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(54) **Title:** PAPER COATING COMPOSITION AND PROCESSES OF MAKING THEREOF

(57) **Abstract:** A novel coating composition comprises an aqueous dispersion of a binder ; pigment ; starch ; and a hydrophobically modified alkali-swellable emulsion which comprises structural units of a carboxylic acid monomer, an acrylate monomer, and a polyethoxylated aralkyl phenol methacrylate. This novel coating composition provides improved thickening efficiency.



PAPER COATING COMPOSITION AND PROCESSES OF MAKING THEREOF

FIELD OF THE INVENTION

The present invention relates to a paper coating composition and a process of making this paper coating composition.

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INTRODUCTION

In the paper making process, a coating composition is commonly applied to the base paper surface to ensure that the paper surface is smooth and free of “peaks and valleys” caused by base paper fibers, before images are printed onto the paper. Paper manufacturers have traditionally added rheology modifiers (*i.e.*, thickeners), to the paper coating materials as additives to enhance physical stability of the coating material and control coat weight.

Hydrophobically-modified alkali-soluble emulsion (“HASE”) polymers are typically used as the preferred rheology modifier for this purpose. Conventional HASE compositions typically use associative monomers with linear aliphatic alkyl chains as ending groups to serve as associative phobes. Examples of such associative monomers are polyoxyethylene dodecyl-stearyl methacrylate, polyoxyethylene lauryl-myrisyl methacrylate

However, when coating compositions containing such conventional HASE polymers are mixed with water soluble additives such as, for example, starch in pre-coating applications, the coating compositions tend to show low low shear viscosity. This phenomenon requires adding more HASE polymer in order to reach the desired viscosity level, therefore incurring additional manufacturing costs. Therefore, it is desirable to provide a coating composition containing a rheology modifier that has a higher thickening efficiency.

SUMMARY OF THE INVENTION

Inventors of the present invention have surprisingly discovered a novel coating composition. Among other applications, this novel coating composition can be applied to paper surfaces during the pre-coating stages of the paper manufacturing process. More specifically, inventors of the present invention discovered, through a series of

experimentations, that coating compositions containing HASE polymers made from certain associative monomers having hydrophobic phenyl radical end groups would have better low shear viscosity and higher thickening efficiency.

In particular, the present invention is a paper coating composition comprising an aqueous dispersion of a binder; pigment; starch and a hydrophobically modified alkali-swella-
 5 ble emulsion which comprises structural units of a carboxylic acid monomer, an acrylate monomer, and a polyethoxylated aralkyl phenol (meth) acrylate.

DETAILED DESCRIPTION OF THE INVENTION

10 In one embodiment of the present invention, the coating composition of the present invention is a paper coating composition comprising an aqueous dispersion of a binder, starch, pigment and an alkali-swella- ble emulsion hydrophobically modified with a polyethoxylated aralkyl phenol.

Aqueous dispersion of a binder

An aqueous dispersion of a binder is preferably chosen from a pure acrylic copolymer, a styrene acrylic copolymer, a styrene butadiene copolymer, or a vinyl acrylic copolymer poly vinyl acetate, vinyl acetate emulsion mixtures of these binders. Suitable unsaturated monomers for use in forming the above-mentioned copolymers are generally ethylenically
 20 unsaturated monomers that include vinylaromatic compounds (*e.g.* styrene, α -methylstyrene, *o*-chlorostyrene, and vinyltoluenes); 1,2-butadiene; conjugated dienes (*e.g.* 1,3-butadiene and isoprene); α,β -monoethylenically unsaturated mono- and dicarboxylic acids or anhydrides thereof (*e.g.* acrylic acid, methacrylic acid, crotonic acid, dimethacrylic acid, ethylacrylic acid, allylacetic acid, vinylacetic acid maleic acid, fumaric acid, itaconic acid, mesaconic
 25 acid, methylenemalonic acid, citraconic acid, maleic anhydride, itaconic anhydride, and methylmalonic anhydride); esters of α,β -monoethylenically unsaturated mono- and dicarboxylic acids having 3 to 6 carbon atoms with alkanols having 1 to 12 carbon atoms (*e.g.* esters of acrylic acid, methacrylic acid, maleic acid, fumaric acid, or itaconic acid, with C₁-C₁₂, C₁-C₈, or C₁-C₄ alkanols such as ethyl, *n*-butyl, isobutyl and 2-ethylhexyl acrylates and
 30 methacrylates, dimethyl maleate and *n*-butyl maleate); acrylamides and alkyl-substituted

acrylamides (e.g. (meth)acrylamide, N-tert-butylacrylamide, and N-methyl(meth)acrylamide); (meth)acrylonitrile; vinyl and vinylidene halides (e.g. vinyl chloride and vinylidene chloride); vinyl esters of C₁-C₁₈ mono- or dicarboxylic acids (e.g. vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl laurate and vinyl stearate); C₁-C₄ hydroxyalkyl esters of C₃-C₆ mono- or dicarboxylic acids, especially of acrylic acid, methacrylic acid or maleic acid, or their derivatives alkoxylated with from 2 to 50 moles of ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, or esters of these acids with C₁-C₁₈ alcohols alkoxylated with from 2 to 50 moles of ethylene oxide, propylene oxide, butylene oxide or mixtures thereof (e.g. hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, and methylpolyglycol acrylate); and monomers containing glycidyl groups (e.g. glycidyl methacrylate). As used herein, the term “(meth)acrylate” means acrylate, methacrylate, and mixtures thereof and the term “(meth)acrylic” used herein means acrylic, methacrylic, and mixtures thereof.

The monomers can also include one or more crosslinkers such as N-alkylolamides of α,β -monoethylenically unsaturated carboxylic acids having 3 to 10 carbon atoms and esters thereof with alcohols having 1 to 4 carbon atoms (e.g., N-methylolacrylamide and N-methylolmethacrylamide); glyoxal based crosslinkers; monomers containing two vinyl radicals; monomers containing two vinylidene radicals; and monomers containing two alkenyl radicals. Exemplary crosslinking monomers include diesters of dihydric alcohols with α,β -monoethylenically unsaturated monocarboxylic acids, of which in turn acrylic acid and methacrylic acid can be employed. Examples of such monomers containing two non-conjugated ethylenically unsaturated double bonds are alkylene glycol diacrylates and dimethacrylates, such as ethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate and propylene glycol diacrylate, divinylbenzene, vinyl methacrylate, vinyl acrylate, allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate and methylenebisacrylamide. In some embodiments, the crosslinking monomers include alkylene glycol diacrylates and dimethacrylates, and/or divinylbenzene. The crosslinking monomers when used in the copolymer can be present in an amount of from 0.2% to 5% by weight, based on the weight of the total monomer and are considered part of the total amount of monomers used in the copolymer.

In addition to the crosslinking monomers, small amounts of molecular weight regulators (*e.g.*, from 0.01% to 4% by weight based on the total dry monomer weight), such as tert-dodecyl mercaptan, can be added. Such substances are preferably added to the polymerization zone in a mixture with the monomers to be polymerized and are considered
5 part of the total amount of unsaturated monomers used in the copolymer.

In certain embodiments, the amount of binder dispersion in the paper coating composition of the present invention may be present in an amount of 3% to 20%, preferably 4% to 15%, and more preferably, 5% to 10% by weight, based on the dry weight of total pigment amount in the paper coating composition.

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Pigment

The coating composition of the present invention further comprises pigments. In certain embodiments, the pigments are inorganic materials such as clays with fine to coarse particle sizes; calcined clay; calcium carbonates including precipitated and ground calcium
15 carbonates; titanium dioxides including anatase and rutile; talc; silica; aluminum silicate; hydrated alumina; and aluminum trihydrate, either alone or as a combination of two kinds or more, dispersed in an aqueous medium in the form of a slurry.

Generally, a dry pigment is first dispersed in water or solvent to form a pigment slurry. The preparation of pigment slurries is well known in the art and may include
20 dispersants such as polyacrylic acid or surfactants to aid in the dispersion and stabilization of the pigment particles.

Hydrophobically modified alkali-swelling emulsion (HASE)

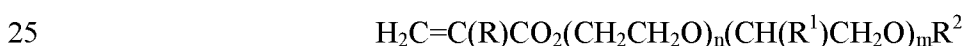
In certain embodiments of the present invention, the coating composition comprises a
25 hydrophobically modified alkali-swelling emulsion (HASE) polymer comprising structural units of the following monomers: a) an α,β -ethylenically unsaturated carboxylic acid monomer, preferably from 35% to 55%, more preferably from 40% to 50%, and most preferably from 45% to 49%, by weight based on the dry weight of the polymer; b) an α,β -ethylenically unsaturated nonionic monomer, from 40% to 55%, preferably from 42% to 53%,
30 and more preferably from 45% to 50%, by weight based on the dry weight of the HASE

polymer; and c) a polyethoxylated aralkyl phenol (meth)acrylate, from 0.5% to 20%, preferably from 1.0% to 15%, and more preferably from 2.5% to 10%, by weight based on the dry weight of the HASE polymer.

Suitable examples of α,β -ethylenically unsaturated carboxylic acid monomers include monobasic acids, such as acrylic, methacrylic, crotonic, and acyloxypropionic acids; and 5 dibasic acid monomers, such as maleic, fumaric, and itaconic acids. In some embodiments, the dibasic acid monomers are used in place of a portion, *e.g.*, up to about 10 weight percent, of the monobasic acid. Monoesters of the dibasic acid monomers, such as monobutyl ester of maleic acid can also be used. Preferably, the α,β -ethylenically unsaturated carboxylic acid 10 monomers are acrylic acid, methacrylic acid, and a combination thereof.

Examples of suitable α,β -ethylenically unsaturated nonionic monomers include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, lauryl acrylate, methyl methacrylate, butyl methacrylate, isodecyl methacrylate, lauryl methacrylate, hydroxyethyl methacrylate and hydroxypropyl methacrylate; methacrylonitrile; 15 ethacrylonitrile; methacrylamide; methacrylamide; amino-functional and ureido-functional monomers; monomers bearing acetoacetate-functional groups; styrene and substituted styrenes; butadiene; ethylene, propylene, α -olefins such as 1-decene; vinyl acetate, vinyl butyrate, vinyl versate and other vinyl esters; and vinyl monomers such as vinyl chloride and vinylidene chloride. Preferred examples are ethyl acrylate, methyl methacrylate, 2- 20 hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, vinyl acetate, acrylonitrile and the mixtures thereof. An especially preferred nonionic monomer is ethyl acrylate.

The polyethoxylated aralkyl phenol (meth) acrylate has the general formula:

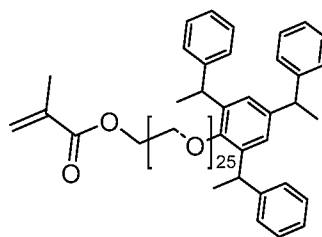


wherein R is H or CH₃; R¹ is C₁-C₂ alkyl; R² is aralkyl phenyl; n is an integer from 6 to 100 and m is an integer from 0 to 50, provided that $n \geq m$ and $m+n$ is from 6 to 100.

Preferably, $m=0$, and n is an integer from 10 to 60; and more preferably, $m=0$, and n is an 30 integer from 20 to 40.

Examples of the polyethoxylated aralkyl phenol (meth) acrylate include polyethoxylated tristyryl phenol methacrylate (commercially available as SIPOMER SEM-25 (60% active), as well as SIPOMER HPM-400 (50% active)) from Solvay Chemicals, Inc.

Specifically, in one embodiment of the present invention, the HASE comprises structural units of a polyethoxylated tristyryl phenol with 25 oxyethylene (EO) units, as represented by the following chemical structure:



The HASE polymer is prepared by emulsion polymerization well-known in the art. In certain embodiments of the present invention, either thermal or redox initiation process may be used as part of the emulsion polymerization process. Examples of suitable free radical initiators include hydrogen peroxide, sodium peroxide, potassium peroxide, t-butyl hydroperoxide, ammonium and/or alkali metal persulfates, sodium perborate, perphosphoric acid, and salts thereof; potassium permanganate, and ammonium or alkali metal salts of peroxydisulfuric acid. The free radical initiators may be used typically at a level of 0.01 to 3.0% by weight, based on the dry weight of monomers.

Redox systems comprising the above described initiators coupled with a suitable reductant may also be used in the emulsion polymerization process. Examples of suitable reductants include sodium sulfoxylate formaldehyde, ascorbic acid, isoascorbic acid, alkali metal and ammonium salts of sulfur-containing acids, such as sodium sulfite, bisulfite, thiosulfate, hydrosulfite, sulfide, hydrosulfide or dithionite, formadinesulfinic acid, hydroxymethanesulfonic acid, acetone bisulfite, glycolic acid, glyoxylic acid hydrate, lactic acid, glyceric acid, malic acid, tartaric acid and salts of the preceding acids. Redox reaction catalyzing metal salts of iron, copper, manganese, silver, platinum, vanadium, nickel, chromium, palladium, or cobalt may be used. Other additives such as, for example, free

radical initiators, oxidants, reducing agents, neutralizers, and dispersants may be added prior to, during, or subsequent to the polymerization reaction.

In certain embodiments, neutralizers can be added to the aqueous emulsion polymer during or after the reaction period to control pH. Neutralizers can be selected from mineral
5 bases such as sodium hydroxide, potassium hydroxide, salts of phosphoric acid, organic amines such as, for example, alkyl hydroxylamine, and ammonia.

Preferably, to ensure that a high solids content in the aqueous compositions of the present invention, chain transfer agents such as, for example, n-dodecyl mercaptan should be used in an amount between 0.01% and 0.3% by weight, or, more preferably, between 0.01%
10 to 0.2% by weight, or, more preferably, between 0.01% and 0.1% by weight, based on the dry weight of monomer mixture. Use of such low amount of the chain transfer agents in an emulsion copolymer avoids possible increase in water swelling or a decrease in elongation abilities.

Other suitable surfactants may include styrenated phenol sulfates, such as HitenolTM
15 BC-1025 (from Montello inc., Tulsa, OK), AerosolTM NPES – 930 (polyoxyethylene) nonylphenol (NP) ammonium sulfate (from Cytec Industries, Woodland Park, NJ), ethoxylated styrenated phenol sulfates, such as E-SperseTM RS-1596 and E-SperseTM RS-1618 (from Ethox Chemicals, Greenville, SC), and sodium dodecylallyl sulfosuccinate such as TREMTM LF-40 (from Cognis, Cincinnati, OH).

20 In certain embodiments, the amount of HASE in the paper coating composition of the present invention may be present in an amount of 0.01% to 1%, preferably 0.03% to 0.6%, and more preferably, 0.05% to 0.4% by weight, based on the dry weight of total pigment amount in the paper coating composition.

25 Starch

In certain embodiments of the present invention, the coating composition further comprises starch. “Starch,” as used herein, encompasses materials known as starches or flours that can come from one or more of a variety of sources, such as corn, wheat, pea, potato, rice, tapioca, and others known in the industry. The starch can be substituted or
30 unsubstituted. A combination of two or more types of starch can be used.

In one embodiment, the starch is a thinned starch. "Thinned starch" means starch whose molecular weight has been reduced, for example by acid or chemical hydrolysis, enzymatic hydrolysis, mechanical forces or other means. An example of a starch product that is suitable for use in some embodiments of the present invention is from National Starch & Chemical Company.

In one embodiment, the starch in the paper coating composition of the present invention may be present in an amount of 0.1% to 10%, and preferably from 1% to 9%, more preferably from 3% to 7%, by weight, based on the dry weight of the pigment amount in the paper coating composition.

The coating composition

The coating composition of the present invention may be prepared by techniques well known in the paper coating art. In one embodiment, the process of preparing the coating composition of the present invention may comprise mixing the aqueous dispersion of a binder, the pigment slurry, the starch solution, the HASE polymer, and water. Neutralizer is added to the dispersion to control pH. Other optional components may also be added as described above. Components in the coating composition may be mixed in any order to provide the coating composition of the present invention. Any of the above-mentioned optional components may also be added to the composition during or prior to the mixing to form the coating composition. In certain embodiments, the amount of solids in the coating composition is between 30%-75% by weight, based on total weight of the coating composition. In certain embodiments, the coating composition of the present invention may comprise dispersant, OBA, dyestuff, biocide, co-solvent and surfactant.

The paper coating compositions may be applied to a paper substrate by techniques well known in the art. For example, after forming a paper substrate, the paper coating compositions may be applied with a rolling applicator such as a metered size press; a blade coater such as a short dwell time applicator; an air knife coater; a slot die coater such as a jet applicator; or a brush. The preferred coating methods for high speed application include blade coater and metered size press.

As discussed above, the coating composition of the present invention is particularly suitable for use as a pre-coating material during the paper making process. In addition, the aqueous coating composition of the present invention can be used alone, or in combination with other coatings to form multi-layer coatings on a paper surface.

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EXAMPLES

The following examples illustrate the advantages of the present invention. Unless otherwise stated, all conditions are standard pressure and room temperature.

10 Raw materials used

Table 1 below lists the binder dispersion used to make the inventive and comparative coating compositions. Likewise, Table 2 below lists the representative raw materials used to make the HASE polymers in the inventive and comparative coating compositions. Table 3 below shows the additional materials that can be added to the binder dispersion and the HASE polymers, in order to make the inventive and comparative coating compositions. Tables 1-3 show the acronyms for these chemicals, the function for each material, and the commercial supplier from which these materials could be obtained.

20

*Table 1 - Representative List of Raw Materials Used to Make the
Binder Dispersion*

Chemical Name	Function	Supplier
Styrene Butadiene	Binder	BASF

*Table 2 - Representative List of Raw Materials Used to Make the
Hydrophobically Modified Alkali-Swellable Emulsion (HASE)*

Raw material	Function	Supplier
Methacrylic acid, MAA	Monomer	SCRC
Ethyl acrylate, EA	Monomer	Dow Chemical
Polyoxyethylene cetyl-stearyl methacrylate	Associative Monomer	Dow Chemical
Polyoxyethylene behenyl-tricosyl	Associative	Solvay Co., Ltd.

methacrylate, SIPOMER BEM	Monomer	
Polyethoxylated tristyryl phenol methacrylate, SIPOMER SEM-25	Associative Monomer	Solvay Co., Ltd.
Disponil ® FES 32	Surfactant	Cognis
n-dodecyl mercaptan (n-DDM)	Chain transfer agent	Dow Chemical
Ammonium persulfate (APS)	Initiator	Dow Chemical
Ferrous sulfate (FeSO ₄ ·7H ₂ O)	Promoter	Sinopharm Chemical Reagent Co., Ltd.
Tert-butylhydroperoxide (t-BHP)	Chaser catalyst	Dow Chemical
Isoascorbic acid (IAA)	Reductant	Dow Chemical
Sodium acetate	Buffer	Sinopharm Chemical Reagent Co., Ltd.
KATHON™ LX biocide (1.5% active)	Biocide	Dow Chemical

Table 3 - Representative List of Additional Raw Materials Used to Make the Comparative and Inventive Coating Compositions

Raw material	Function	Supplier
CaCO ₃ Slurry	Pigment slurry	Omya Company
Sodium Hydroxide (10% Active)	Neutralizer	Sinopharm Chemical Reagent Co., Ltd.
Starch	Water soluble Binder	GFE Company

5 Analytical Methods

The viscosities of the inventive and comparative coating composition samples were analyzed. In particular, Brookfield (BF) viscosity (measured in cps), representing the low-shear viscosity of the coating composition, is measured by a Brookfield viscometer DV-II+Pro EXTRA device, available from Brookfield Engineering Laboratories, Inc., at a low-shear rate at 50 rpm with a spindle 5. In general, a higher Brookfield viscosity reading indicates better thickening efficiency.

Sample Preparations

1. Starch solution for the comparative and inventive coating compositions

100 grams of starch powder was dispersed into 186 grams of DI water by stirring at 200-1500 rpm for 5 minutes, and then heated to 90-95°C for 20 minutes with continuous stirring at 500-2000 rpm. After the powder was dissolved, the aqueous starch solution was obtained.

5 2. Preparation of HASE for the inventive coating compositions

Charge 500.00 grams of DI water and 16.10 g of DISPONIL FES 32 emulsifier into a five-liter, four-necked flask equipped with a mechanical stirrer, a nitrogen sweep, a thermocouple, and a condenser. Heat the flask to 86°C. Dissolve 1.12 grams of ammonium persulfate (APS) in 16 grams of DI water, and added into the flask to initiate the
10 polymerization process. Wait two minutes, and then add into the flaks a monomer mixture including: 291.90 grams of EA, 287.80 grams of MAA, 51.75 grams SIPOMER SEM-25, 16.10 grams of DISPONIL FES 32 emulsifier mixed in 600.00 grams of DI water, as well as an additional charge of initiator mixture consisting of 0.34grams of APS dissolved in 58.0 grams of DI water, being co-fed into the flask with the monomer mixture over a period of 80
15 minutes while the flask temperature was maintained at 86°C.

Thereafter, the flask temperature was held at 86°C for ten minutes and then cooled to 60°C. A chaser mixture consists of 20.0 grams of FeSO₄ solution (0.15 %), 0.42 grams of t-BHP mixed in 10.00grams of DI water, and 0.21 grams of IAA mixed in 14.00 grams of DI water were then added into the flaks. After holding at 60°C for 15 minutes, the same amount
20 of chaser mixture was charged again into the flask. The flask was then cooled to 40°C, and a buffer solution of 1.1 grams of sodium acetate mixed in 130.00 grams of DI water was added into the flask over 10 minutes. Thereafter, a biocide solution consists of 3.71 grams of KATHON LX biocide (1.5% active) mixed in 12 grams of DI water was added into the flask over a span of 10 minutes. After the completion of polymerization process, the resulting
25 HASE emulsion was cooled to ambient temperature and filtered through a 325 mesh size screen.

The procedure described above illustrates the method for making the HASE polymer used in Inventive Coating Composition 1, which results in a HASE polymer that contains 5% of SIPOMER SEM-25 in its composition.

The procedure for making the HASE polymer to be used in Inventive Coating Composition 2 is substantially similar, except with a 7% SEM-25 in its composition.

3. Preparation of HASE for the comparative coating compositions

Several comparative coating compositions were prepared to demonstrate the advantages of the present invention. Notably, the procedure for making the HASE polymers used in these comparative coating compositions is similar to that described above for the inventive coating compositions.

One significant difference is that instead of using SIPOMER SEM-25 as an associate monomer to make the HASE, polyoxyethylene cetyl-stearyl methacrylate is used along with EA and MAA to make the HASE for Comparative Coating Composition 1. Unlike SIPOMER SEM-25, which contains multiple hydrophobic alkyl phenyl groups, polyoxyethylene cetyl-stearyl (C₁₆₋₁₈) methacrylate is a linear alkyl chain. For Comparative Coating Composition 1, it contains a 5% of polyoxyethylene cetyl-stearyl methacrylate in its composition.

Similarly, for Comparative Coating Composition 2, polyoxyethylene behenyl-tricosyl methacrylate (commercially obtainable as SIPOMER BEM) is used along with EA and MAA to make the HASE polymer for that coating composition. Similar to polyoxyethylene cetyl-stearyl methacrylate used in Comparative Coating Composition 1, polyoxyethylene behenyl-tricosyl (C₂₂₋₂₃) methacrylate is also a linear alkyl radical except that it has a longer carbon chain. For Comparative Coating Composition 2, it contains a 3% of polyoxyethylene behenyl-tricosyl methacrylate in its composition.

4. Preparation of coating compositions

After the starch solution, the pigment slurry, and the HASE polymers have been prepared, the inventive and comparative coating compositions were made. To make Inventive Coating Composition 1, 400 grams of the pigment slurry (calcium carbonate slurry) was mixed with 55.7 grams of the starch solution, as well as 36 grams of styrene-butadiene binder under room temperature, in to a 1L barrel with constant stirring at 300 rpm. Then, 1.6 grams of sodium hydroxide (10% active) were slowly added into the mixture to raise the

pH of the coating composition to above 9. At the same time, 0.8 grams of HASE was diluted with the same amount of DI water, and then added into the coating composition to reduce the percent solid of the coating composition to 68%. Finally, the coating composition was being stirred at 800 rpm for 8 minutes before the Brookfield viscosity is tested.

- 5 To make the Inventive Coating Composition 2, Comparative Coating Composition 1, and Comparative Coating Composition 2, the same steps described above were used.

Analytical Results

- 10 Table 4 below compares the thickening efficiencies of the inventive and comparative coating compositions, measured in terms of viscosity reading on the Brookfield viscometer.

Table 4 – Thickening Efficiencies of Coating Compositions Analyzed

Coating Composition Samples	Amount of HASE added (as wt.% of coating composition)	Hydrophobic Associative Monomer Used in HASE	Thickening Efficiency (as viscosity reading in cps)
Inventive Coating Composition 1	0.08%	Polyoxyethylene 2, 4, 6-triphenethyl benzyl methacrylate (SIPOMER SEM-25)	5880
Inventive Coating Composition 2	0.08%	Polyoxyethylene 2, 4, 6-triphenethyl benzyl methacrylate (SIPOMER SEM-25)	6275
Comparative Coating Composition 1	0.08%	Polyoxyethylene cetyl-stearyl methacrylate	3413
Comparative Coating Composition 2	0.08%	Polyoxyethylene behenyl-tricosyl methacrylate	3584

- 15 As shown in Table 4 above, with the same percentage of HASE polymers being introduced into the coating composition, the Inventive Coating Compositions 1 and 2 shows

much higher thickening efficiencies than that of Comparative Coating Compositions 1 and 2. These results indicate that variations in carbon chain lengths for the associative monomers in the HASE polymers do not have any positive effect on the thickening efficiency, as demonstrated by the lower thickening efficiencies in both Comparative Coating

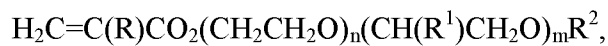
5 Compositions 1 and 2.

Rather, when a HASE polymer is made from associative monomers with polyethoxylated tristyryl phenol as end groups (such as the case for Inventive Coating Compositions 1 and 2); the coating composition shows a drastic improvement in thickening efficiency. Such improvement in thickening efficient would result in cost savings.

10

What is claimed is:

1. A paper coating composition comprising 1) an aqueous dispersion of a binder; 2) pigment; 3) starch; and 4) a hydrophobically modified alkali-swella-
5 ble emulsion which comprises structural units of a carboxylic acid monomer, an acrylate monomer, and an polyethoxylated aralkyl phenol (meth)acrylate having the following formula:



- 10 wherein R is H or CH₃, R¹ is methyl or ethyl; R² is aralkyl phenyl; n is an integer from 6 to 100 and m is an integer from 0 to 50, provided that n ≥ m and m+n is from 6 to 100.
2. The paper coating composition as claimed in claim 1, wherein R² is tristyryl phenyl, n is an integer from 20 to 30, and m is 0.
- 15 3. The paper coating composition as claimed in claim 1, wherein the hydrophobically modified alkali-swellaable emulsion is present in an amount from 0.01% to 1% by weight, based on dry weight of the total pigment amount in the paper coating composition.
- 20 4. The paper coating composition as claimed in claim 1, wherein said pigment is clay, titanium dioxide, or calcium carbonate, or talc, or silica, or aluminum silicate, or hydrated alumina, or aluminum trihydrate or mixture thereof.
5. The paper coating composition as claimed in claim 1, wherein the hydrophobically modified alkali-swellaable emulsion comprises by weight, based on dry weight of the 25 hydrophobically modified alkali-swellaable emulsion, from 35% to 55% structural units of a methacrylic acid, from 40% to 55% structural units of ethyl acrylate, and from 0.5% to 20% of an polyethoxylated aralkyl phenol methacrylate.

6. The paper coating composition as claimed in claim 1, wherein the aqueous dispersion of the binder is an aqueous dispersion of a) an acrylic copolymer, b) a styrene acrylic copolymer, c) styrene butadiene copolymers, or d) vinyl acrylic copolymers, and mixtures thereof.

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7. The paper coating composition as claimed in claim 1, wherein the aqueous dispersion of the binder comprises from 3% to 20% by weight, based on the dry weight of the pigment amount in the paper coating composition.

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8. The paper coating composition as claimed in claim 1, wherein the starch comprises from 0.1% to 10%, preferably from 1.0% to 9.0%, and more preferably from 3.0% to 7.0% by weight, based on the dry weight of pigment amount in the paper coating composition.

9. A coated paper substrate comprising the coating composition of any one of claims 1-8.

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10. A method of forming a coated paper substrate comprising: (a) forming a paper substrate, (b) forming a coating composition comprising mixing an aqueous dispersion of a binder, pigment, a hydrophobically modified alkali-swellaable emulsion, and starch under stirring, wherein the hydrophobically modified alkali-swellaable emulsion comprises

20 structural units of a carboxylic acid monomer, an acrylate monomer, and an polyethoxylated aralkyl phenol methacrylate; and (c) applying the coating composition onto one or more surfaces of the paper substrate.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/076724

A. CLASSIFICATION OF SUBJECT MATTER

D21H 21/00(2006.01)i; C08F 212/04(2006.01)i; C08F 220/00(2006.01)i; D21H 19/36(2006.01)i

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)

D21H 21/-; C08F 212/-; C08F220/-; D21H 19/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

WPI, EPODOC, CNKI, CNPAT: paper, coat+, alkali, hydrophobic+, emulsion, tristyryl, phenyl, aralkyl, phenol, ethoxy+, acrylate, acrylic, carboxylic, acid, pigment, starch, binder

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 1283206 A (RHODIA CHIM) 07 February 2001 (2001-02-07) description, page 2 lines 9-27, page 3 line 17 to page 4 line 1, page 4 lines 8-23, page 3 lines 17-29, page 7 lines 10-15, page 8 lines 4-5, examples 1-2	1-10
A	US 2010038046 A1 (COATEX S.A.S.) 18 February 2010 (2010-02-18) claims 1-28, discription, paragraphs [0127]-[0131], [0207]-[0224]	1-10
A	EP 2368923 A1 (ROHM AND HAAS COMPANY) 28 September 2011 (2011-09-28) all document	1-10
A	WO 2006127050 A1 (HERCULES INCOPRORATED) 30 November 2006 (2006-11-30) all document	1-10
A	EP 2712898 A1 (ROHM AND HAAS COMPANY) 02 April 2014 (2014-04-02) all document	1-10

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* 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

10 November 2016

Date of mailing of the international search report

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Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2016/076724

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