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(71) Applicant (for all designated States except US): **ROHM AND HAAS COMPANY** [US/US]; 100 Independence Mall West, 7th Floor, Philadelphia, Pennsylvania 19106 (US).

(72) Inventor; and

(71) Applicant (for US only): **LI, Ling** [US/CN]; 936 Zhangheng Road, Shanghai 201203 (CN).

(74) Agent: **SHANGHAI PATENT & TRADEMARK LAW OFFICE, LLC**; 435 Guiping Road, Shanghai 200233 (CN).

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(54) Title: A MULTI-STAGE POLYMER AS A GRINDING ADDITIVE AND PREPARATION PROCESS THEREOF

(57) Abstract: Provided are a multi-stage polymer comprising a first stage and second stage polymer as a grinding additive and the preparation process thereof. The first stage polymer is prepared from a mixture of: a) 0.1-50 wt% of a nonionic macro-monomer; b) 30-70 wt% an α , β - ethylenically β unsaturated carboxylic acid monomer; and c) 30-70 wt% α , β - ethylenically unsaturated nonionic monomer. The polymerization units of the second stage polymer comprise: e) 10-70 wt% of a α , β - ethylenically unsaturated carboxylic acid monomer; and f) 30-90 wt% nonionic α , β - ethylenically unsaturated monomer.



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A MULTI-STAGE POLYMER AS A GRINDING ADDITIVE AND PREPARATION PROCESS THEREOF

Field

This invention generally relates to a multi-stage polymer as a grinding additive and a method of producing the same.

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Background

In a typical paint-making process, a dispersant is added in the grinding stage to help pigments and extenders to stably disperse. Polyacid homopolymers or copolymers are commonly used as dispersants. In the same grinding stage, 10 thickeners are added to provide high enough viscosity to grind pigment/extender to fine sizes, as well as to deliver the proper viscosity for the final paint. Thickeners used in grinding stage, typically, are Hydroxyethyl Cellulose (HEC) and Hydrophobically-modified Ethylene Oxide Urethane (HEUR). In the letdown stage, more thickeners are added to reach the target viscosity for the final paint. In 15 economy paint space, HEC and polyacid dispersant are added in the grinding stage to deliver dispersion and viscosity, and minimal thickeners could be added in the letdown stage to reach the target viscosity.

In the effort of replacing HEC for cost saving and better flow/leveling, Hydrophobically-modified Alkali Soluble Emulsion (HASE) was added in the letdown 20 stage to reach the target viscosity. However, this approach will make the paint film more hydrophilic and lead to significant loss on scrub resistance (washability). To make the paint film more hydrophobic, hydrophobic copolymer dispersant (such as Orotan 2002 of Dow Coating Materials) can be used to replace the polyacid dispersant in the grinding stage. However, HASE is not very compatible with 25 hydrophobic dispersant, and sometimes causes many grids.

It is still desirable to paint formulators a compatible composition of HASE and hydrophobic dispersant, which will provide the paint formulation basic paint properties, such as the proper washability and opacity.

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Summary

The present invention provides a multi-stage polymer comprising, based on the total weight of the multi-stage polymer, from 1 wt.% to 99 wt.% of a first stage polymer, and from 1 wt.% to 99 wt.% of a second stage polymer, wherein the first stage polymer comprises, as polymerization units, based on the total weight of the first stage polymer: (a) from 0.1 wt.% to 50 wt.%, of a nonionic macromonomer, characterized by the following formula: $\text{H}_2\text{C}=\text{C}(\text{R})\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}(\text{R}')\text{CH}_2\text{O})_m\text{R}''$, wherein R is H or CH_3 , R' is $\text{C}_1\text{-C}_2$ alkyl; R'' is $\text{C}_8\text{-C}_{30}$ alkyl, $\text{C}_8\text{-C}_{16}$ alkylphenyl or $\text{C}_{13}\text{-C}_{36}$ aralkylphenyl; n is an integral number from 6 to 100 and m is an integral number from 0 to 50, provided that $n \geq m$ and $m+n$ is from 6 to 100; (b) from 30 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated carboxylic acid monomer; and (c) from 30 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated nonionic monomer; wherein the first stage polymer has a weight average molecular weight of at least 50,000 Daltons; and the second stage polymer comprises, as polymerization units, based on the total weight of the second stage polymer: (e) from 10 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated carboxylic acid monomer; and (f) from 30 wt.% to 90 wt.%, of a nonionic α,β -ethylenically unsaturated monomer; wherein the second stage polymer has a weight average molecular weight of from 500 to 20,000 Daltons, and the second stage polymer contains a substantial absence of the nonionic macromonomer.

The multi-stage polymer of the present invention may comprise a first stage polymer further comprising, as polymerization units, based on the total weight of the first stage polymer, from 0.01 wt.% to 5 wt.%, a polyethylenically unsaturated crosslinking monomer.

The multi-stage polymer of the present invention preferably comprises a second stage polymer containing an absence of the nonionic macromonomer.

The present invention further provides a method for preparing a multi-stage polymer which comprises the steps: i) contacting under emulsion polymerization conditions a first monomer composition comprising: (a) from 0.1 wt.% to 50 wt.%, of a nonionic macromonomer, characterized by the following formula: $\text{H}_2\text{C}=\text{C}(\text{R})\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}(\text{R}')\text{CH}_2\text{O})_m\text{R}''$, wherein R is H or CH_3 , R' is $\text{C}_1\text{-C}_2$ alkyl; R'' is $\text{C}_8\text{-C}_{30}$ alkyl, $\text{C}_8\text{-C}_{16}$ alkylphenyl or $\text{C}_{13}\text{-C}_{36}$ aralkylphenyl; n is an integral number from 6 to 100 and m is an integral number from 0 to 50, provided that $n \geq m$ and $m+n$ is from 6 to 100; (b) from 30 wt.% to 70 wt.%, of an α,β -ethylenically

unsaturated carboxylic acid monomer; and (c) from 30 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated nonionic monomer; to obtain a first stage polymer having a weight average molecular weight of at least 50,000 Daltons; and ii) contacting under emulsion polymerization the first stage polymer with a second monomer composition comprising, based on the weight of the second monomer composition: (e) from 10 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated carboxylic acid monomer; and (f) from 30 wt.% to 90 wt.%, of an α,β -ethylenically unsaturated nonionic monomer; to obtain a second stage polymer having a weight average molecular weight of from 500 to 20,000 Daltons, and the second stage polymer contains a substantial absence of the nonionic macromonomer.

The method for preparing a multi-stage polymer of the present invention may comprise a first monomer composition further comprising, based on the total weight of the first polymer composition, from 0.01 wt.% to 5 wt.%, a polyethylenically unsaturated crosslinking monomer.

The method for preparing a multi-stage polymer of the present invention preferably comprises a second monomer composition containing an absence of the nonionic macromonomer.

The present invention further provides a coating composition comprising from 0.1% to 2%, by weight based on the total weight of the coating composition, of the multi-stage polymer according to claim 1, a pigment, an extender, and a binder.

Detailed Description

Exemplary embodiments in accordance with the present invention will be described. Various modifications, adaptations or variations of the exemplary embodiments described herein may become apparent to those skilled in the art as such are disclosed. It will be understood that all such modifications, adaptations or variations that rely upon the teachings of the present invention, and through which these teachings have advanced the art, are considered to be within the scope and spirit of the present invention.

As used herein and throughout the specification, the term "multi-stage polymer" means a composite polymer particle prepared by a sequential or staged polymerization process wherein first sequence or stage of monomer repeating units

is polymerized before the subsequent or second sequence or stage of repeating units are polymerized.

As used herein, the term “(meth)acrylic” acid is meant to include both acrylic acid and methacrylic acid.

5 The multi-stage polymer as a grinding additive of the present invention includes a first stage polymer, and a second stage polymer. The first stage polymer is a Hydrophobically-modified Alkali Soluble Emulsion (HASE) polymer, and comprises, as polymerization units, based on the total weight of the first stage polymer:

10 (a) from 0.1 wt.% to 50 wt.%, preferably from 1 wt.% to 30 wt.%, and most preferably from 2 wt.% to 20 wt.%, of a nonionic macromonomer;

(b) from 30 wt.% to 70 wt.%, preferably from 35 wt.% to 60 wt.%, and most preferably from 40 wt.% to 50 wt.%, of an α,β -ethylenically unsaturated carboxylic acid monomer; and

15 (c) from 30 wt.% to 70 wt.%, preferably from 35 wt.% to 65 wt.%, and most preferably from 40 wt.% to 60 wt.%, of an α,β -ethylenically unsaturated nonionic monomer.

Optionally, the first stage polymer further comprises, as polymerization units, based on the total weight of the first stage polymer, d) from 0.01 wt.% to 5 wt.%,
20 preferably from 0.03 wt.% to 1 wt.%, and most preferably from 0.05 wt.% to 0.5 wt.%, of a polyethylenically unsaturated crosslinking monomer.

The second stage polymer is a hydrophobic polymer dispersant, and comprises, as polymerization units, based on the total weight of the second stage polymer:

25 (e) from 10 wt.% to 70 wt.%, preferably from 20 wt.% to 60 wt.%, and most preferably from 25 wt.% to 50 wt.%, of an α,β -ethylenically unsaturated carboxylic acid monomer; and

(f) from 30 wt.% to 90 wt.%, preferably from 35 wt.% to 80 wt.%, and most preferably from 40 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated nonionic
30 monomer.

The proportions of the monomers in the first stage polymer can vary widely within above mentioned ranges to obtain thickening agents possessing a variety of

rheological properties. The resulting first stage polymer, upon neutralization of at least a portion of the carboxyl groups, can be soluble in water and thicken the paint.

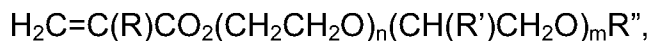
The proportions of the monomers in the second stage polymer can vary widely within the above mentioned ranges to achieve requested balance of dispersion efficiency and hydrophobicity. The resulting second stage polymer, upon neutralization of at least a portion of the carboxyl groups, can be soluble in water and disperse pigment and extenders in the grinding stage of paint making process.

In the multi-stage polymer composite of the present invention, the first stage polymer can vary from 1% to 99% by weight, and the second stage polymer can also vary from 1% to 99% by weight, based on the total weight of the multi-stage polymer composite. It is preferred for the first stage polymer being from 30% to 90% by weight, and the second stage polymer being from 10% to 70% by weight, while most preferably, the first stage polymer is from 40% to 65% by weight, and the second stage polymer is from 30% to 60% by weight.

The first stage polymer has a weight average molecular weight of at least 50,000 Daltons as determined by gel permeation chromatography. To provide most effective thickening with polymers which are water-soluble when neutralized, molecular weight within the range of from 80,000 to 5,000,000 Daltons is preferred, while most preferably, it is from 100,000 to 1,000,000 Daltons. The second stage polymer has a weight average molecular weight of from 500 to 20,000 Daltons as determined by gel permeation chromatography. To provide most effective dispersing with polymers which are water-soluble when neutralized, molecular weights within the range of from 800 to 15,000 Daltons is preferred, while most preferably, it is from 1,000 to 10,000 Daltons. Weight average molecular weight, M_w , is measured by gel permeation chromatography (GPC) using polyacrylic acid standards, as is known in the art. The techniques of GPC are discussed in detail in "Modern Size Exclusion Chromatography", W. W. Yau, J. J. Kirkland, D. D. Bly; Wiley-Interscience, 1979, and in "A Guide to Materials Characterization and Chemical Analysis", J. P. Sibilio; VCH, 1988, p. 81-84. The molecular weights reported herein are all in weight average molecular weights and are all in units of Dalton.

In general, more nonionic macromonomers will lead to stronger associative thickening behavior with the binder particles. On the other hand, the higher level of acid monomers will provide stronger thickening to the aqueous phase.

The nonionic macromonomer of the present invention has the formula:



wherein R is H or CH₃, R' is C₁-C₂ alkyl; R'' is C₈-C₃₀ alkyl, C₈-C₁₆ alkylphenyl or C₁₃-C₃₆ aralkylphenyl; n is an integral number from 6 to 100 and m is an integral number from 0 to 50, provided that n≥m and m+n is from 6 to 100. Preferably, m=0, and n is an integral number from 10 to 60; and most preferably, m=0, and n is an integral number from 20 to 40.

Suitable examples of the nonionic macromonomer include, but are not limited to, SIPOMERTM BEM (50% active), SIPOMERTM SEM-25 (60% active), SIPOMERTM HPM-100 (50% active), SIPOMERTM HPM-200 (50% active), SIPOMERTM HPM-400 (50% active), available from Rhodia, and MA-20 (70% active), available from Dow Chemical Company. Preferably used examples are SIPOMERTM BEM (50% active), SIPOMERTM HPM-400 (50% active), and MA-20 (70% active).

The second stage polymer contains a substantial absence of the nonionic macromonomer (i.e., less than 1 part by weight, preferably less than 0.1 part, more preferably less than 0.01 part, of the nonionic macromonomer per 100 parts by weight of the nonionic macromonomer in the first stage polymer). In a most preferred embodiment, the second stage polymer contains an absence of the nonionic macromonomer.

α,β-ethylenically unsaturated carboxylic acid monomers are α,β-ethylenically unsaturated monomers containing at least one carboxylic acid group. α,β-ethylenically unsaturated carboxylic acid monomers suitably used in the present invention include, but are not limited to, monobasic acids, such as acrylic, methacrylic, crotonic, and acyloxypropionic acid; and dibasic acid monomers, such as maleic, fumaric, and itaconic acid. Dibasic acid monomers, when applying, are used in place of a portion, e.g. up to about 10 weight percent, of the monobasic acid. Monomers which are monoesters of dibasic acids, such as the monobutyl ester of maleic acid can also be used. Preferably used examples are acrylic acid, methacrylic acid, and a combination thereof.

α,β-ethylenically unsaturated nonionic monomers are α,β-ethylenically unsaturated monomers without bearing an ionic charge between pH=1-14. α,β-ethylenically unsaturated nonionic monomers suitably used in the present invention include, but are not limited to, (meth)acrylic ester monomers, where (meth)acrylic ester designates methacrylic ester or acrylic ester, including methyl acrylate, ethyl

acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, lauryl acrylate, methyl methacrylate, butyl methacrylate, isodecyl methacrylate, lauryl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate; (meth)acrylonitrile; (meth)acrylamide; amino-functional and ureido-functional monomers; monomers
 5 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, vinylidene chloride. The most preferably used examples are ethyl acrylate, methyl methacrylate, 2-hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl
 10 methacrylate, vinyl acetate and acrylonitrile and a combination thereof.

Polyethylenically unsaturated cross-linking monomers are optional in the first stage polymer's polymerization. They work as crosslinkers that are utilized to generate a polymer having either a partially or substantially crosslinked three-dimensional network. Exemplary polyethylenically unsaturated cross-linking
 15 monomers include, but are not limited to, di(meth)acrylate compounds such as ethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,6-butylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 2,2'-bis(4-(acryloxy-propyloxyphenyl)propane, 2,2'-
 20 bis(4-(acryloxydiethoxy-phenyl)propane, and zinc acrylate (i.e., $2(\text{C}_3\text{H}_3\text{O}_2)\text{Zn}^{++}$); tri(meth)acrylate compounds such as, trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, and tetramethylolmethane tri(meth)acrylate; tetra(meth)acrylate compounds such as ditrimethylolpropane tetra(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, and pentaerythritol tetra(meth)acrylate;
 25 hexa(meth)acrylate compounds such as dipentaerythritol hexa(meth)acrylate; allyl compounds such as allyl (meth)acrylate, diallylphthalate, diallyl itaconate, diallyl fumarate, and diallyl maleate; polyallyl ethers of sucrose having from 2 to 8 allyl groups per molecule, polyallyl ethers of pentaerythritol such as pentaerythritol diallyl ether, pentaerythritol triallyl ether, and pentaerythritol tetraallyl ether; polyallyl ethers
 30 of trimethylolpropane such as trimethylolpropane diallyl ether and trimethylolpropane triallyl ether. Other suitable polyethylenically unsaturated cross-linking monomers include divinyl glycol, divinyl benzene, and methylenebisacrylamide.

Preferably, the suitable examples of polyethylenically unsaturated cross-linking monomers are ethylene glycol di(meth)acrylate, ally (meth)acrylate, diallylphthalate, and the composition thereof.

In another aspect, suitable polyethylenically unsaturated cross-linking monomers can be synthesized via an esterification reaction of a polyol made from ethylene oxide or propylene oxide or combinations thereof with unsaturated anhydride such as maleic anhydride, citraconic anhydride, itaconic anhydride, or an addition reaction with unsaturated isocyanate such as 3-isopropenyl-a-a-dimethylbenzene isocyanate.

In addition, the following unsaturated compounds can be utilized as crosslinkers which are reactive with pendant carboxyl groups on the polymer backbone: polyhaloalkanols such as 1,3-dichloroisopropanol and 1,3-dibromoisopropanol; sulfonium zwitterions such as the tetrahydrothiophene adduct of novolac resins; haloepoxyalkanes such as epichlorohydrin, epibromohydrin, 2-methyl epichlorohydrin, and epiiodohydrin; polyglycidyl ethers such as 1,4-butanediol diglycidyl ether, glycerine-1,3-diglycidyl ether, ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, diethylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, polypropylene glycol diglycidyl ethers, bisphenol A-epichlorohydrin epoxy resins and mixtures of the foregoing. Mixtures of two or more of the foregoing polyunsaturated compounds can also be utilized to crosslink the first stage polymer component of the present invention.

The multi-stage grinding additive of the present invention can be conveniently prepared by using the above-described monomers and by conventional staged- or sequential-emulsion polymerization techniques at an acid pH lower than about 5.0 using free-radical producing initiators, usually in an amount from 0.01 percent to 3 percent based on the total weight of the monomers. Polymerization at an acid pH lower than about 5.0 permits direct preparation of an aqueous colloidal dispersion with relatively high solids content without problems of undue viscosity.

The first stage polymer is synthesized in a first emulsion polymerization stage from a monomer mixture emulsified in an aqueous phase of a first monomer composition comprising a), b), c) , and optionally d), as disclosed above. The emulsified first monomers are polymerized in the presence of a suitable free radical forming initiator to provide an emulsion of a HASE stage polymer. Correspondingly, a second stage polymer is formed in a second emulsion polymerization stage. In this

second stage, an emulsified monomer mixture of a second monomer composition comprising e), and f), as previously disclosed, is polymerized in the presence of the previously prepared first stage polymer and additional free radical forming initiator. The end-product is a multi-stage polymer composite comprising a HASE surrounded or partially surrounded with a dispersant. Alternatively, a preformed HASE seed emulsion polymer can be utilized as the first stage polymer followed by the formation of the second stage polymer in a second stage as described above.

The emulsified monomer mixture of the second monomer composition contains a substantial absence of the nonionic macromonomer (i.e., less than 1 part by weight, preferably less than 0.1 part, more preferably less than 0.01 part, of the nonionic macromonomer per 100 parts by weight of the nonionic macromonomer in the first stage polymer). In a most preferred embodiment, the second monomer composition contains an absence of the nonionic macromonomer.

Each stage of the multi-stage polymer of the invention can be prepared from a monomer mixture comprising one or more chain transfer agents. The chain transfer agent can be any chain transfer agent which reduces the molecular weight of the staged polymers of the invention. Suitable chain transfer agents include, but are not limited to, thio and disulfide containing compounds, such as C₁-C₁₈ alkyl mercaptans, mercaptocarboxylic acids, mercaptocarboxylic esters, thioesters, C₁-C₁₈ alkyl disulfides, aryldisulfides, polyfunctional thiols such as trimethylolpropane-tris-(3-mercaptopropionate), pentaerythritol-tetra-(3-mercaptopropionate), pentaerythritol-tetra-(thioglycolate), and pentaerythritol-tetra-(thiolactate), dipentaerythritol-hexa-(thioglycolate), and the like; phosphites and hypophosphites; haloalkyl compounds, such as carbon tetrachloride, bromotrichloromethane, and the like; and catalytic chain transfer agents such as, for example, cobalt complexes (e.g., cobalt (II) chelates).

In one aspect of the invention, the chain transfer agent is selected from octyl mercaptan, n-dodecyl mercaptan, t-dodecyl mercaptan, hexadecyl mercaptan, octadecyl mercaptan (ODM), isooctyl 3-mercaptopropionate (IMP), butyl 3-mercaptopropionate, 3-mercaptopropionic acid, butyl thioglycolate, isooctyl thioglycolate, and dodecyl thioglycolate.

When utilized, the chain transfer agent can be present in an amount ranging from about 0.1 % to 10% by weight, based on the total monomer mixture weight.

The emulsion polymerization can be carried out in a staged batch process, in a staged metered monomer addition process, or the polymerization can be initiated as a batch process and then the bulk of the monomers can be continuously staged into the reactor (seed process). Typically, the polymerization process is carried out at a reaction temperature in the range of about 20 to about 99°C, however, higher or lower temperatures can be used. To facilitate emulsification of the monomer mixture, the emulsion polymerization is carried out in the presence of at least one surfactant. In one embodiment, the emulsion polymerization is carried out in the presence of surfactant ranging in the amount of about 1% to about 10% by weight in one aspect, from about 3% to about 8% in another aspect, and from about 3.5% to about 7% by weight in a further aspect, based on a total emulsion weight basis. The emulsion polymerization reaction mixture also includes one or more free radical initiators which are present in an amount ranging from about 0.01% to about 3% by weight based on total monomer weight. The polymerization can be performed in an aqueous or aqueous alcohol medium.

Surfactants for facilitating emulsion polymerizations include anionic, nonionic, amphoteric, and cationic surfactants, as well as mixtures thereof. Most commonly, anionic and nonionic surfactants can be utilized as well as mixtures thereof.

Suitable anionic surfactants for facilitating emulsion polymerizations are well known in the art and include, but are not limited to, sodium lauryl sulfate, sodium dodecyl benzene sulfonate, sodium (C₆-C₁₆) alkyl phenoxy benzene sulfonate, disodium (C₆-C₁₆) alkyl phenoxy benzene sulfonate, disodium (C₆-C₁₆) di-alkyl phenoxy benzene sulfonate, disodium laureth-3 sulfosuccinate, sodium dioctyl sulfosuccinate, sodium di-sec-butyl naphthalene sulfonate, disodium dodecyl diphenyl ether sulfonate, disodium n-octadecyl sulfosuccinate, phosphate esters of branched alcohol ethoxylates, and the like.

Nonionic surfactants suitable for facilitating emulsion polymerizations are well known in the polymer art, and include, without limitation, linear or branched C₈-C₃₀ fatty alcohol ethoxylates, such as capryl alcohol ethoxylate, lauryl alcohol ethoxylate, myristyl alcohol ethoxylate, cetyl alcohol ethoxylate, stearyl alcohol ethoxylate, cetearyl alcohol ethoxylate, sterol ethoxylate, oleyl alcohol ethoxylate, and, behenyl alcohol ethoxylate; alkylphenol alkoxyates, such as octylphenol ethoxylates; and polyoxyethylene polyoxypropylene block copolymers, and the like. Additional fatty alcohol ethoxylates suitable as non-ionic surfactants are described below. Other

useful nonionic surfactants include C₈-C₂₂ fatty acid esters of polyoxyethylene glycol, ethoxylated mono- and diglycerides, sorbitan esters and ethoxylated sorbitan esters, C₈-C₂₂ fatty acid glycol esters, block copolymers of ethylene oxide and propylene oxide, and combinations thereof. The number of ethylene oxide units in each of the foregoing ethoxylates can range from 2 and above in one aspect, and from 2 to about 150 in another aspect.

Exemplary free radical initiators include, but are not limited to, water-soluble inorganic persulfate compounds, such as ammonium persulfate, potassium persulfate, and sodium persulfate; peroxides such as hydrogen peroxide, benzoyl peroxide, acetyl peroxide, and lauryl peroxide; organic hydroperoxides, such as cumene hydroperoxide and t-butyl hydroperoxide; organic peracids, such as peracetic acid; and oil soluble, free radical producing agents, such as 2,2'-azobisisobutyronitrile, and the like, and mixtures thereof. Peroxides and peracids can optionally be activated with reducing agents, such as sodium bisulfite, sodium formaldehyde, or ascorbic acid, transition metals, hydrazine, and the like. Particularly suitable free-radical polymerization initiators include water soluble azo polymerization initiators, such as 2,2'-azobis(tert-alkyl) compounds having a water solubilizing substituent on the alkyl group. Preferred azo polymerization catalysts include the Vazo[®] free-radical polymerization initiators, available from DuPont, such as Vazo[®] 44 (2,2'-azobis(2-(4,5-dihydroimidazolyl)propane), Vazo[®] 56 (2,2'-azobis(2-methylpropionamidine) dihydrochloride), and Vazo[®] 68 (4,4'-azobis(4-cyanovaleric acid)).

Optionally, other emulsion polymerization additives and processing aids which are well known in the emulsion polymerization art, such as auxiliary emulsifiers, solvents, buffering agents, chelating agents, inorganic electrolytes, polymeric stabilizers, and pH adjusting agents can be included in the polymerization system.

In a typical two-stage polymerization, a mixture of first stage monomers is added to a first reactor under inert atmosphere to a solution of emulsifying surfactant (e.g., anionic surfactant) in water. Optional polyethylenically unsaturated cross-linking monomers, and processing aids can be added as desired (e.g., auxiliary emulsifier(s)). The contents of the reactor are agitated to prepare a monomer emulsion. To a second reactor equipped with an agitator, an inert gas inlet, and feed pumps are added under inert atmosphere a desired amount of water and additional anionic surfactant and optional processing aids. The contents of the second reactor

are heated with mixing agitation. After the contents of the second reactor reaches a temperature in the range of about 55 to 98°C, a free radical initiator is injected into the so formed aqueous surfactant solution in the second reactor, and a portion of the monomer emulsion from the first reactor is gradually metered into the second reactor over a period typically ranging from about one half to about four hours. The reaction temperature is controlled in the range of about 45 to about 95°C. After the addition of the first stage monomer, an additional quantity of free radical initiator can optionally be added to the second reactor, if desired, and the resulting reaction mixture is typically held at a temperature of about 45 to 95°C for a time period sufficient to accomplish the polymerization reaction and obtain a first stage polymer particle emulsion.

While a typical two-stage polymer process is generally described immediately above, multi-staged or multi-layered polymers can be formed through the sequential emulsion polymerization of monomer charges in the presence of polymer particles of a previously formed emulsion polymer.

The polymer composite preferably comprises all the polymer stages which are base-soluble. "Base-soluble" as used herein means that the polymer is substantially soluble in aqueous medium which has been adjusted with base to a pH of about 5.0 or greater.

This neutralization can occur in situ when the multi-stage polymer composite is blended with an aqueous solution containing a suitable base.

The multi-stage polymer composite of the present invention can be added, as a grinding additive in the grinding stage at a content range of from 0.1% to 2%, preferably from 0.3% to 1.5%, and most preferably from 0.6% to 1.0% by weight based on the total weight of the coating composition, and binder and other additives can be added in the letdown stage, to make a coating formulation.

Coating formulations include, but are not limited to, latex paint formulations, cosmetic formulations, dentifrices, hand lotions, automotive coatings formulations, architectural and industrial coatings formulations, caulks, adhesives, and sealants.

Examples of suitable binders include, but are not limited to, acrylic-, vinyl-acrylic-, styrene-acrylic, vinyl acetate/ethylene-, urethane-, melamine-, epoxy-, alkyd-, acrylonitrile-, styrene-, polybutadiene-, polyisoprene-, ethylene-propylene-, polyvinyl alcohol-, vinyl chloride-, vinylidene chloride-, epoxy-based homopolymers and copolymers, and blends of binders. The binder is typically present in the formulation

at levels ranging from 2 to 50% by weight, based on the total weight of the coating formulation. The coating formulation may also include colorants containing colored pigments that provide tint to coating compositions such as paints and semitransparent stains. One factor affecting the amount of colorant added to a coating composition to obtain a desired color is the light scattering efficiency and the light absorbing efficiency of the colored pigments. The scattering and absorbing efficiencies of colored pigments are affected by the extent of dispersion of the colored pigments in the coating composition. Colored pigment particles that are well dispersed and separated from each other are believed to provide increased color and optionally, increased hiding. The coating formulation can be formulated to a desired color with lower levels of the colored pigments than compositions in which the colored pigments are poorly dispersed. Alternatively, a coating formulation having well dispersed colored pigments typically display more intense colors, and permit the preparation of colored coatings with a broader color palette.

The coating composition according to the present invention may further include one or more of the following additives: Solvents; fillers; pigments, such as titanium dioxide, mica, calcium carbonate, silica, zinc oxide, milled glass, aluminum trihydrate, talc, antimony trioxide, fly ash, and clay; polymer encapsulated pigments, such as polymer-encapsulated or partially encapsulated opacifying pigment particles such as titanium dioxide, zinc oxide, or lithopone particles; polymers or polymer emulsions adsorbing or bonding to the surface of pigments such as titanium dioxide; hollow pigments, including pigments having one or more voids; dispersants, such as aminoalcohols and polycarboxylates; surfactants; defoamers; preservatives, such as biocides, mildewcides, fungicides, algacides, and combinations thereof; flow agents; leveling agents; and additional neutralizing agents, such as hydroxides, amines, ammonia, and carbonates.

For example, the coatings composition may include polymer-encapsulated opacifying pigment particles comprising i) opacifying pigment particles, such as titanium dioxide particles, having a diameter in the range of 100 nm to 500 nm and an index of refraction of at least 1.8; ii) an encapsulating polymer, and iii) a polymeric dispersant for the encapsulated opacifying pigment particles and the polymer. Such polymer-encapsulated opacifying pigment particles are described, for example, in U.S. Patent Publication US 2010/0298483 A1. In another example, the coating

composition may include polymer-encapsulated opacifying pigment particles as described in WO 2007/112503 A1.

A coating formulation that provides a colored coating having a higher degree of opacity, a measure of substrate covering power, may be desired. A formulation
5 suitable for providing colored coatings having a higher degree of color saturation, a measure of color intensity, may also be desired. Alternatively, a formulation that can be tinted to a desired color with lower level of colorants than conventional coating formulations may also be desired. A coating formulation having less variation in the efficiencies of a range of different colorant particles, to provide consistent colors
10 when mixtures of colorant particles are employed, may also be desired.

The pigment particles contained in the formulation are white and nonwhite pigments. The colorant particles provide any color including white to the coating composition. Colorant particles include colored pigments, white pigments, black pigments, metal effect pigments, and luminescent pigments such as fluorescent
15 pigments and phosphorescent pigments. The term "colorant particles", as used herein includes white pigment particles such as titanium dioxide, zinc oxide, lead oxide, zinc sulfide, lithophone, zirconium oxide, and antimony oxide. Examples of colors for the pigmented polymer composition include black, magenta, yellow, and cyan, as well as combinations of these colors such as orange, blue, red, pink, green,
20 and brown. Other suitable colors for the pigmented polymer composition include fluorescent colors; metallic colors such as silver, gold, bronze, and copper; and pearlescent pigments. These colors are obtained by employing one or more different types of colorant particles.

The colorant particles include inorganic colorant particles and organic colorant
25 particles. Typically, the colorant particles have average particle diameters in the range of from 10 nm to 50 μ m, preferably in the range of from 40 nm to 2 μ m.

Suitable inorganic colorant particles include, but are not limited to, titanium dioxide pigments, iron oxide pigments such as goethite, lepidocrocite, hematite, maghemite, and magnetite; chromium oxide pigments; cadmium pigments such as
30 cadmium yellow, cadmium red, and cadmium cinnabar; bismuth pigments such as bismuth vanadate and bismuth vanadate molybdate; mixed metal oxide pigments such as cobalt titanate green; chromate and molybdate pigments such as chromium yellow, molybdate red, and molybdate orange; ultramarine pigments; cobalt oxide pigments; nickel antimony titanates; lead chrome; blue iron pigments; carbon black;

and metal effect pigments such as aluminum, copper, copper oxide, bronze, stainless steel, nickel, zinc, and brass.

Suitable organic colorant particles include, but are not limited to, azo pigments, monoazo pigments, diazo pigments, azo pigment lakes, β -naphthol pigments, naphthol AS pigments, benzimidazolone pigments, diazo condensation pigment, metal complex pigments, isoindolinone, and isoindoline pigments, polycyclic pigments, phthalocyanine pigments, quinacridone pigments, perylene and perinone pigments, thioindigo pigments, anthrapyrimidone pigments, flavanthrone pigments, anthanthrone pigments, dioxazine pigments, triarylcarbonium pigments, quinophthalone pigments, and diketopyrrolo pyrrole pigments.

Suitable extender include, but are not limited to a particulate inorganic material having a refractive index of less than or equal to 1.8 and greater than 1.3 and includes, for example, calcium carbonate, clay, calcium sulfate, aluminosilicates, silicates, zeolites, mica, diatomaceous earth, solid or hollow glass, and ceramic beads. The aqueous coating composition may optionally contain solid or hollow polymeric particles having a Tg of greater than 60°C, such polymeric particles are classified as extenders for purposes of PVC calculations herein. The details of hollow polymeric particles are described in EP22633, EP915108, EP959176, EP404184, US5360827, WO 00/68304, and US20100063171. The solid polymeric particles have particle size from 1-50 microns, preferably from 5-20 microns.

Examples

I. Raw materials

A) Materials used in making Polymer compound	
Compound	Chemical Nature
MAA	Methacrylic Acid
EA	Ethyl acrylate
EHA	2-Ethylhexyl acrylate
MA-20	a mixture of 70% methacrylate ester of a 20 ethoxylate of cetyl-stearyl alcohol, 20% methacrylic acid, and 10% water.

B) Starting materials used in paint formulation			
Material	Function	Chemical nature	Supplier
Disponil TM Fes-32	Emulsifier	Fatty polyglycol ether sulphate, Na ⁺ salt	BASF
Aerosol TM A-102	Emulsifier	Disodium ethoxylated alcohol [C10-C12] half ester of sulfosuccinic acid	Cytec Industries Inc.
Ammonium	Initiator	Ammonium persulfate	The Dow Chemical Company

persulfate			
tert-Butyl hydroperoxide	Chaser	tert-Butyl hydroperoxide	The Dow Chemical Company
Isoascorbic acid	Chaser	Isoascorbic acid	The Dow Chemical Company
Sodium acetate	Buffer	Sodium acetate	The Dow Chemical Company
Kathon TM LX 1.5%	Biocide	Methyl and chlorisothiazolinone	The Dow Chemical Company
Natrolso TM 250HBR	Thickener	Hydrophobic modified cellulose	Ashland Inc.
AMP TM -95	Neutralizer	2-Amino-2-methyl-1-propanol (5% water)	The Dow Chemical Company
Orotan TM 1288	Dispersant	Polyacrylic acid	The Dow Chemical Company
Fomaster TM NXZ	Defoamer	Hydrocarbon and surfactant	BASF
DB-80	Extender	Alumina Silicate	Shanxi Jinyang Calcined Kaolin Ltd. (China)
Ti-Pure TM R-706	Pigment	Titanium dioxide	Dupont
Talc 8E	Extender	Magnesium silicate	Shandong Huasheng Fine Chemical Co., Ltd. Qixia
CC-700	Extender	Calcium carbonate	Guangfu Building Materials Group (China)
Texanol TM	Coalescent	Propanoic acid, 2-methyl-, monoester with 2,2,4-trimethyl-1,3-pentanediol	Eastman Chemical Company
Propylene Glycol	Anti-freeze	Propylene Glycol	The Dow Chemical Company
Primal TM AS-380	Binder	Styrene-Acrylic polymer	The Dow Chemical Company

II. Processes

Performance evaluation methods

i) KU viscosity

- 5 The formulated paints were obtained as control formulation and inventive formulation.

“KU viscosity” is a measure of the mid-shear viscosity as measured by a Krebs viscometer. The Krebs viscometer is a rotating paddle viscometer that is compliant with ASTM-D562. KU viscosity was measured on a Brookfield Krebs Unit

10 Viscometer KU-1+ available from Brookfield Engineering Labs (Middleboro, MA, USA). “KU” shall mean Krebs unit.

“Brookfield 4/6” is the low-shear viscosity, expressed in units of cps, measured on a Brookfield viscometer at a low-shear rate, 6 rpm, with spindle 4. The Brookfield viscosity of the paint typically correlates with the “in-can appearance”

15 of the paint.

ii) Washability (Wet-Scrub Resistance) The scrub resistance of paints is determined using a modified version of the ASTM Test Method D 2486-74A. As compared to the standard ASTM method, there are four modification in the test method used here. First, the scrub medium for the paints with PVC greater than 55%
5 used in a 0.5 wt% household detergent solution but the abrasive scrub medium was used for the paints with fewer pigments. Second, the coating films were laid down on vinyl charts vertical to the longer side. Third, there are no shims on the aluminum metal plates of scrub machines. The last difference is the material used for making the hairs of the test brush. The brushes used here were made of pig hairs rather
10 than nylon fibers. On each vinyl chart, four coatings were applied with always making one of them derived from the same paint as control and three others being samples so that relative ratings between control and samples can be obtained. For a given paint, four coating specimens were made and the final rating was obtained by averaging the results of the four specimens. The coatings were dried for 7 days in a
15 constant temperature room with a temperature of 25°C and a humidity of 50% prior to scrub test.

III. Experimental examples

Comparative example 1 – dispersant polymer 1

20 This example illustrates the preparation of an emulsion polymer for use solely as a dispersant with weight composition: 70 EHA/30 MAA/2.55 MMP.

A five-liter, four-necked flask equipped with a mechanical stirrer, nitrogen sweep, thermocouple, and condenser was charged with 750.00 gram of water and 6.35 grams of DisponilTM Fes-32. The kettle solution was heated at 82°C. An initiator,
25 2.10 grams of ammonium persulfate (APS) dissolved in 35.00 grams of water, was added. Two minutes later, the monomer emulsion, 700.00 grams of 2-ethylhexyl acrylate, 300.00 grams of methacrylic acid, 25.50 grams of chain transfer agent, methyl mercaptopropionate (MMP), and 60.87 grams of DisponilTM Fes-32 in 419.36
grams of water, and an initiator, 1.75 grams of APS dissolved in 90.80 grams of
30 water, were cofed over a period of 90 minutes while the kettle temperature was maintained at 82°C. The kettle temperature was held at 82°C for fifteen minutes after the end of the feeds and then cooled to 60°C. A chaser system, 10.00 grams of

ferrous sulfate solution (0.15%), 1.18 grams of tert-butyl hydroperoxide (t-BHP) in 25.00 grams of water and 0.58 grams of Isoascorbic acid (IAA) in 25.00 grams of water were then added. After holding at 60°C for 15 minutes, the same chaser system was charged again. The batch was cooled down to 40°C, then a biocide solution of 7.41grams of Kathon™ LX 1.5% in 28.00 grams of water was added over 10 minutes. The After completion of the polymerization, the copolymer emulsion was cooled to ambient temperature and filtered through a 325 mesh size screen. The resulting emulsion polymer had total solids of 39.2 % with 0.15 gram wet gel at PH 1.86.

Comparative example 2 – HASE polymer 1

This example illustrates the preparation of an emulsion polymer for use solely as a HASE thickener with weight composition: 47 EA/48 MAA/5 MA-20.

A five-liter, four-necked flask equipped with a mechanical stirrer, nitrogen sweep, thermocouple, and condenser was charged with 720.00 gram of water and 34.32 grams of Disponil™ Fes-32. The kettle solution was heated at 86°C. An initiator, 1.30 grams of ammonium persulfate (APS) dissolved in 31.00 grams of water, was added. Two minutes later, the monomer emulsion, 621.00 grams of ethyl acrylate, 541.16 grams of methacrylic acid, 88.71 grams of MA-20 and 34.32 grams of Disponil™ Fes-32 in 900.00 grams of water, and an initiator, 0.56 grams of APS dissolved in 115.5.00 grams of water, were cofed over a period of 90 minutes while the kettle temperature was maintained at 86°C. The kettle temperature was held at 86°C for fifteen minutes after the end of the feeds and then cooled to 60°C. A chaser system, 30.80 grams of ferrous sulfate solution (0.15%), 1.66 grams of tert-butyl hydroperoxide (t-BHP) in 19.00 grams of water and 0.83 grams of Isoascorbic acid (IAA) in 27.00 grams of water were then added. After holding at 60°C for 15 minutes, the same chaser system was charged again. The batch was cooled down to 40°C, and a buffer solution of 2.19 grams of sodium acetate in 258.00 grams of water was added over 10 minutes, then a biocide solution of 7.41grams of Kathon™ LX 1.5% in 28.00 grams of water was added over 10 minutes. After completion of the polymerization, the copolymer emulsion was cooled to ambient temperature and

filtered through a 325 mesh size screen. The resulting emulsion polymer had total solids of 35.6 % with 0.45 gram wet gel at PH 4.50.

Example 1 – multi-stage polymer 1

5 This example illustrates the preparation of a multi-stage polymer for use as a grinding additive, with a different composition with weight composition: 70 (47 EA/48 MAA/5 MA-20)//30 (62 EHA/38 MAA/2.55 MMP).

A five-liter, four-necked flask equipped with a mechanical stirrer, nitrogen sweep, thermocouple, and condenser was charged with 720.00 gram of water and
10 34.32 grams of AerosolTM A-102. The kettle solution was heated at 86°C. An initiator, 1.30 grams APS dissolved in 31.00 grams of water, was added. Two minutes later, the first-stage monomer emulsion, 408.60 grams of ethyl acrylate, 405.10 grams of methacrylic acid, 62.10 grams of MA-20 and 24.03 grams of AerosolTM A-102 in 630.00 grams of water, and an initiator, 0.37 grams of APS dissolved in 77.00 grams
15 of water, were cofed over a period of 60 minutes while the kettle temperature was maintained at 86°C. After 60 minutes, the second-stage monomer emulsion, 244.95 grams of 2-ethylhexyl acrylate, 104.98 grams of methacrylic acid, 8.92 grams of MMP, and 19.19 grams of AerosolTM A-102 in 225.00 grams of water, and an initiator, 1.05 grams of APS dissolved in 70.00 grams of water, were cofed over a
20 period of 30 minutes while the kettle temperature was maintained at 86°C. The kettle temperature was held at 86°C for fifteen minutes after the end of the feeds and then cooled to 60°C. A chaser system, 30.80 grams of ferrous sulfate solution (0.15%), 1.66 grams of tert-butyl hydroperoxide (t-BHP) in 19.00 grams of water and 0.83 grams of Isoascorbic acid (IAA) in 27.00 grams of water were then added. After
25 holding at 60°C for 15 minutes, the same chaser system was charged again. The batch was cooled down to 40°C, and a buffer solution of 2.19 grams of sodium acetate in 258.00 grams of water was added over 10 minutes, then a biocide solution of 7.41grams of KathonTM LX 1.5% in 28.00 grams of water was added over 10 minutes. After completion of the polymerization, the copolymer emulsion was cooled
30 to ambient temperature and filtered through a 325 mesh size screen. The resulting emulsion polymer had total solids of 35.5 % with 0.40 gram wet gel at PH 4.13.

Example 2 – multi-stage polymer 2

This example illustrates the preparation of a multi-stage polymer for use as a grinding additive with weight composition: 70 (47 EA/45 MAA/8 MA-20)/30 (62
5 EHA/38 MAA/2.55 MMP).

A five-liter, four-necked flask equipped with a mechanical stirrer, nitrogen sweep, thermocouple, and condenser was charged with 720.00 gram of water and 44.72 grams of DisponilTM Fes-32. The kettle solution was heated at 86°C. An initiator, 1.30 grams of ammonium persulfate (APS) dissolved in 31.00 grams of
10 water, was added. Two minutes later, the first-stage monomer emulsion, 408.60 grams of ethyl acrylate, 371.35 grams of methacrylic acid, 99.36 grams of MA-20 and 31.30 grams of DisponilTM Fes-32 in 630.00 grams of water, and an initiator, 0.37 grams of APS dissolved in 77.00 grams of water, were cofed over a period of 60 minutes while the kettle temperature was maintained at 86°C. After 60 minutes,
15 the second-stage monomer emulsion, 216.96 grams of 2-ethylhexyl acrylate, 132.97 grams of methacrylic acid, 8.92 grams of chain transfer agent, methyl mercaptopropionate (MMP), and 25.01 grams of DisponilTM Fes-32 in 225.00 grams of water, and an initiator, 1.05 grams of APS dissolved in 70.00 grams of water, were cofed over a period of 30 minutes while the kettle temperature was maintained at
20 86°C. The kettle temperature was held at 86°C for fifteen minutes after the end of the feeds and then cooled to 60°C. A chaser system, 30.80 grams of ferrous sulfate solution (0.15%), 1.66 grams of tert-butyl hydroperoxide (t-BHP) in 19.00 grams of water and 0.83 grams of Isoascorbic acid (IAA) in 27.00 grams of water were then added. After holding at 60°C for 15 minutes, the same chaser system was charged
25 again. The batch was cooled down to 40°C, and a buffer solution of 2.19 grams of sodium acetate in 258.00 grams of water was added over 10 minutes, then a biocide solution of 7.41grams of KathonTM LX 1.5% in 28.00 grams of water was added over 10 minutes. After completion of the polymerization, the copolymer emulsion was cooled to ambient temperature and filtered through a 325 mesh size screen. The
30 resulting emulsion polymer had total solids of 35.5 % with 0.45 gram wet gel at PH 3.27.

Example 3 – multi-stage polymer 3

This example illustrates the preparation of a multi-stage emulsion polymer for use as a grinding additive, with a different composition with weight composition: 70(47 EA/45 MAA/8 MA-20)//30(65 BMA/35 MAA/2.55 MMP).

5 A five-liter, four-necked flask equipped with a mechanical stirrer, nitrogen sweep, thermocouple, and condenser was charged with 720.00 gram of water and 34.32 grams of AerosolTM A-102. The kettle solution was heated at 86°C. An initiator, 1.30 grams APS dissolved in 31.00 grams of water, was added. Two minutes later, the first-stage monomer emulsion, 408.60 grams of ethyl acrylate, 371.35 grams of
10 methacrylic acid, 99.36 grams of MA-20 and 24.03 grams of AerosolTM A-102 in 630.00 grams of water, and an initiator, 0.37 grams of APS dissolved in 77.00 grams of water, were cofed over a period of 60 minutes while the kettle temperature was maintained at 86°C. After 60 minutes, the second-stage monomer emulsion, 227.45 grams of n-butyl acrylate, 122.48 grams of methacrylic acid, 8.92 grams of MMP,
15 and 19.19 grams of AerosolTM A-102 in 225.00 grams of water, and an initiator, 1.05 grams of APS dissolved in 70.00 grams of water, were cofed over a period of 30 minutes while the kettle temperature was maintained at 86°C. The kettle temperature was held at 86°C for fifteen minutes after the end of the feeds and then cooled to 60°C. A chaser system, 30.80 grams of ferrous sulfate solution (0.15%), 1.66 grams
20 of tert-butyl hydroperoxide (t-BHP) in 19.00 grams of water and 0.83 grams of Isoascorbic acid (IAA) in 27.00 grams of water were then added. After holding at 60°C for 15 minutes, the same chaser system was charged again. The batch was cooled down to 40°C, and a buffer solution of 2.19 grams of sodium acetate in 258.00 grams of water was added over 10 minutes, then a biocide solution of 7.41grams of
25 KathonTM LX 1.5% in 28.00 grams of water was added over 10 minutes. After completion of the polymerization, the copolymer emulsion was cooled to ambient temperature and filtered through a 325 mesh size screen. The resulting emulsion polymer had total solids of 35.5 % with 0.40 gram wet gel at PH 4.13.

Example 4 – multi-stage polymer 4

This example illustrates the preparation of a multi-stage polymer for use as a grinding additive with weight composition: 50 (47 EA/48 MAA/5 MA-20)/50 (70 EHA/30 MAA/2.55 MMP).

A five-liter, four-necked flask equipped with a mechanical stirrer, nitrogen sweep, thermocouple, and condenser was charged with 720.00 gram of water and 34.32 grams of DisponilTM Fes-32. The kettle solution was heated at 86°C. An initiator, 1.30 grams of ammonium persulfate (APS) dissolved in 31.00 grams of water, was added. Two minutes later, the first-stage monomer emulsion, 286.59 grams of ethyl acrylate, 283.97 grams of methacrylic acid, 43.55 grams of MA-20 and 16.85 grams of DisponilTM Fes-32 in 450.00 grams of water, and an initiator, 0.27 grams of APS dissolved in 57.60 grams of water, were cofed over a period of 45 minutes while the kettle temperature was maintained at 86°C. After 45 minutes, the second-stage monomer emulsion, 426.83 grams of 2-ethylhexyl acrylate, 182.94 grams of methacrylic acid 15.54 grams of chain transfer agent, methyl mercaptopropionate (MMP), and 33.45 grams of DisponilTM Fes-32 in 225.00 grams of water, and an initiator, 1.89 grams of APS dissolved in 126.00 grams of water, were cofed over a period of 45 minutes while the kettle temperature was maintained at 86°C. The kettle temperature was held at 86°C for fifteen minutes after the end of the feeds and then cooled to 60°C. A chaser system, 30.80 grams of ferrous sulfate solution (0.15%), 1.66 grams of tert-butyl hydroperoxide (t-BHP) in 19.00 grams of water and 0.83 grams of Isoascorbic acid (IAA) in 27.00 grams of water were then added. After holding at 60°C for 15 minutes, the same chaser system was charged again. The batch was cooled down to 40°C, and a buffer solution of 2.19 grams of sodium acetate in 258.00 grams of water was added over 10 minutes, then a biocide solution of 7.41grams of KathonTM LX 1.5% in 28.00 grams of water was added over 10 minutes. After completion of the polymerization, the copolymer emulsion was cooled to ambient temperature and filtered through a 325 mesh size screen. The resulting emulsion polymer had total solids of 35.5 % with 0.10 gram wet gel at PH 2.86.

Example 5 – multi-stage polymer 5

This example illustrates the preparation of a multi-stage polymer for use as a grinding additive with weight composition: 70 (47 EA/48 MAA/5 MA-20/0.08 n-DDM)/30 (70 EHA/30 MAA/2.55 MMP).

A five-liter, four-necked flask equipped with a mechanical stirrer, nitrogen sweep, thermocouple, and condenser was charged with 720.00 gram of water and 34.32 grams of DisponilTM Fes-32. The kettle solution was heated at 86°C. An initiator, 1.30 grams of ammonium persulfate (APS) dissolved in 31.00 grams of water, was added. Two minutes later, the first-stage monomer emulsion, 408.60 grams of ethyl acrylate, 405.10 grams of methacrylic acid, 62.10 grams of MA-20, 0.70 gram of chain transfer agent, n-dodecyl mercaptan (n-DDM) and 24.03 grams of DisponilTM Fes-32 in 630.00 grams of water, and an initiator, 0.37 grams of APS dissolved in 77.00 grams of water, were cofed over a period of 60 minutes while the kettle temperature was maintained at 86°C. After 60 minutes, the second-stage monomer emulsion, 244.95 grams of 2-ethylhexyl acrylate, 104.98 grams of methacrylic acid 8.92 grams of chain transfer agent, methyl mercaptopropionate (MMP), and 19.19 grams of DisponilTM Fes-32 in 225.00 grams of water, and an initiator, 1.05 grams of APS dissolved in 70.00 grams of water, were cofed over a period of 30 minutes while the kettle temperature was maintained at 86°C. The kettle temperature was held at 86°C for fifteen minutes after the end of the feeds and then cooled to 60°C. A chaser system, 30.80 grams of ferrous sulfate solution (0.15%), 1.66 grams of tert-butyl hydroperoxide (t-BHP) in 19.00 grams of water and 0.83 grams of Isoascorbic acid (IAA) in 27.00 grams of water were then added. After holding at 60°C for 15 minutes, the same chaser system was charged again. The batch was cooled down to 40°C, and a buffer solution of 2.19 grams of sodium acetate in 258.00 grams of water was added over 10 minutes, then a biocide solution of 7.41grams of KathonTM LX 1.5% in 28.00 grams of water was added over 10 minutes. After completion of the polymerization, the copolymer emulsion was cooled to ambient temperature and filtered through a 325 mesh size screen. The resulting emulsion polymer had total solids of 35.5 % with 0 gram wet gel at PH 3.31.

Table 1: Grinding additive composition (Examples 1 to 5)

No.	Grinding additive	HASE stage composition	Dispersant stage composition
Example 1	multi-stage polymer 1	70 (47 EA/48 MAA/5 MA-20)	30 (62 EHA/38 MAA/2.55 MMP)
Example 2	multi-stage polymer 2	70 (47 EA/45 MAA/8 MA-20)	30 (62 EHA/38 MAA/2.55 MMP)
Example 3	multi-stage polymer 3	70 (47 EA/45 MAA/8 MA-20)	30 (65 BMA/35 MAA/2.55 MMP)
Example 4	multi-stage polymer 4	50 (47 EA/48 MAA/5 MA-20)	50 (70 EHA/30 MAA/2.55 MMP)
Example 5	multi-stage polymer 5	70 (47 EA/48 MAA/5 MA-20/0.08 n-DDM)	30 (70 EHA/30 MAA/2.55 MMP)

IV. Paint formulations

Control paint #1 (77% PVC)

Grind	
Water	300.000
Natrosol TM 250 HBR	6.000
AMP TM -95	1.000
Orotan TM 1288	3.800
Fomaster TM NXZ	1.000
DB-80	119.000
Ti-Pure TM R-706	29.600
Talc 8E	75.000
CC-700	270.000
Sub totals	805.400
LetDown	
Water	72.600
Texanol TM	10.000
Fomaster TM NXZ	2.000
Propylene Glycol	5.000
Primal TM AS-380	105.000
Premix Sub-total	1000.00

5

Control paint #2 (81% PVC)

Grind	
Water	300.000
Natrosol TM 250 HBR	6.000
AMP TM -95	1.000
Orotan TM 1288	3.800
Fomaster TM NXZ	1.000
DB-80	119.000
Ti-Pure TM R-706	29.600
Talc 8E	75.000
CC-700	270.000
Sub totals	805.400

LetDown	
Water	92.600
Texanol TM	10.000
Fomaster TM NXZ	2.000
Propylene Glycol	5.000
Primal TM AS-380	85.000
Premix Sub-total	1000.00

Comparative paint (81% PVC)

Grind	
Water	300.000
Propylene Glycol	5.000
Natrosol TM 250 HBR	1.500
AMP TM 95	2.000
Dispersant polymer 1	1.84
HASE polymer 1	4.90
Fomaster TM NXZ	1.000
DB-80	119.000
Ti-Pure TM R-706	29.600
Talc 8E	75.000
CC-700	270.000
Sub totals	809.840
LetDown	
Water	93.1600
Texanol TM	10.000
Fomaster TM NXZ	2.000
Primal TM AS-380	85.000
Premix Sub-total	1000.00

Inventive paint # 1 - 5 (81% PVC)

Grind	
Water	300.000
Propylene Glycol	5.000
Natrosol TM 250 HBR	1.500
AMP TM 95	2.000
multi-stage polymer 1-5	7.000
Fomaster TM NXZ	1.000
DB-80	119.000
Ti-Pure TM R-706	29.600
Talc 8E	75.000
CC-700	270.000
Sub totals	810.100
LetDown	
Water	92.900
Texanol TM	10.000

Fomaster TM NXZ	2.000
Primal TM AS-380	85.000
Premix Sub-total	1000.00

V. Paint Results

Table 2

Paints Nos.	Control #1	Control #2	Comparative	Inventive #1
Binder, g	105	85	85	85
HEC, g	6.00	6.00	1.50	1.50
Kuaiyi, g	3.80	3.80	N/A	N/A
KU eq	106	103	111	107
Brk 4/6, eq	19,200	15,900	25,800	23,100
Opacity%	91.4	93.1	92.6	93.5
Washability	100%	43%	90%	170%
Δ KU, 50°C oven, 7 days	-4	-5	-1	-1

5 Washability is the key performance to pursue in the low cost, economy formulation spaces at high PVC (typically 75-85 PVC).

Control paint #1 is a typical 77% PVC paint with 10.5% binder loading and commercially used thickener, NatrolsolTM 250HBR, and dispersant, OrotanTM 1288.

10 Control paint #2 is a typical 81% PVC paint with 8.5% binder loading and commercially used thickener, NatrolsolTM 250HBR, and dispersant, OrotanTM 1288.

Comparative paint is an 81% PVC paint with 8.5% binder loading and cold blended HASE thickener (Comparative Example 2 (HASE polymer 1)) and hydrophobic dispersant (Comparative Example 1 (dispersant polymer 1)).

15 Inventive paint #1 to #5 is respectively 81% PVC paint with 8.5% binder loading and inventive multi-stage polymer as grinding additive.

It is highly desirable to use less binder in economy paints for cost saving. However, with original additive package, less binder loading will lead to a sacrifice in washability. As shown in Table 2, Control paint #2 (with 8.5% binder and original additive package) has a washability compromise over 60% comparing to Control paint #1 (with 10.5% binder loading and same original additive package). While
20 using inventive grinding additives, Inventive paint #1 has a 70% washability increase over Control paint #1, even with only 8.5% binder dosage comparing to 10.5% binder dosage of Control paint #1 (over 20% lower dosage), not to mention the comparison with Control paint #2 (over 120% washability increase).

Also, the paint made from the inventive grinding additive has reasonable rheology profile (~100-110 KU) and reasonable heat-age stability (less than 5 KU rise over 7 days heat age).

The Comparative paint is a cold blend of 1.84 gram second stage polymer (dispersant polymer 1) and 4.90 gram of first stage polymer (HASE polymer 1) which is an equivalent to 7.00 gram of multi-stage polymer 1 - on both composition and weight. The inventive paint #1 with grinding additive of the present invention has significantly higher washability comparing to that of the comparative paint with cold-blended HASE and dispersant. The inventive paint #1 has a 170% washability, while the paint with the HASE/dispersant cold-blended in grinding (Control paint #1) has only 90% washability.

In addition, with lower dosage of binders, the actual PVC is higher than 77% (Control paint #2, Comparative paint, and Inventive paint #1 at 81% PVC). Therefore, the opacity of the paint film is at least 1.2% higher than the typical 77% PVC paint (Control paint #1). The paint with a higher opacity will provide a film with better hiding. Or, on the other hand, the formulators could also achieve the same hiding with lower TiO₂ dosage with significant cost saving. However, the original additive package cannot maintain reasonable washability (Control paint #2) with lower binder dosage. With the excellent washability, the inventive grinding additive can lead to a paint film with better hiding, or decrease the requested TiO₂ usage for cost saving.

Table 3

Per 1000g paint	Control #1	Control #2	Inventive #1	Inventive #2	Inventive #3	Inventive #4	Inventive #5
Binder, g	105	85.00	85.00	85.00	85.00	85.00	85.00
HEC, g	6.00	6.00	1.50	1.50	1.50	1.50	1.50
Orotan Kuaiyi, g	3.80	3.80	N/A	N/A	N/A	N/A	N/A
Grinding additive, g		N/A	7.00	7.00	7.00	7.00	7.00
KU eq	106	103	107	101	103	96	116
Brk 4/6 eq	19,200	15,900	23,100	23,600	21,300	17,600	21,300
Opacity %	91.4	93.1	93.5	92.9	92.6	92.7	93.2
Washability	100%	43%	170%	126%	110%	130%	110%

As shown in Table 3, with the composition variation on both first (HASE) and second (dispersant) stage polymer, the grinding additives with multi-stage

morphology consistently deliver significantly higher washability to inventive paints (#1 - #5) comparing to that of Control paint #2 (43% v.s. 110% to 170%), and higher opacity comparing to Control paint #1 (91.4% v.s. 92.6% to 93.5%). Comparing with Inventive paint #1, Inventive paint #2 has higher percentage of nonionic macromonomer, MA-20. Inventive paint #3 has butyl methacrylate, instead of 2-ethylhexyl methacrylate in the dispersant polymer composition, comparing to Inventive paint #2. Inventive paint #4 has a 50:50 weight ratio of HASE and dispersant stage polymer, while others Inventive paints are in 70 to 30. Inventive paint #5 used a small amount of chain transfer agent, n-DDM, when preparing HASE stage polymer (details are shown in Table 1).

The inventive grinding additive of the present invention can replace most or all HEC and polyacid dispersant in the grinding stage, and the resulting paint film has the significantly enhanced washability, as well as the improved hiding performance. The inventive grinding additive has simplified paint making process, reduced the formulator's cost from additive package, binder dosage, and possibly TiO₂ loading as well.

Claims

1. A multi-stage polymer comprising, based on the total weight of the multi-stage polymer, from 1 wt.% to 99 wt.% of a first stage polymer, and from 1 wt.% to
5 99 wt.% of a second stage polymer,

wherein the first stage polymer comprises, as polymerization units, based on the total weight of the first stage polymer:

(a) from 0.1 wt.% to 50 wt.%, of a nonionic macromonomer, characterized by the following formula: $\text{H}_2\text{C}=\text{C}(\text{R})\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}(\text{R}')\text{CH}_2\text{O})_m\text{R}''$, wherein R is H
10 or CH_3 , R' is $\text{C}_1\text{-C}_2$ alkyl; R'' is $\text{C}_8\text{-C}_{30}$ alkyl, $\text{C}_8\text{-C}_{16}$ alkylphenyl or $\text{C}_{13}\text{-C}_{36}$ aralkylphenyl; n is an integral number from 6 to 100 and m is an integral number from 0 to 50, provided that $n \geq m$ and $m+n$ is from 6 to 100;

(b) from 30 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated carboxylic acid monomer; and

15 (c) from 30 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated nonionic monomer;

wherein the first stage polymer has a weight average molecular weight of at least 50,000 Daltons; and

the second stage polymer comprises, as polymerization units, based on the
20 total weight of the second stage polymer:

(e) from 10 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated carboxylic acid monomer; and

(f) from 30 wt.% to 90 wt.%, of a nonionic α,β -ethylenically unsaturated monomer;

25 wherein the second stage polymer has a weight average molecular weight of from 500 to 20,000 Daltons, and the second stage polymer contains a substantial absence of the nonionic macromonomer.

2. The multi-stage polymer according to claim 1, wherein the first stage polymer further comprises, as polymerization units, based on the total weight of the
30 first stage polymer, from 0.01 wt.% to 5 wt.%, a polyethylenically unsaturated crosslinking monomer.

3. The multi-stage polymer according to claim 1, wherein the second stage polymer contains an absence of the nonionic macromonomer.

4. The multi-stage polymer according to claim 1, wherein the α,β -ethylenically unsaturated carboxylic acid monomer is acrylic acid, methacrylic acid or a combination thereof.

5 5. The multi-stage polymer according to claim 1, wherein the α,β -ethylenically unsaturated nonionic monomer is ethyl acrylate, methyl methacrylate, 2-hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, vinyl acetate or acrylonitrile or a combination thereof.

6. A method for preparing a multi-stage polymer which comprises the steps:

10 i) contacting under emulsion polymerization conditions a first monomer composition comprising:

(a) from 0.1 wt.% to 50 wt.%, of a nonionic macromonomer, characterized by the following formula: $\text{H}_2\text{C}=\text{C}(\text{R})\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}(\text{R}')\text{CH}_2\text{O})_m\text{R}''$, wherein R is H or CH_3 , R' is $\text{C}_1\text{-C}_2$ alkyl; R'' is $\text{C}_8\text{-C}_{30}$ alkyl, $\text{C}_8\text{-C}_{16}$ alkylphenyl or $\text{C}_{13}\text{-C}_{36}$ aralkylphenyl; n is an integral number from 6 to 100 and m is an integral number
15 from 0 to 50, provided that $n \geq m$ and $m+n$ is from 6 to 100;

(b) from 30 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated carboxylic acid monomer; and

(c) from 30 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated nonionic monomer; to obtain a first stage polymer having a weight average molecular weight
20 of at least 50,000 Daltons; and

ii) contacting under emulsion polymerization the first stage polymer with a second monomer composition comprising, based on the weight of the second monomer composition:

25 (e) from 10 wt.% to 70 wt.%, of an α,β -ethylenically unsaturated carboxylic acid monomer; and

(f) from 30 wt.% to 90 wt.%, of an α,β -ethylenically unsaturated nonionic monomer; to obtain a second stage polymer having a weight average molecular weight of from 500 to 20,000 Daltons, and the second stage polymer contains a substantial absence of the nonionic macromonomer.

30 7. The method for preparing a multi-stage polymer according to claim 6, wherein the first monomer composition further comprises, based on the total weight of the first polymer composition, from 0.01 wt.% to 5 wt.%, a polyethylenically unsaturated crosslinking monomer.

8. The method for preparing a multi-stage polymer according to claim 6, wherein the second monomer composition contains an absence of the nonionic macromonomer.

5 9. The method for preparing a multi-stage polymer according to claim 6, wherein the α,β -ethylenically unsaturated carboxylic acid monomer is acrylic acid or methacrylic acid or a combination thereof.

10 10. The method for preparing a multi-stage polymer according to claim 6, wherein the α,β -ethylenically unsaturated nonionic monomer is ethyl acrylate, methyl methacrylate, 2-hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, vinyl acetate or acrylonitrile or a combination thereof.

11. A coating composition comprising from 0.1% to 2%, by weight based on the total weight of the coating composition, of the multi-stage polymer according to claim 1, a pigment, an extender, and a binder.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/081470

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: C08F265/04, C08F265/06, C08F265/00, C08L51/00

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)

EPODOC, WPI, CNABS, CNKI, CA: polymer, stage, grind+, additive?, dispersant, thickener, ethylene oxide, nonionic, ethylenical+, unsaturated, carboxylic acid, acrylate, MA 1w 20, SIPOMER, BEM, SEM, HPM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 1047322 A (ROHM AND HAAS COMPANY) 28. November 1990 (28.11.1990) page 28 line 23 to page 29 line 12, page 37 paragraph 3 and Table I	1-11

☐ 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
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The State Intellectual Property Office, the P.R.China
6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China
100088
Facsimile No. 86-10-62019451

Authorized officer

LI, Yanfang

Telephone No. (86-10)82246929

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2012/081470

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN 1047322 A	28.11.1990	EP0398576A	22.11.1990
		AU5497590A	15.11.1990
		NO902063A	16.11.1990
		PT94033A	08.01.1991
		CA2015832A	15.11.1990
		FI902402A	16.11.1990
		ZA9003607A	30.01.1991
		JPH0372511A	27.03.1991
		BR9002257A	30.07.1991
		NZ233653A	27.01.1993
		EP0398576A3	27.12.1991
		US5266646A	30.11.1993
		EP0398576B1	02.08.1995
		DE69021266T2	04.01.1996
		US5451641A	19.09.1995
		JP2845570B2	13.01.1999
		CA2015832C	28.05.2002

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/081470

Continuation of A. CLASSIFICATION OF SUBJECT MATTER:

C08F265/04 (2006.01)i

C08F265/06 (2006.01)i

C08F265/00 (2006.01)i

C08L51/00 (2006.01)i