50%, with about 40% solids being exemplary. The b-fraction may also be mixed with one or more of the aforementioned dispersing agents.

[052] The b-fraction may thereafter be subjected to delamination. Delamination may be accomplished by any known or after-discovered methods, such as, for example, sand or attrition grinding, bead milling, and/or ball milling. Delamination may be achieved in any proprietary grinder or commercially available apparatus including, but not limited to, a Denver attrition scrubber, a Drias mill, a Netsch mill, a Matter mill, and vibo-energy mill.

[053] The delaminated b-fraction and/or fine fraction may thereafter be subjected to one or more beneficiation processes to improve brightness and to remove impurities as desired. According to some embodiments, the delaminated b-fraction and/or fine fraction may be subjected to magnetic separation and/or reductive bleaching to remove iron- and/or titanium-containing impurities, as well as other impurities as desired. Appropriate magnetic separators include any commercial or proprietary “high intensity” magnetic separator with a minimum applied field strength of, for example, 0.5 tesla. Suitable equipment may include the Carpco reciprocating magnet or a PEM HIMS (High Intensity Magnetic Separator). Permanent magnet systems, copper coil electromagnet systems, and/or superconducting magnet systems can be employed.

[054] Exemplary reductive bleaching agents include sodium hydrosulfite (hydros) in doses ranging from about 0.5 to about 5 pounds per ton of mineral (e.g., kaolin), for example, less than about 4 pounds per ton on a dry basis. Any other suitable reductive bleaching agents, such as, for example, formamidine sulphinic acid, may be employed. Reductive bleaching using hydros may be preferably carried out in acidic pH, such as, for example, a pH in the range of from about 2.0 to about 4.5. Any mineral, organic acid, and/or alum solution may be used to adjust the pH to the desired value. For example, pH modifiers include sulfuric acid, with a pH of from about 2.5 to about 3.5, and alum solution, with a pH of from about 3.5 to about 4.5. In both cases, sodium hydrosulfite may act as the reductive bleaching agent. According to some embodiments, the mineral slurry may be mixed with a chosen acidifying agent(s) to bring the pH to the desired value, as dictated by kinetics and other considerations.

[055] The fully beneficiated mineral (e.g., kaolin) may thereafter be advantageously filtered and redispersed to form an aqueous slurry as described herein.

[056] The refined, neutral mineral may thereafter be subjected to evaporation and/or spray-drying as desired, and its solids level adjusted to an upper limit as dictated by the rheological characteristics desired for the intended mineral composition. In the case of the mineral compositions according to exemplary embodiments, the upper limit may be about 65% solids, but lower solids concentrations may be achieved according to the desired specification.

[057] According to some embodiments, a coating composition may include a mineral composition, and the mineral composition may be treated with styrene-based polymer. According to some embodiments, a fully beneficiated mineral slurry may be

treated with styrene-based polymer, for example, by adding styrene-based polymer to the fully beneficiated mineral filter cake.

[058] According to some embodiments, styrene-based polymer may be added to mineral compositions without it being desirable to substantially or slightly modify mineral production parameters, production processes, and/or formulations for preparing coating compositions. Thus, treating the mineral composition with styrene-based polymer may be transparent to mineral processors and/or coating manufacturers.

[059] According to some embodiments, a commercially available kaolin composition may be treated with styrene-based polymer, for example, by adding styrene-based polymer to a composition containing the commercially available kaolin composition.

[060] Cellulose substrates coated with some embodiments of coating compositions disclosed herein may be used in printing processes. Normal paper, LWC paper, and/or ULWC paper, or any other suitable substrates, may optionally be used. Products and compositions disclosed herein may be used in the production of all paper grades, for example, from ULWC paper to coated or filled board (e.g., corrugated linerboard). Paper and paperboard products may comprise a coating, which may improve the brightness and/or opacity of the coated paper or coated board.

[061] According to some embodiments, the paper coating compositions may include a mineral (e.g., calcined kaolin) and materials generally used in the production of paper coatings and paper fillers. For example, the coating compositions may include a binder and a pigment, such as, for example, TiO_2 . According to some embodiments, the coating compositions may include, but are not limited to, other additives (e.g., polyvinyl alcohol), such as, for example, dispersants, cross-linkers, water retention aids, viscosity modifiers or thickeners, lubricity or calendaring aids, antifoamers/defoamers, gloss-ink

hold-out additives, dry- or wet-rub improvement or abrasion-resistance additives, dry- or wet-pick improvement additives, optical brightening agents or fluorescent whitening agents, dyes, biocides, leveling or evening aids, grease- or oil-resistance additives, water-resistance additives, and/or insolubilizers.

EXAMPLE

[062] In this Example, commercially-available BARRISURF HX® (available from IMERYS of Roswell, Georgia), a particulate kaolin clay, was used to form a coating composition for coating paper prior to water absorption testing to determine the Cobb value of the coated paper. The Table below lists the parameters used during a method of making a kaolin slurry, including kaolin treated with a styrene-based polymer in accordance with an embodiment of the present invention.

[063] BARRISURF HX® is a commercially-available particulate kaolin clay that has a shape factor of approximately 90, a d50 of 1.535, and a steepness of 27. The typical particle size distribution is as follows: 62% by weight less than 2 µm; 37% by weight less than 1 µm; 26% by weight less than 0.5 µm; 11% by weight less than 0.25 µm. The GE Brightness is 86. The styrene maleic anhydride-treated kaolin sample (e.g., with the styrene maleic anhydride having a styrene-to-maleic anhydride ratio of about 1:1) was made from filter cake and mixed in the Cowles mixer at 2,000 rpms for 20 minutes. The sample was produced at high solids. The Brookfield viscosity (#2 spindle) was taken at ambient temperature.

Table

Filter Cake Solids	Slurry Solids	Brookfield viscosity 20 rpms	Brookfield viscosity 100 rpms	Temperature °F	pH	SMA dose
49.5	49.1	68	162	113	7.86	40 pounds/dry ton kaolin

[064] An analogous sample was produced with an untreated BARRISURF HX kaolin. The kaolin compositions were then used in a 8 gsm coating including 200 parts per hundred binder, 4% ammonium zirconium carbonate (AZC) based on dry latex amount, and caustic for pH control that was applied to an uncoated freesheet base paper and then tested for their Cobb values. The respective Cobb values are shown in Fig. 1. From these results, it can be seen that styrene-based polymer treatment of the kaolin improves the water barrier property of the coated paper.

[065] Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

WHAT IS CLAIMED IS:

1. A mineral composition for use in a coating on a paper product, the composition comprising:

a mineral treated with a styrene-based polymer, wherein the paper product has a first Cobb value less than a second Cobb value of the paper product with the coating being devoid of the mineral composition.

2. The mineral composition of claim 1, further comprising an aqueous solution substantially devoid of sodium.

3. The mineral composition of claim 1, wherein the first Cobb value ranges from about 1 g/m² to about 25 g/m².

4. The mineral composition of claim 1, wherein the mineral has a shape factor of at least about 20.

5. The mineral composition of claim 1, wherein the mineral composition further comprises a pH adjuster.

6. The mineral composition of claim 5, wherein the pH adjuster comprises ammonium hydroxide.

7. The mineral composition of claim 1, wherein the styrene-based polymer is styrene maleic anhydride in an amount ranging from about 5 to about 400 pounds of styrene maleic anhydride per dry ton of kaolin.

8. The mineral composition of claim 1, wherein the mineral has a conductivity less than about 12,000 μS .

9. The mineral composition of claim 1, the mineral is selected from the group consisting of kaolin, talc, gypsum, diatomaceous earth, calcium carbonate, attapulgite, bentonite, montmorillonite, natural clays, and synthetic clays.

10. The mineral composition of claim 1, further comprising a dispersant selected from the group consisting of phosphate, silicate, and acrylate, wherein the dispersant is devoid of sodium.

11. The mineral composition of claim 1, wherein the coating is printable.

12. A method for making a mineral slurry, the method comprising:
dispersing a mineral treated with styrene-based polymer in an aqueous composition.

13. The method of claim 12, wherein the aqueous solution is substantially devoid of sodium.

14. A method for making a coating for a paper product, the method comprising:
providing mineral slurry in the coating, wherein the paper product has a first Cobb value less than a second Cobb value of the paper product with the coating devoid of the mineral.
15. The method of claim 14, wherein the first Cobb value ranges from about 1 g/m² to about 25 g/m².
16. The method of claim 12, wherein the mineral has a shape factor of at least about 20.
17. The method of claim 12, wherein the aqueous composition further comprises a pH adjuster.
18. The method of claim 17, wherein the pH adjuster comprises ammonium hydroxide.
19. The method of claim 12, wherein the styrene-based polymer is styrene maleic anhydride in an amount ranging from about 5 to about 400 pounds of styrene maleic anhydride per ton of mineral.
20. The method of claim 12, wherein the mineral has a conductivity less than about 12,000 μ S.

21. The method of claim 12, wherein the mineral slurry comprises a mineral selected from the group consisting of talc, gypsum, diatomaceous earth, calcium carbonate, attapulgite, bentonite, montmorillonite, natural clays, and synthetic clays.

22. The method of claim 12, wherein the aqueous composition comprises a dispersant selected from the group consisting of phosphate, silicate, and acrylate, and wherein the dispersant is devoid of sodium.

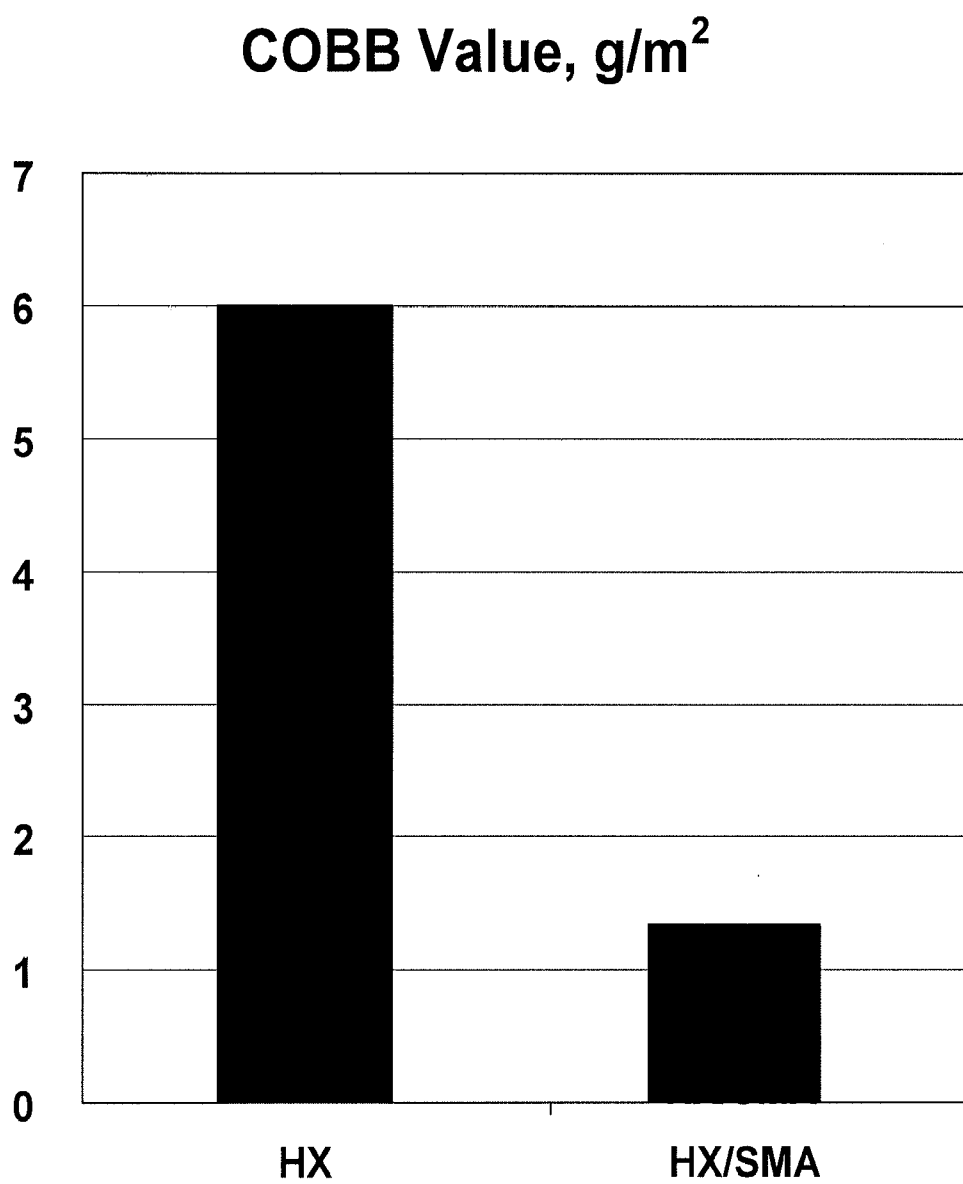
23. The method of claim 14, wherein the coating is printable.

24. The mineral composition of claim 1, wherein the mineral comprises at least one of kaolin and talc.

25. The method of claim 12, wherein the mineral comprises at least one of kaolin and talc.

26. The method of claim 14, wherein the mineral comprises at least one of kaolin and talc.

1/1

**FIG. 1**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/54777

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - D21H 19/46, D21H 19/64 (2012.01)

USPC - 427/411

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 19/46, D21H 19/64 (2012.01)

USPC - 427/411

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 162/173; 162/174; 162/175; 162/181.1

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

PatBase - talc kaolin styrene maleic anhydride polystyrene latex Cobb hydrophobic barrier slurry coat coating Imerys MEIZANIS

PRUETT YILDIRIM

Google - (talc OR kaolin)-coated-with-(styrene maleic anhydride) paper (hydrophobic OR Cobb)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 2004/0023004 A1 (KIMPIMAKI, ET AL.) 05 February 2004 (05.02.2004), paras [0060], [0066]-[0069], [0076]-[0077]	1-3, 5, 9-11, 14-15, 23-24, 26 ----- 4, 6-8
Y	US 2006/0032405 A2 (JONES ET AL.) 16 February 2006 (16.02.2006), especially para [0002], [0022], [0098], [0118], [0159],	4, 7-8
Y	US 2006/0249051 A1 (PRUETT ET AL.) 09 November 2006 (09.11.2006), especially para [0002], [0036], [0063],	6
A	US 2010/0310883 A1 (BRUNGARDT) 09 December 2010 (09.12.2010), entire document	1-11, 14-15, 23-24, 26
A	US 2010/0151255 A1 (WILLIAMS, ET AL.) 17 June 2010 (17.06.2010), entire document	1-11, 14-15, 23-24, 26
A	WO 2009/114071 A1 (FARRELL, ET AL.) 17 September 2009 (17.09.2009), entire document	1-11, 14-15, 23-24, 26
A	US 2006/0124033 A1 (PRUETT ET AL.) 15 June 2006 (15.06.2006), entire document	1-11, 14-15, 23-24, 26

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

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

29 November 2012 (29.11.2012)

Date of mailing of the international search report

09 JAN 2013

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/54777

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.:
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:

*** Please see extra sheet ***

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.:
Group I: Claims 1-11, 14-15, 23-24 and 26

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.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/54777

Box No. III: Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-11, 14-15, 23-24 and 26 relate to a mineral slurry for use in coating a paper product which include a mineral component, such as a mineral treated with a styrene-based polymer, wherein the paper product has a first Cobb value less than a second Cobb value of the paper product with the coating being devoid of the mineral composition.

Group II: Claims 12-13, 16-22 and 25 relate to method of making a mineral slurry, the method comprising dispersing a mineral treated with styrene-based polymer in an aqueous composition.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Groups I does not include the inventive concept of being related to coating a paper product, including wherein the coated paper product has a first Cobb value less than a second Cobb value of the paper product with the coating being devoid of the mineral composition, as required by Group I.

Groups I and II share the technical features of being related to a mineral slurry treated with styrene-based polymer, and dispersed in an aqueous composition.

However, the shared technical features fail to make a contribution over the prior art US 2004/0023004 A1 to Kimpimaki et al. (05 February 2004), which discloses a talc slurried in a polymer latex comprising water and a 'styrene-butadiene-based polymer latex'. As mineral slurries treated with styrene-based polymer and dispersed in an aqueous compositions were known, as evidenced by the disclosure of Kimpimaki, this cannot be considered a special technical feature that would otherwise unify the groups.

Groups I-II therefore lack unity under PCT Rule 13.1 because they do not share a same or corresponding special technical feature.