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(54) Title: VINYL ACETATE-ETHYLENE COPOLYMER EMULSION AND PAPER COATING COMPOSITION BASED ON THE SAME

(57) Abstract: The present invention relates to a vinyl acetate-ethylene copolymer emulsion and a paper coating composition based on the same. More specifically, the present invention relates to a vinyl acetate-ethylene copolymer emulsion based paper coating composition with low odor. The present invention also relates to processes for preparing the vinyl acetate-ethylene copolymer emulsion and the paper coating composition, and uses thereof.



Vinyl acetate-ethylene copolymer emulsion and paper coating composition
based on the same

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a vinyl acetate-ethylene copolymer emulsion and a paper coating composition based on the same. More specifically, the present invention relates to a vinyl acetate-ethylene copolymer emulsion based paper coating composition with low odor. The present invention also relates to processes for preparing the vinyl acetate-ethylene copolymer emulsion and the paper coating composition, and uses thereof.

2. Description of the Related Art

[0002] Aqueous emulsions, such as styrene-butadiene copolymer emulsion, styrene-acrylate copolymer emulsion, acrylate copolymer emulsion, vinyl acetate homopolymer emulsion, vinyl acetate-ethylene copolymer emulsion, etc., are commonly used as binder for paper surface coating in paper industry, and styrene-butadiene copolymer emulsion are the most widely used aqueous emulsion among others. With the advancement in modern printing package techniques, the requirements to the papers for using in printing and packing are also enhancing, in particular to those printing packages with high qualities such as cigarette package and food package which require that the package material *per se* has a low odor. Especially as the application of Ultra-Violet (UV) curable ink and electron beam radiation curable ink printing techniques recently, a higher requirement to the odor of the package material and therefore to the odor of the emulsion for surface coating has raised. However, traditional aqueous emulsions tend to be odorous and cannot meet the requirement of low odor paper coating, especially printing packages with high qualities such as cigarette package and food package.

[0003] Although a low odor aqueous emulsion is required in the art, few researches have been done to lower the odor of the aqueous emulsion used in paper making industry, and the factors which directly influence the odor of the emulsion are still unknown up to now. Furthermore, the odors of various kinds of emulsion polymers which have already cured under UV and electron beam radiation are still unpredictable respectively to the technicians in the art based on their past experiences.

[0004] Therefore, a need still exists for low odor aqueous emulsion and paper coating composition based on the same for application in printing packages with high qualities.

BRIEF SUMMARY OF THE INVENTION

[0005] It has been surprisingly found by the present inventors that, by using a specific vinyl acetate-ethylene copolymer emulsion according to the present invention instead of commonly used aqueous emulsion such as styrene-butadiene emulsion as binder for paper coating compositions, especially high qualities paper coating compositions used in UV curable ink and electron beam radiation curable ink, such as those used in cigarette package and food package, a vinyl acetate-ethylene copolymer emulsion and a paper coating composition based on the same with extraordinary low odor are obtained.

[0006] The vinyl acetate-ethylene copolymer emulsion according to the present invention is obtained through aqueous emulsion polymerization of vinyl acetate and ethylene. It has been surprisingly found by the present inventors that the package paper made by using the inventive vinyl acetate-ethylene copolymer emulsion as binder for paper surface coating exhibits a extremely low odor after application of Ultra-Violet (UV) curable ink and electron beam radiation curable ink printing techniques, which can meet the low odor requirement sufficiently as needed by the market. Without wishing to be bound by any theory, but the applicant believes that the low odor performances as provided by the vinyl acetate-ethylene copolymer emulsion according to the present invention is partially attributed to following factors, such as the structure/composition properties of the vinyl acetate-ethylene copolymer emulsion and/or its advantages over commonly used styrene-butadiene copolymer emulsion, which could include: the vinyl acetate-ethylene copolymer emulsion is free of organic phenylic monomer, and the polymerization process is carried out without addition of phenylic derived monomer, therefore the residue of volatile phenylic derivative which has special odor such as 4-phenyl cyclohexene is avoided; ethylene, one of the monomers, is gas, thus can hardly retained in the emulsion; the vinyl acetate monomer and other possible volatile organic residues can be further reduced by chemical and physical process during or after the end of the polymerization, whereby the content of residue vinyl acetate monomer can be reduced to less than about 800 ppm, preferably less than about 600 ppm, more preferably less than about 400 ppm; furthermore, vinyl acetate ethylene copolymer will not release odorous substances by further chemical reaction under exposure to UV or electron beam radiation.

[0007] Thus, one object of the present invention is to provide a low odor vinyl acetate-ethylene copolymer emulsion.

[0008] Another object of the present invention is to provide a process for preparing said vinyl acetate-ethylene copolymer emulsion.

[0009] Still another object of the present invention is to provide a use of the vinyl acetate-ethylene copolymer emulsion for low odor paper coating composition.

[0010] Furthermore, one object of the present invention is to provide a low odor paper coating composition.

[0011] Another object of the present invention is to provide a process for preparing said low odor paper coating composition.

[0012] Still another object of the present invention is to provide a use of the low odor paper coating composition in printing packages with high qualities, such as cigarette package and food package.

DETAILED DESCRIPTION OF THE INVENTION

[0013] For the purposes of this description, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the description and claims are to be understood as being modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following description and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0014] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific Examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0015] It is noted that, as used in this description and the appended claims, the singular forms "a", "an" and "the" include plural referents unless expressly and unequivocally limited to one referent.

[0016] According to one aspect of the present invention, a vinyl acetate-ethylene copolymer-based emulsion for low odor paper coating composition is provided, wherein the copolymer comprises, based on the total

weight of the copolymer:

(1) about 65-95pphm (parts by weight / 100 parts by weight of monomers used for preparing the emulsion), preferably about 75-90 pphm of a moiety derived from vinyl acetate;

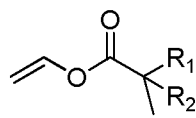
(2) about 5-35pphm, preferably about 10-20 pphm of a moiety derived from ethylene; and

(3) about 0-10pphm, preferably about 0-5 pphm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization of the monomers in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid.

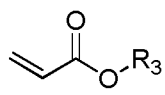
[0017] In some non-limiting embodiments of the present invention, the monomers used in emulsion polymerization can be composed of about 65-95pphm of vinyl acetate, about 5-35pphm of ethylene and about 0-10pphm of other comonomers or functional monomers. Examples of other comonomers or functional monomers suitable for the present invention include, but not limited to, one or more selected from the group of:

- vinyl esters of polyacid, wherein the specific monomer can include:



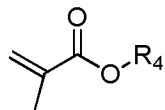
, wherein each of R_1 and R_2 is hydrogen or alkyl group, provided that the total carbon atom number of R_1 and R_2 is from 1 to 14;

- acrylates, wherein the specific monomer can include:



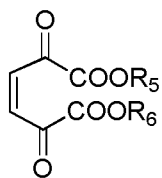
, wherein R_3 is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- methacrylates, wherein the specific monomer can include:



, wherein R_4 is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- maleate esters, wherein the specific monomer can include:



, wherein each of R_5 and R_6 is alkyl group with 1 to 16 carbon atom(s);

- acrylic acid; methacrylic acid; maleic acid; maleic anhydride; fumaric acid; crotonic acid; itaconic acid; acrylonitrile; methylacrylonitrile; sodium vinylsulfonate; sodium vinyl benzenesulfonate; mono-sodium 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propylsulfonate; methacrylate ethyl trimethyl ammonium chloride; acrylamide; hydroxymethylacrylamide; hydroxyethylacrylamide; hydroxypropylacrylamide; vinyltrimethoxysilane; vinyltriethoxysilane; vinyltri(2-methoxyethoxy)silane; methylacryloxypropyltrimethoxysilane; ethylene glycol acrylate; propylene glycol acrylate; glycidyl acrylate; diallyl maleate; diallyl phthalate; triallyl cyanurate; allyl methacrylate; ethylene glycol dimethylacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; ethyl acetoacetoxymethylacrylate; diacetone acrylamide; allyl acrylamide; or mixtures thereof.

[0018] In some non-limiting embodiments of the present invention, said surfactant can be selected from anionic surfactants, nonionic surfactants or combination thereof.

[0019] Examples of anionic surfactants suitable for the present invention include, but not limited to: alkylsulfates, alkylsulfonates, alkyl benzenesulfonates, alkyl polyoxyethylene ether sulfates, alkylpolyoxyethylene-propylene ether sulfates, sodium fatty alcohol succinic acid mono ester sulfonates, disodium fatty alcohol polyoxyethylene ether sulfosuccinates, disodium fatty alcohol polyoxyethylene-propylene ether sulfosuccinates, alkylpolyoxyethylene phosphates, alkylpolyoxyethylene-propylene phosphates and alkali metal salts of fatty acids. Specific examples of anionic surfactants suitable for the present invention include, but not limited to: sodium dodecylbenzene sulfonate, sodium dodecylsulfonate, sodium dodecylsulfate, disodium dodecyldiphenylether sulfonate, octadecyl sulfosuccinic acid and sodium dioctylsulfosuccinate. In some non-limiting embodiments of the present invention, the anionic surfactants as mentioned above can be used in the form of aqueous solution.

[0020] Examples of nonionic surfactants suitable for the present invention include, but not limited to: linear alkyl alcohol polyoxyethylene ethers, linear alkyl alcohol polyoxyethylene-propylene ethers, branched alkyl alcohol polyoxyethylene ethers, branched alkyl alcohol polyoxyethylene-propylene

ethers, fatty acid polyoxyethylenemonoesters, fatty acid polyoxyethylene-propylenemonoesters. Specific examples of nonionic surfactants suitable for the present invention include, but not limited to: isometric tridecyl alcohol polyoxyethylene monoether, cetyl alcohol polyoxyethylenemonoether, octadecyl alcohol polyoxyethylenemonoether lauroylhydroxypolyoxyethylene, etc., wherein the EO numbers of polyoxyethylene section are chosen according to the desired HLB value of the surfactant, typically in the range of about 20 to 40. In some non-limiting embodiments of the present invention, the nonionic surfactants as mentioned above can be used in the form of aqueous solution.

[0021] In some non-limiting embodiments of the present invention, the surfactant can be used in an amount of about 1-5 ppm, preferably about 2-5 ppm, more preferably about 2-4 ppm.

[0022] In some non-limiting embodiments of the present invention, the polymeric protective colloid can be selected from partially hydrolyzed polyvinyl alcohols, cellulose ethers and polyvinyl pyrrolidone. Specific examples of polymeric protective colloids suitable for the present invention include, but not limited to: polyvinyl alcohols having a degree of alcoholysis of about 75 to 95%, more preferably about 70 to 92% and a degree of polymerization of about 200 to 4000, more preferably polyvinyl alcohols having a degree of alcoholysis of about 80 to 90% and a degree of polymerization of about 200 to 4000. Cellulose ethers as polymeric protective colloid suitable for the present invention include, but not limited to, hydroxymethyl cellulose ether, hydroxyl ethylcellulose ether and hydroxypropyl cellulose ether. In some non-limiting embodiments of the present invention, the polymeric protective colloid can be used in an amount of about 0-10 ppm, preferably about 0-5 ppm.

[0023] According to one aspect of the present invention, a low odor paper coating composition, comprising a solid component and a binder, characterized in that said binder comprises:

(a) a vinyl acetate-ethylene copolymer-based emulsion, wherein the copolymer comprises, based on the total weight of the copolymer:

(1) about 65-95ppm, preferably about 75-90 ppm of a moiety derived from vinyl acetate;

(2) about 5-35ppm, preferably about 10-20 ppm of a moiety derived from ethylene; and

(3) about 0-10ppm, preferably about 0-5 ppm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization

of the monomers in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid,

(b) additional water.

[0024] The low odor paper coating composition comprises the solid component and the binder. In some non-limiting embodiments of the present invention, the weight ratio of solid component to binder is about 100:6 to 100:19, preferably about 100:8 to 100:16.

[0025] The solid component used in low odor paper coating composition can comprise, but not limited to, kaolin, calcium carbonate or a mixture thereof.

[0026] The binder used in low odor paper coating composition comprises mainly vinyl acetate-ethylene copolymer-based emulsion and additional water. In some non-limiting embodiments of the present invention, the binder can have a solid content of about 40 to 70%, more commonly about 50 to 60% by weight.

[0027] In some non-limiting embodiments of the present invention, the binder used in low odor paper coating composition essentially consists of vinyl acetate-ethylene copolymer-based emulsion, additional water and other conventional additives.

[0028] The conventional additives added to the aqueous phase of the binder may include those known in the art which are useful in the emulsion polymerization system or improve the stability or pot life of the final emulsion. For example, those additives can be redox reaction promoter, pH adjusting agents, ion intensity regulators, molecular weight modifiers, defoamers, fungicides, chelating agents, and the like.

[0029] In some non-limiting embodiments of the present invention, the emulsion polymerization is conducted in the presence of a redox initiator. The oxidizing agent and reducing agent used to make up of the redox initiator include, but not limited to water soluble oxidizing agents and reducing agents known in the art. Examples of oxidizing agents and reducing agents suitable for the present invention may include, but not limited to, ammonium persulfate, sodium persulfate, hydrogen peroxide, tert-butyl peroxide, sodium formaldehyde-sulfoxylate, disodium 2-hydroxyl-2-sulfinatoacetate, ascorbic acid, erythorbic acid, alkali metal salts of ascorbic acid, alkali metal salts of erythorbic acid, sodium bisulfite, sodium sulfite, sodium metabisulfite, sodium thiosulfate, etc.. Typically, the oxidizing agent and reducing agent can be each added in an amount of about 0.05 to 5 pphm.

[0030] According to another aspect of the present invention, a process for preparing the vinyl acetate-ethylene copolymer-based emulsion is provided. Said process comprises emulsion polymerizing a monomeric composition comprising:

- (1) about 65-95pphm of a moiety derived from vinyl acetate;
- (2) about 5-35pphm of a moiety derived from ethylene; and
- (3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid.

[0031] According to another aspect of the present invention, a process for preparing the low odor paper coating composition is provided, said process comprises

(a) forming an ethylene-vinyl acetate copolymer-based emulsion by emulsion polymerizing a monomeric composition comprising:

- (1) about 65-95pphm of a moiety derived from vinyl acetate;
- (2) about 5-35pphm of a moiety derived from ethylene; and
- (3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid;

(b) mixing said ethylene-vinyl acetate copolymer-based emulsion with additional water to form a binder;

(c) mixing said binder with a solid component.

[0032] In a preferable embodiment of the present invention, the emulsion may be obtained by the following steps: forming an aqueous phase by adding surfactant and protective colloid, as emulsifier, and other additives such as defoamers, pH adjusting agents, ion intensity regulators, molecular weight modifiers, etc. into water under stirring; feeding the aqueous phase to a reactor under slow stirring; evacuating the reactor under vacuum and purging with nitrogen several times for removing any air; raising the temperature of the reactor to about 40-70°C, then increasing the speed of stirring, adding to the reactor part of the vinyl acetate monomer or mixture of the vinyl acetate monomer and the other comonomers or functional monomers, together with

part of ethylene gas; after the temperature and pressure of the reactor becomes stable, adding dropwise oxidizing agent and reducing agent, as polymerization initiator, so that polymerization takes place, with increasing of temperature; adding remaining monomers when the temperature of the reactor reaches a predetermined value, about 50-90°C, until the consumption of the monomers. The temperature of the reactor was controlled at about 50-90°C during the emulsion polymerization process. After completion of polymerization, the reactor is cooled to selected temperature, about 50-70°C, and the polymerization product therein was transferred to a post-treatment reactor, while the unreacted ethylene gas was discharged as exhaust gas. Subsequently, certain amount of oxidizing agent and reducing agent were added to the post-treatment reactor, to reduce the amount of residual monomers by further initiating the polymerization of residual monomers. Alternatively, the amount of residual monomers can be further reduced by extraction of water vapor. Finally, the emulsion parameters of the copolymer-based emulsion thus obtained can be adjusted by feeding with additional water and/or other conventional additives, such as fungicides, pH adjusting agents, etc.. The emulsion thus obtained can have a solid content of about 40 to 70%, most commonly about 50 to 60% by weight, and can be used as binder for the low odor paper coating composition according to the present invention.

[0033] In some non-limiting embodiments of the present invention, a vinyl acetate-ethylene copolymer-based emulsion was obtained according to the above mentioned formulation and process, and the vinyl acetate-ethylene copolymer-based emulsion thus obtained can be used to formulate the low odor paper coating composition.

[0034] In a preferable embodiment of the present invention, the low odor paper coating composition may be obtained by the following steps: forming an slurry by mixing the solid component with water, dispersing agents, defoamers and the like; the slurry thus obtained is added with the binder derived from the vinyl acetate-ethylene copolymer-based emulsion and co-adjuvants such as fluorescent whiteners, rheology modifiers, etc., and mixed under stirring to obtain a homogeneous paper coating composition.

[0035] In some non-limiting embodiments of the present invention, the low odor paper coating composition according to the present invention comprises:

100 parts of solid component, which comprises kaolin, calcium carbonate or a mixture thereof;

- about 6-19 parts, preferably about 8-16 parts of binder;

- about 0.05-1 part, preferably about 0.1-0.5 part of dispersing agents, suitable examples of which may include, but not limited to: acrylate dispersing agents, such as sodium acrylate, ammonium acrylate, potassium acrylate, etc.; polyphosphate dispersing agents, such as sodium tripolyphosphate, tetrasodium pyrophosphate, sodium hexametaphosphate, etc.; sulfonate dispersing agents, such as lignin sulfonate, aromatic sulfonate, aliphatic sulfonate, sodium succinsulfonate, etc.; or mixtures thereof;
- about 0.05-0.5 part, preferably about 0.1-0.3 part of defoamers, suitable examples of which may include, but not limited to: polyol defoamers, polyether defoamers, mineral oil defoamers, silicone defoamers, or mixtures thereof;
- about 0.05-1 part, preferably about 0.1-0.4 part of rheology modifiers, suitable examples of which may include, but not limited to: associative rheology modifiers, alkali swelling rheology modifiers, cellulosic rheology modifiers, natural polymer rheological modifiers and the like, such as polyurethane thickeners, sodium acrylate thickeners, acrylate thickeners, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropylmethyl cellulose, carrageenin, agar, sodium alginate, etc.; or mixtures thereof;
- about 0-0.8 part, preferably about 0.3-0.6 part of fluorescent whiteners, suitable examples of which may include, but not limited to: diaminodistyrenedisulfonate, diaminodistyrenetetrasulfonate, and diaminodistyrenehexasulfonate, or mixtures thereof;
- about 0.1-0.4 part of pH adjusting agents, which is used to keep the pH value of the paper coating composition between 8 to 11, suitable examples of which may include, but not limited to: sodium hydroxide, potassium hydroxide, ammonia and organic amine modifiers, or mixtures thereof.

[0036] According to the concept of the present invention, the present invention comprises the following items:

1. A low odor paper coating composition, comprising a solid component and a binder, characterized in that said binder comprises:

(a) a vinyl acetate-ethylene copolymer-based emulsion, wherein the copolymer comprises, based on the total weight of the copolymer:

- (1) about 65-95pphm of a moiety derived from vinyl acetate;
- (2) about 5-35pphm of a moiety derived from ethylene; and
- (3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization of the monomers in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid,

(b) additional water.

2. The paper coating composition according to any of the preceding items, wherein the surfactant is selected from anionic surfactants, nonionic surfactants or combination thereof.

3. The paper coating composition according to any of the preceding items, wherein the anionic surfactants are selected from alkylsulfates, alkylsulfonates, alkyl benzenesulfonates, alkyl polyoxyethylene ether sulfates, alkylpolyoxyethylene-propylene ether sulfates, sodium fatty alcohol succinic acid mono ester sulfonates, disodium fatty alcohol polyoxyethylene ether sulfosuccinates, disodium fatty alcohol polyoxyethylene-propylene ether sulfosuccinates, alkylpolyoxyethylene phosphates, alkylpolyoxyethylene-propylene phosphates, alkali metal salts of fatty acids, or mixtures thereof.

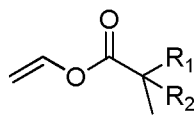
4. The paper coating composition according to any of the preceding items, wherein the nonionic surfactants are selected from linear alkyl alcohol polyoxyethylene ethers, linear alkyl alcohol polyoxyethylene-propylene ethers, branched alkyl alcohol polyoxyethylene ethers, branched alkyl alcohol polyoxyethylene-propylene ethers, fatty acid polyoxyethylenemonoesters, fatty acid polyoxyethylene-propylenemonoesters, or mixtures thereof.

5. The paper coating composition according to any of the preceding items, wherein the polymeric protective colloid is selected from partially hydrolyzed polyvinyl alcohols, cellulose ethers, polyvinyl pyrrolidone, or mixtures thereof.

6. The paper coating composition according to any of the preceding items, wherein the polyvinyl alcohol has a degree of alcoholysis of about 75 to 95%, more preferably about 70 to 92% and a degree of polymerization of about 200 to 4000, preferably a degree of alcoholysis of about 80 to 90% and a degree of polymerization of about 200 to 4000.

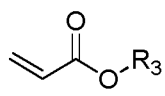
7. The paper coating composition according to any of the preceding items, wherein other comonomers or functional monomers are selected from:

- vinyl esters of polyacid, wherein the specific monomer can include:



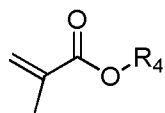
, wherein each of R_1 and R_2 is hydrogen or alkyl group, provided that the total carbon atom number of R_1 and R_2 is from 1 to 14;

- acrylates, wherein the specific monomer can include:



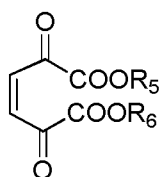
, wherein R_3 is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- methacrylates, wherein the specific monomer can include:



, wherein R_4 is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- maleate esters, wherein the specific monomer can include:



, wherein each of R_5 and R_6 is alkyl group with 1 to 16 carbon atom(s);

- acrylic acid; methacrylic acid; maleic acid; maleic anhydride; fumaric acid; crotonic acid; itaconic acid; acrylonitrile; methylacrylonitrile; sodium vinylsulfonate; sodium vinyl benzenesulfonate; mono-sodium 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propylsulfonate; methacrylate ethyl trimethyl ammonium chloride; acrylamide; hydroxymethylacrylamide; hydroxyethylacrylamide; hydroxypropylacrylamide; vinyltrimethoxysilane; vinyltriethoxysilane; vinyltri(2-methoxyethoxy)silane; methylacryloxypropyltrimethoxysilane; ethylene glycol acrylate; propylene glycol acrylate; glycidyl acrylate; diallyl maleate; diallyl phthalate; triallyl cyanurate; allyl methacrylate; ethylene glycol dimethylacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; ethyl acetoacetoxymethylacrylate; diacetone acrylamide; allyl acrylamide; or mixtures thereof.

8. The paper coating composition according to any of the preceding items, wherein the solid component comprises kaolin, calcium carbonate or a mixture thereof.

9. The paper coating composition according to any of the preceding items, wherein the weight ratio of solid component to binder is about 100:6 to 100:19, preferably about 100:8 to 100:16.

10. The paper coating composition according to any of the preceding items, wherein the content of residue vinyl acetate monomer is less than about 800 ppm, preferably less than about 600 ppm, more preferably less than about 400 ppm.

11. A process for preparing the low odor paper coating composition according to any of the preceding items, said process comprises

(a) forming an ethylene-vinyl acetate copolymer-based emulsion by emulsion polymerizing a monomeric composition comprising:

- (1) about 65-95pphm of a moiety derived from vinyl acetate;
- (2) about 5-35pphm of a moiety derived from ethylene; and
- (3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid;

(b) mixing said ethylene-vinyl acetate copolymer-based emulsion with additional water to form a binder;

(c) mixing said binder with a solid component.

12. A vinyl acetate-ethylene copolymer-based emulsion for low odor paper coating composition, wherein the copolymer comprises, based on the total weight of the copolymer:

- (1) about 65-95pphm of a moiety derived from vinyl acetate;
- (2) about 5-35pphm of a moiety derived from ethylene; and
- (3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization of the monomers in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid.

13. The vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items, wherein the surfactant is selected from anionic surfactants, nonionic surfactants or combination thereof.

14. The vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items, wherein the anionic surfactants are selected from

alkylsulfates, alkylsulfonates, alkyl benzenesulfonates, alkyl polyoxyethylene ether sulfates, alkylpolyoxyethylene-propylene ether sulfates, sodium fatty alcohol succinic acid mono ester sulfonates, disodium fatty alcohol polyoxyethylene ether sulfosuccinates, disodium fatty alcohol polyoxyethylene-propylene ether sulfosuccinates, alkylpolyoxyethylene phosphates, alkylpolyoxyethylene-propylene phosphates, alkali metal salts of fatty acids, or mixtures thereof.

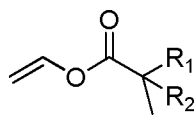
15. The vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items, wherein the nonionic surfactants are selected from linear alkyl alcohol polyoxyethylene ethers, linear alkyl alcohol polyoxyethylene-propylene ethers, branched alkyl alcohol polyoxyethylene ethers, branched alkyl alcohol polyoxyethylene-propylene ethers, fatty acid polyoxyethylenemonoesters, fatty acid polyoxyethylene-propylenemonoesters, or mixtures thereof.

16. The vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items, wherein the polymeric protective colloid is selected from partially hydrolyzed polyvinyl alcohols, cellulose ethers, polyvinyl pyrrolidone, or mixtures thereof.

17. The vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items, wherein the polyvinyl alcohol has a degree of alcoholysis of about 75 to 95%, more preferably about 70 to 92% and a degree of polymerization of about 200 to 4000, preferably a degree of alcoholysis of about 80 to 90% and a degree of polymerization of about 200 to 4000.

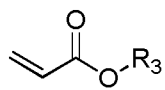
18. The vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items, wherein other comonomers or functional monomers are selected from:

- vinyl esters of polyacid, wherein the specific monomer can include:



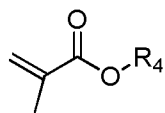
, wherein each of R_1 and R_2 is hydrogen or alkyl group, provided that the total carbon atom number of R_1 and R_2 is from 1 to 14;

- acrylates, wherein the specific monomer can include:



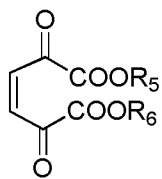
, wherein R_3 is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- methacrylates, wherein the specific monomer can include:



, wherein R₄ is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- maleate esters, wherein the specific monomer can include:



, wherein each of R₅ and R₆ is alkyl group with 1 to 16 carbon atom(s);

- acrylic acid; methacrylic acid; maleic acid; maleic anhydride; fumaric acid; crotonic acid; itaconic acid; acrylonitrile; methylacrylonitrile; sodium vinylsulfonate; sodium vinyl benzenesulfonate; mono-sodium 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propylsulfonate; methacrylate ethyl trimethyl ammonium chloride; acrylamide; hydroxymethylacrylamide; hydroxyethylacrylamide; hydroxypropylacrylamide; vinyltrimethoxysilane; vinyltriethoxysilane; vinyltri(2-methoxyethoxy)silane; methylacryloxypropyltrimethoxysilane; ethylene glycol acrylate; propylene glycol acrylate; glycidyl acrylate; diallyl maleate; diallyl phthalate; triallyl cyanurate; allyl methacrylate; ethylene glycol dimethylacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; ethyl acetoacetoxymethylacrylate; diacetone acrylamide; allyl acrylamide; or mixtures thereof.

19. The vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items, wherein the copolymer-based emulsion has a solid content of about 40 to 70%, most commonly about 50 to 60% by weight based on the total weight of the emulsion.

20. The vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items, wherein the content of residue vinyl acetate monomer is less than about 800 ppm, preferably less than about 600 ppm, more preferably less than about 400 ppm.

21. A process for preparing the vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items, said process comprises emulsion polymerizing a monomeric composition comprising:

- (1) about 65-95pphm of a moiety derived from vinyl acetate;
- (2) about 5-35pphm of a moiety derived from ethylene; and
- (3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid.

22. The process according to any of the preceding items, wherein the emulsion polymerization is carried out in the presence of a redox initiator.

23. The process according to any of the preceding items, wherein the initiator is selected from ammonium persulfate, sodium persulfate, hydrogen peroxide, tert-butyl peroxide, sodium formaldehyde-sulfoxylate, disodium 2-hydroxyl-2-sulfonatoacetate, ascorbic acid, erythorbic acid, alkali metal salts of ascorbic acid, alkali metal salts of erythorbic acid, sodium bisulfite, sodium sulfite, sodium metabisulfite, sodium thiosulfate, or mixtures thereof.

24. Use of the vinyl acetate-ethylene copolymer-based emulsion according to any of the preceding items or obtainable by the process according to any of the preceding items in low odor paper coating composition.

25. Use of the low odor paper coating composition according to any of the preceding items in high end packaging application, such as cigarette package and food package.

[0037] The inventive paper coating composition has extraordinary low odor, even after application of Ultra-Violet (UV) curable ink and electron beam radiation curable ink printing techniques. In the context of this application, the term "low odor" means that the inventive paper coating composition pass the odor evaluation test as described hereinafter.

[0038] The odor evaluation test can be carried out as follows:

1. Preparation of paper sample.

A paper sample is prepared by the following steps: the binder derived from vinyl acetate-ethylene copolymer-based emulsion produced by aqueous emulsion polymerization as described above is mixed with solid component, dispersing agents, fluorescent whiteners and rheology modifiers to obtain a paper coating composition; the paper coating composition thus obtained is applied to both sides of a raw paper in an amount of 10-15gsm/10-15gsm/10-15gsm for pre-coating/middle coating/top-coating; the coated white paperboard is calendered through a calender and sealed inside a plastic bag for storing.

2. UV curing

The paper sample thus obtained is withdrawn from the plastic bag, curable in a UV drier, and then sealed again inside a plastic bag for storing. The

parameters used in UV radiation are: UV lamp, 6wx4; wavelength, 254 nm; radiation time, 30 min.

3. Odor evaluation

The odor evaluation is carried out in 12 hours after UV curing. The odor evaluation procedures are as follows: a sealed plastic bag containing the paper sample is placed in front of the nose of an evaluator and then opened; the evaluator breathes in the air released from the plastic bag immediately after the plastic bag is opened, and scores the smell by a value ranging from 1 to 5, with the value of 1 represents the highest odor and the worst score, and the value of 5 represents the lowest odor and the best score. Each paper sample is evaluated by ten random selected persons respectively and the sum of the scores is output as the final result for each paper sample. The sum of the scores of each paper sample is compared with those of other paper samples, whereby a final score evaluation to each paper sample is obtained. Typically, a value of 5 represents the lowest odor which cannot be obviously smelled by the evaluator, a value of 1 represents the highest odor, which means that the tested sample exhibits severe sour smell, bitter smell or other chemical's smell to the evaluator, while a value ranging from 4 to 2 represents a slight odor, obvious odor or heavier odor sequentially.

[0039] In some non-limiting embodiments of the present invention, the inventive low odor paper coating composition made from vinyl acetate-ethylene copolymer-based emulsion produce by aqueous emulsion polymerization as described above exhibits a final score of greater than 30, more preferably greater than 40 when compared with other paper coating composition made from traditional aqueous emulsions, such as styrene-butadiene copolymer emulsion, styrene-acrylate copolymer emulsion, acrylate copolymer emulsion, vinyl acetate homopolymer emulsion, vinyl acetate-ethylene copolymer emulsion, etc..

[0040] The following Examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the Examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

EXAMPLES

[0041] Unless indicated to the contrary, all parts and percentages are by weight.

TEST

[0042] The odor of the inventive paper coating composition and other comparative paper coating compositions are tested according to the odor evaluation test as described above.

Example 1

[0043] To a 10L reactor was added 2.4 kg deionized water, 116 g polyvinyl alcohol having an alcoholysis degree of 88% and a viscosity of 5 mPa.s in 4% aqueous solution at 20°C and 120g polyvinyl alcohol having an alcoholysis degree of 88% and a viscosity of 23 mPa.s in 4% aqueous solution at 20°C with stirring (300 rpm). The reactor was heated to 99°C and maintained for 1 hour to obtain a sufficiently dissolved solution. The reactor was then cooled to 55°C. 33 g Disponil A3065 (Cognis, with a concentration of 65%), 3 g sodium acetate and 6 g 85% phosphoric acid solution (which were used to adjust the pH of the solution), 2 g silicone defoamer and 0.2g 40% ferric chloride solution were added sequentially into the reactor to provide a catalyst for the polymerization reaction. The reactor was evacuated and purged with nitrogen for three times to remove residual air. The stirring speed was then increased to 600 rpm. 2.9 kg vinyl acetates were added into the reactor by feeding pump, and 550g ethylene gases were fed into the reactor at the same time. The pressure of the reactor was equilibrated for 5 mins, and then the reactor was charged with 35 g of 1.7wt% aqueous solution of disodium 2-hydroxy-2-sulfinatoacetate. The reactor was kept under 55°C and equilibrated for 5 mins. The polymerization reaction was initiated by feeding into the reactor with the following initiators: 1.5wt% aqueous solution of *t*-butyl peroxide with a starting feeding rate of 94.5g/h, 1.7wt% aqueous solution of disodium 2-hydroxy-2-sulfinatoacetate with a starting feeding rate of 94.5g/h. When the temperature of the reactor reached 57°C, the reaction temperature was controlled by adjusting the flow rates of the initiators so that the reaction temperature increased to 85°C in 20 mins and then was maintained under 85°C. When temperature of the reactor reached 72°C, 230 g ethylene gases were added, and the maximum pressure inside the reactor was maintained below 60bar. When temperature of the reactor reached 80°C, 1.24kg vinyl acetates were added into the reactor with a feeding rate of 1.26kg/h.

[0044] After completion of adding the initiators, the reactor was cooled to 55°C. The obtained emulsion was transferred to post-treatment reactor.

[0045] The post-treatment reactor was stirred at a speed of 200 rpm and charged with 90g of 3.1wt% aqueous solution of disodium 2-hydroxy-2-sulfinatoacetate in 30 mins, then 90g of mixture of 1wt% aqueous solution of *t*-butyl peroxide and 1wt% aqueous solution of hydrogen peroxide in 30 mins. The post-treatment reactor was kept under a vacuum degree of -0.3bar. When the temperature of the post-treatment reactor reached 65°C, a total amount of 105g water vapor was charged in to the post-treatment reactor for extraction. Finally, the post-treatment reactor was cooled to 40°C. 30 g 1.5% CIT/MIT fungicides were added into the post-treatment reactor.

[0046] The properties of the obtained vinyl acetate-ethylene copolymer-based emulsion (Emulsion 1) are listed in Table 1.

Table 1 Properties of Emulsion 1

solid content	56.42% by weight
pH	4.3
viscosity (BVF, 20 rpm)	5670 mPa.s
particle size (D90)	2.0 μ m
Residual Monomers	291 ppm

Example 2

[0047] A vinyl acetate-ethylene copolymer-based emulsion (Emulsion 2) was prepared according to the procedure in Example 1, except that the post-treatment reactor has not subjected to water vapor extraction. The obtained vinyl acetate-ethylene copolymer-based emulsion (Emulsion 2) has a residual monomer content of 685 ppm.

Comparative Example 1

[0048] A commercial available styrene-butadiene copolymer emulsion (Comparative Emulsion 1) for paper coating was obtained, which has a residual monomer content of 60 ppm.

Comparative Example 2

[0049] A commercial available styrene-acrylate copolymer emulsion (Comparative Emulsion 2) for paper coating was obtained, which has a residual monomer content of 550 ppm.

Results and Discussion

[0050] The emulsions as obtained in Example 1-2 and Comparative Example 1-2 were used to prepare paper coating compositions respectively according to the formulation as listed in Table 2.

Table 2, Formulation of the paper coating compositions

Component	Amount, parts by weight
Emulsion, on dry basis	14
Kaolin	30
Calcium carbonate C95	70
Dispersing agent 5040	0.1
Fluorescent whitener OBA	0.75
Thickener CMC	0.4
Defoamer Foamaster NXZ	0.1
Sodium hydroxide	0.1

[0051] The paper coating compositions thus obtained were tested according to the odor evaluation test as described above respectively and the results are summarized in Table 3.

Table 3, Results of odor evaluation test

	Residual Monomer Content of emulsion, ppm	Score of the odor evaluation test
Paper coating composition prepared from Emulsion 1	291	41
Paper coating composition prepared from Emulsion 2	685	34
Ppaper coating composition prepared from Comparative Emulsion 1	60	24
Ppaper coating composition prepared from Comparative Emulsion 2	550	27

[0052] According to results of Table 3, although the residual monomer content of Emulsion 1 (291 ppm) is higher than that of Comparative Emulsion 1 (60 ppm), the paper coating composition prepared from Emulsion 1 according to the present invention exhibits a much higher score than that of the paper coating composition prepared from Comparative Emulsion 1. The paper coating composition prepared from Emulsion 2 with a high residual monomer content of 685 ppm also passes the odor evaluation test with a value of greater than 30, which suggests that the vinyl acetate-ethylene copolymer-based emulsion according to the present invention can provide low odor to the paper coating composition prepared therefrom, especially after exposure to UV drier according to the procedure of odor evaluation test, therefore is useful as binder for printing packages with high qualities, such as cigarette package, food package and the like.

[0053] All of the methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the products and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A low odor paper coating composition, comprising a solid component and a binder, characterized in that said binder comprises:

(a) a vinyl acetate-ethylene copolymer-based emulsion, wherein the copolymer comprises, based on the total weight of the copolymer:

(1) about 65-95pphm of a moiety derived from vinyl acetate;

(2) about 5-35pphm of a moiety derived from ethylene; and

(3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization of the monomers in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid,

(b) additional water.

2. The paper coating composition according to claim 1, wherein the surfactant is selected from anionic surfactants, nonionic surfactants or combination thereof.

3. The paper coating composition according to claim 2, wherein the anionic surfactants are selected from alkylsulfates, alkylsulfonates, alkyl benzenesulfonates, alkyl polyoxyethylene ether sulfates, alkylpolyoxyethylene-propylene ether sulfates, sodium fatty alcohol succinic acid mono ester sulfonates, disodium fatty alcohol polyoxyethylene ether sulfosuccinates, disodium fatty alcohol polyoxyethylene-propylene ether sulfosuccinates, alkylpolyoxyethylene phosphates, alkylpolyoxyethylene-propylene phosphates, alkali metal salts of fatty acids, or mixtures thereof.

4. The paper coating composition according to claim 2, wherein the nonionic surfactants are selected from linear alkyl alcohol polyoxyethylene ethers, linear alkyl alcohol polyoxyethylene-propylene ethers, branched alkyl alcohol polyoxyethylene ethers, branched alkyl alcohol polyoxyethylene-propylene ethers, fatty acid polyoxyethylenemonoesters, fatty acid polyoxyethylene-propylenemonoesters, or mixtures thereof.

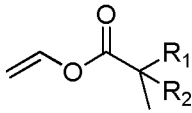
5. The paper coating composition according to claim 1, wherein the polymeric protective colloid is selected from partially hydrolyzed polyvinyl alcohols,

cellulose ethers, polyvinyl pyrrolidone, or mixtures thereof.

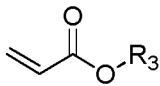
6. The paper coating composition according to claim 5, wherein the polyvinyl alcohol has a degree of alcoholysis of about 75 to 95%, more preferably about 70 to 92% and a degree of polymerization of about 200 to 4000, preferably a degree of alcoholysis of about 80 to 90% and a degree of polymerization of about 200 to 4000.

7. The paper coating composition according to claim 1, wherein other comonomers or functional monomers are selected from:

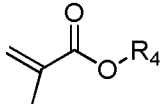
- vinyl esters of polyacid, wherein the specific monomer can include:

, wherein each of R₁ and R₂ is hydrogen or alkyl group, provided that the total carbon atom number of R₁ and R₂ is from 1 to 14;

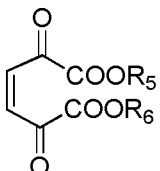
- acrylates, wherein the specific monomer can include:

, wherein R₃ is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- methacrylates, wherein the specific monomer can include:

, wherein R₄ is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- maleate esters, wherein the specific monomer can include:

, wherein each of R₅ and R₆ is alkyl group with 1 to 16 carbon atom(s);

- acrylic acid; methacrylic acid; maleic acid; maleic anhydride; fumaric acid; crotonic acid; itaconic acid; acrylonitrile; methylacrylonitrile; sodium vinylsulfonate; sodium vinyl benzenesulfonate; mono-sodium 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propylsulfonate; methacrylate ethyl trimethyl ammonium chloride; acrylamide; hydroxymethylacrylamide; hydroxyethylacrylamide; hydroxypropylacrylamide; vinyltrimethoxysilane; vinyltriethoxysilane; vinyltri(2-methoxyethoxy)silane; methylacryloxypropyltrimethoxysilane; ethylene glycol acrylate; propylene glycol acrylate; glycidyl acrylate; diallyl maleate; diallyl phthalate; triallyl

cyanurate; allyl methacrylate; ethylene glycol dimethylacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; ethyl acetoacetoxymethylacrylate; diacetone acrylamide; allyl acrylamide; or mixtures thereof.

8. The paper coating composition according to claim 1, wherein the solid component comprises kaolin, calcium carbonate or a mixture thereof.

9. The paper coating composition according to claim 1, wherein the weight ratio of solid component to binder is about 100:6 to 100:19, preferably about 100:8 to 100:16.

10. A process for preparing the low odor paper coating composition according to any one of claims 1 to 9, said process comprises

(a) forming an ethylene-vinyl acetate copolymer-based emulsion by emulsion polymerizing a monomeric composition comprising:

(1) about 65-95pphm of a moiety derived from vinyl acetate;

(2) about 5-35pphm of a moiety derived from ethylene; and

(3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid;

(b) mixing said ethylene-vinyl acetate copolymer-based emulsion with additional water to form a binder;

(c) mixing said binder with a solid component.

11. A vinyl acetate-ethylene copolymer-based emulsion for low odor paper coating composition, wherein the copolymer comprises, based on the total weight of the copolymer:

(1) about 65-95pphm of a moiety derived from vinyl acetate;

(2) about 5-35pphm of a moiety derived from ethylene; and

(3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization of the monomers in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5 pphm of a polymeric protective colloid as emulsifier / protective colloid.

12. The vinyl acetate-ethylene copolymer-based emulsion according to claim 11, wherein the surfactant is selected from anionic surfactants, nonionic surfactants or combination thereof.

13. The vinyl acetate-ethylene copolymer-based emulsion according to claim 12, wherein the anionic surfactants are selected from alkylsulfates, alkylsulfonates, alkyl benzenesulfonates, alkyl polyoxyethylene ether sulfates, alkylpolyoxyethylene-propylene ether sulfates, sodium fatty alcohol succinic acid mono ester sulfonates, disodium fatty alcohol polyoxyethylene ether sulfosuccinates, disodium fatty alcohol polyoxyethylene-propylene ether sulfosuccinates, alkylpolyoxyethylene phosphates, alkylpolyoxyethylene-propylene phosphates, alkali metal salts of fatty acids, or mixtures thereof.

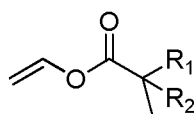
14. The vinyl acetate-ethylene copolymer-based emulsion according to claim 12, wherein the nonionic surfactants are selected from linear alkyl alcohol polyoxyethylene ethers, linear alkyl alcohol polyoxyethylene-propylene ethers, branched alkyl alcohol polyoxyethylene ethers, branched alkyl alcohol polyoxyethylene-propylene ethers, fatty acid polyoxyethylenemonoesters, fatty acid polyoxyethylene-propylenemonoesters, or mixtures thereof.

15. The vinyl acetate-ethylene copolymer-based emulsion according to claim 11, wherein the polymeric protective colloid is selected from partially hydrolyzed polyvinyl alcohols, cellulose ethers, polyvinyl pyrrolidone, or mixtures thereof.

16. The vinyl acetate-ethylene copolymer-based emulsion according to claim 15, wherein the polyvinyl alcohol has a degree of alcoholysis of about 75 to 95%, more preferably about 70 to 92% and a degree of polymerization of about 200 to 4000, preferably a degree of alcoholysis of about 80 to 90% and a degree of polymerization of about 200 to 4000.

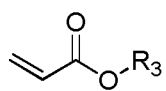
17. The vinyl acetate-ethylene copolymer-based emulsion according to claim 11, wherein other comonomers or functional monomers are selected from:

- vinyl esters of polyacid, wherein the specific monomer can include:



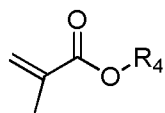
, wherein each of R_1 and R_2 is hydrogen or alkyl group, provided that the total carbon atom number of R_1 and R_2 is from 1 to 14;

- acrylates, wherein the specific monomer can include:



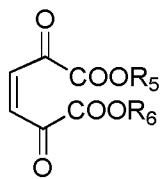
, wherein R_3 is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- methacrylates, wherein the specific monomer can include:



, wherein R₄ is hydrogen or alkyl group with 1 to 16 carbon atom(s);

- maleate esters, wherein the specific monomer can include:



, wherein each of R₅ and R₆ is alkyl group with 1 to 16 carbon atom(s);

- acrylic acid; methacrylic acid; maleic acid; maleic anhydride; fumaric acid; crotonic acid; itaconic acid; acrylonitrile; methylacrylonitrile; sodium vinylsulfonate; sodium vinyl benzenesulfonate; mono-sodium 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propylsulfonate; methacrylate ethyl trimethyl ammonium chloride; acrylamide; hydroxymethylacrylamide; hydroxyethylacrylamide; hydroxypropylacrylamide; vinyltrimethoxysilane; vinyltriethoxysilane; vinyltri(2-methoxyethoxy)silane; methylacryloxypropyltrimethoxysilane; ethylene glycol acrylate; propylene glycol acrylate; glycidyl acrylate; diallyl maleate; diallyl phthalate; triallyl cyanurate; allyl methacrylate; ethylene glycol dimethylacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; ethyl acetoacetoxymethylacrylate; diacetone acrylamide; allyl acrylamide; or mixtures thereof.

18. The vinyl acetate-ethylene copolymer-based emulsion according to claim 11, wherein the copolymer-based emulsion has a solid content of about 40 to 70%, most commonly about 50 to 60% by weight based on the total weight of the emulsion.

19. A process for preparing the vinyl acetate-ethylene copolymer-based emulsion according to any one of claims 11 to 18, said process comprises emulsion polymerizing a monomeric composition comprising:

- (1) about 65-95pphm of a moiety derived from vinyl acetate;
- (2) about 5-35pphm of a moiety derived from ethylene; and
- (3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-10pphm, preferably about 0-5

pphm of a polymeric protective colloid as emulsifier / protective colloid.

20. The process according to claim 19, wherein the emulsion polymerization is carried out in the presence of a redox initiator.

21. The process according to claim 20, wherein the initiator is selected from ammonium persulfate, sodium persulfate, hydrogen peroxide, tert-butyl peroxide, sodium formaldehyde-sulfoxylate, disodium 2-hydroxyl-2-sulfinatoacetate, ascorbic acid, erythorbic acid, alkali metal salts of ascorbic acid, alkali metal salts of erythorbic acid, sodium bisulfite, sodium sulfite, sodium metabisulfite, sodium thiosulfate, or mixtures thereof.

22. Use of the vinyl acetate-ethylene copolymer-based emulsion according to any one of claims 11 to 18 or obtainable by the process according to any one of claims 19 to 21 in low odor paper coating composition.

23. Use of the low odor paper coating composition according to any one of claims 1-9 in high end packaging application, such as cigarette package and food package.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/075432

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

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: C09D1/-; C09D9/-; C09D131/-; C08F2/-; C08F210/-; C08F218/-

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) CNKI, CA on CD, CNABS, CNTXT, DWPI, SIPOABS, vinyl acetate, ethylene, emulsion?, paper?, coating?, polymeriz+, monomer, surfactant, emulsifier, protective colloid, polyvinyl alcohol, PVA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN1954039A (CELANESE EMULSIONS GMBH CELANESE EMULSIONS GMBH) 25 Apr.2007 (25.04.2007), see description pages 2,4-8, and 11	1-21
X	JP2005-194387A (DENKI KAGAKU KOGYO KK) 21 Jul.2005 (21.07.2005), see example 1,[0002],[0018]-[0019]	1, 6, 22-23

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

* 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 24 Jan.2013 (24.01.2013)	Date of mailing of the international search report 28 Feb. 2013 (28.02.2013)
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Information on patent family members

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A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC

C09D131/04 (2006.01) i

C08F218/08 (2006.01) i

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