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(54) Title: ACRYLIC EMULSIONS WITH INHERENT MATTE PROPERTY

(57) Abstract: Disclosed herein are acrylic emulsion compositions with an inherent matte property and methods of synthesizing and using the emulsion compositions.

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ACRYLIC EMULSIONS WITH INHERENT MATTE PROPERTY

FIELD OF THE DISCLOSURE

[001] This disclosure relates generally to acrylic emulsions, and more particularly to acrylic emulsions with an inherent matte property, and to methods of synthesizing and using the emulsion compositions.

BACKGROUND OF THE DISCLOSURE

[002] Aqueous based coatings, such as for example latex or emulsion polymer coatings, constitute a significant segment of all coatings in use today. Aqueous based coatings present advantages over conventional oil-based coatings because they contain fewer undesirable volatile organic solvents and therefore are more environmentally friendly. These polymeric products are dispersed in an aqueous medium and are stable in this condition but can form continuous dry film upon removal of the water. Many polymeric coatings, once cured, are glossy which may be desirable on a variety of substrates including flooring tiles, wood, metal, and fabrics. On the other hand, matte coating films based upon polymeric dispersions typically have low gloss, normally at a level of 30 or below on a 60-degree Gardner Gloss scale measurement. The glossiness of the polymer-based films is directly related to micro-scale surface roughness.

SUMMARY OF THE DISCLOSURE

[003] Disclosed herein are aqueous dispersions of an acrylic polymer comprising particles of the acrylic polymer dispersed in an aqueous medium, wherein the acrylic emulsion can inherently diffuse rays of incident light to provide a matte effect. The matte effect is achieved without the use of organic or inorganic matting agents and provides the coating with an aesthetic looking natural appearance. In another aspect, provided herein are processes for making the aqueous dispersion of acrylic polymers described here. In some embodiments, the aqueous polymer dispersion is prepared using a free radical emulsion polymerization process. In some embodiments, the free radical emulsion polymerization process is performed in a dual feed reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

[004] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate several embodiments of the disclosure and together with the description, serve to explain the principles of the disclosure.

[005] **Figure 1** provides a schematic of the dual feed polymerization reactor used in the syntheses of the acrylic emulsions of the present disclosure.

[006] **Figure 2** provides shows the stages of film formation of the aqueous based emulsions of the present disclosure

DETAILED DESCRIPTION

[007] The term "comprising" and variations thereof as used herein is used synonymously with the term "including" and variations thereof and are open, non-limiting terms. Although the terms "comprising" and "including" have been used herein to describe various embodiments, the terms "consisting essentially of" and "consisting of" can be used in place of "comprising" and "including" to provide for more specific embodiments and are also disclosed. As used in this disclosure and in the appended claims, the singular forms "a", "an", "the", include plural referents unless the context clearly dictates otherwise. The disclosure of percentage ranges and other ranges herein includes the disclosure of the endpoints of the range and any integers provided in the range.

[008] <u>I. Acrylic Emulsions with an Inherent Matte Property</u>

[009] The present disclosure provides acrylic emulsions with an inherent matte property, as well as synthesis methods for the aforementioned emulsions. The acrylic emulsions may be prepared via a free radical emulsion polymerization in a dual-feed reactor. The resulting emulsion polymers demonstrate an aesthetic natural appearance without the use of an organic or inorganic matting agent. Because of the absence of a matting agent, the films of the present disclosure are advantageous for reasons of chemical resistance, scratch resistance, mar resistance, dry-film clarity, haze-level, shelf life, and viscosity.

[0010] Common matting agents include silica, polyurea, polyacrylate, polyethylene, polytetrafluoroethene, organic wax, aluminum stearate, calcium stearate, polymethyl methacrylate, and mixtures thereof. These matting agents are undesirable in polymeric films because they may add complexity to the formulation through changes in viscosity and pH. Additionally, excess use of matting agents may affect the stabilization of a coating throughout the product's shelf life or cause gelling in the films if too much filler is added. Ultra-low matte films often require multiple particle sizes for matting agents. The use of inorganic silica, in particular, results in excessive crystalline dust during production which is a significant safety hazard.

[0011] A typical formulation for the emulsions of the present disclosure may comprise a copolymer, a chain transfer agent, and a surfactant. Other ingredients may be added to harden or soften the product. Colorants may also be added. Defoamers may be added.

[0012] The acrylic emulsions of the present invention may be acrylic or styrene-acrylic copolymers. Suitable monomers employed in the preparation of the emulsion include, but are not limited to, acrylic acid in an amount of from about 0% - 2.0% by weight, methacrylic acid in an amount of from about 0% - 2.0% by weight, styrene in an amount of from about 0% - 55% by weight, hydroxyethylmethacrylate in an amount of from about 0% - 5% by weight, butyl acrylate in an amount of from about 0% - 48% by weight, butyl methacrylate in an amount of from about 0% - 25% by weight, methyl methacrylate in an amount of from about 0% - 55% by weight, diacetone acrylamide in an amount of from about 0% - 5% by weight, methacrylate in an amount of from about 0% - 15% by weight, ethyl acrylate in an amount of from about 0% - 15% by weight, glycidyl methacrylate in an amount of from about 0% - 5% by weight, 2-ethylhexyl acrylate in an amount of from about 0% - 40% by weight, isobutyl acrylate in an amount of from about 0% - 10% by weight, and isobutyl methacrylate in an amount of from about 0% - 10% by weight, based on the total weight of the composition.

[0013] In some embodiments, the copolymer may be a carboxylic acid-functional resin. In some embodiments, the carboxylic acid-functional resin may be an alkali soluble resin. In other words, the carboxylic acid-functional resin may react with alkali materials to form ion salts at the carboxylate groups of the polymer, thereby enhancing the water solubility characteristics of the resin. Suitable monomers for preparation of the carboxylic acid-functional resin and the low molecular weight copolymer include monomers such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, crotonic acid, acrylic anhydride, methacrylic anhydride, itaconic anhydride, maleic anhydride, fumaric anhydride, crotonic anhydride, styrene, methyl styrene, alpha-methyl styrene, ethyl styrene, isopropyl styrene, tertiary-butyl styrene, ethyl methacrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, ethyl acrylate, vinyl acetate, methyl acrylate, open-chain conjugated dienes, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, methylol acrylamide, glycidyl acrylate, glycidyl methacrylate, vinyl esters, vinyl chloride, or mixtures of any two or more such monomers. In some embodiments, the carboxylic acid-functional support resin includes polymerized monomers of one or more of ethyl methacrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, ethyl acrylate, vinyl acetate, methyl acrylate, 2-

hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, glycidyl acrylate, glycidyl methacrylate, or mixtures of any two or more such monomers. In one embodiment, the carboxylic acid-functional resin includes polymerized monomers of one or more acrylic acid, ethyl methacrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, ethyl acrylate, vinyl acetate, methyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, glycidyl acrylate, glycidyl methacrylate, styrene, methyl styrene, alpha-methyl styrene, diacetone acrylamide, ureido methacrylate, or a mixture of any two or more such monomers. In some embodiments, the carboxylic acid-functional resin may include a co-polymer including two or more of styrene, methyl methacrylate, and acrylic acid. In some embodiments, the carboxylic acid-functional support resin may include a copolymer of acrylic acid and styrene.

[0014] The polymer or polymers used within the emulsions may have a glass transition temperature (Tg) for the individual polymer from -60 °C to 130 °C or any subrange or value within this range. For example, any given polymer within an emulsion may have a Tg from -60 °C to 100 °C, from -60 °C to 75 °C, from -60 °C to 50 °C, from -15 °C to 50 °C, from -15 °C to 45 °C, from -15 °C to 40 °C, from -15 °C to 35 °C, from -15 °C to 30 °C, from -15 °C to 25 °C, from -15 °C to 20 °C, from -15 °C to 15 °C, from -15 °C to 10 °C, from -15 °C to 5 °C, from -15 °C to 0 °C, from 0 °C to 50 °C, from 0 °C to 45 °C, from 0 °C to 40 °C, from 0 °C to 35 °C, from 0 °C to 30 °C, from 0 °C to 20 °C, from 0 °C to 15 °C, from 0 °C to 10 °C, from 10 °C to 50 °C, from 10 °C to 45 °C, from 10 °C to 40 °C, from 10 °C to 35 °C, from 10 °C to 30 °C, from 10 °C to 25 °C, from 10 °C to 20 °C, or any range including any two of these values as endpoints.

[0015] The emulsion or combination of polymers may have a glass transition temperature (Tg) for the individual polymer from -60 °C to 130 °C or any subrange or value within this range. For example, any given polymer within an emulsion may have a Tg from -60 °C to 100 °C, from -60 °C to 75 °C, from -60 °C to 50 °C, from -15 °C to 50 °C, from -15 °C to 45 °C, from -15 °C to 40 °C, from -15 °C to 35 °C, from -15 °C to 30 °C, from -15 °C to 25 °C, from -15 °C to 20 °C, from -15 °C to 15 °C, from -15 °C to 10 °C, from -15 °C to 5 °C, from -15 °C to 0 °C, from 0 °C to 50 °C, from 0 °C to 45 °C, from 0 °C to 40 °C, from 0 °C to 35 °C, from 0 °C to 30 °C, from 0 °C to 20 °C, from 0 °C to 15 °C, from 0 °C to 10 °C, from 10 °C to 50 °C, from 10 °C to 45 °C, from 10 °C to 40 °C, from 10 °C to 35 °C, from 10 °C to 30 °C, from 10 °C to 25 °C, from 10 °C to 20 °C, or any range including any two of these values as endpoints.

[0016] The polymers may be formed from emulsion-polymerizable monomers. Emulsion-polymerizable monomers are known in the art, *see e.g.* U.S. Patents Nos. 4,820,762;

7,253,218; 7,893,149; and U.S. Patent Publication No. 2015/0166803. The emulsion polymerizable monomer may include an ethylenically unsaturated monomer. In some embodiments, emulsion polymerizable monomer may include at least one ethylenically unsaturated nonionic monomer. By "nonionic monomer" herein is meant that the copolymerized monomer residue does not bear an ionic charge between pH 1 and 14. Suitable ethylenically unsaturated nonionic monomers include, but are not limited to, (meth)acrylic ester monomers 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; ureido-functional monomers; monomers bearing acetoacetate-functional groups; styrene and substituted styrenes; butadiene; ethylene, propylene, .alpha.-olefins such as 1-decene; vinyl acetate, vinyl butyrate and other vinyl esters; and vinyl monomers such as vinyl chloride, vinylidene chloride.

[0017] The emulsion-polymerizable monomer may include acrylate monomers, methacrylate monomers, styrene monomers, or a mixture of any two or more thereof. In some embodiments, the emulsion polymerizable monomer does not include styrene monomers.

[0018] In some embodiments, the at least one emulsion polymerizable monomer may be a C_1-C_4 acrylate, a C_1-C_4 (meth)acrylate, or a mixture of any two or more thereof. In some embodiments, the emulsion-polymerizable monomer may be n-butyl acrylate, 2-ethylhexyl acrylate, methyl acrylate, methyl methacrylate, styrene, ethyl acrylate, or a mixture of any two or more thereof.

[0019] In some embodiments, the emulsion polymerizable polymer may include one or more keto-functional monomers. Examples of keto-functional monomers include diacetone acrylamide, diacetone methacrylamide, diacetone acrylate, diacetone methacrylate, acetoacetoxymethyl (meth)acrylate, 2-(acetoacetoxy)ethyl (meth) acrylate, 2-acetoacetoxypropyl(meth)acrylate, butanediol-1,4-acrylate-acetylacetate, vinyl methyl ketone, vinyl ethyl ketone, and vinyl isobutyl ketone, allyl acetoacetate, vinyl acetoacetate, or vinyl acetoacetamide. In one embodiment, the emulsion polymerizable polymer includes a repeat unit derived from diacetone acrylamide.

[0020] The emulsions may be formed thorough an emulsion polymerization reaction, which may involve at least one emulsion polymerizable monomer, a low molecular weight copolymer, and other ingredients and/or reagents, such as an initiator. In some embodiments, the emulsion polymerization occurs in a dual-feed reactor.

[0021] The initiator may be a water-soluble compound for ready mixing and blending with the emulsions. Non-limiting examples of water-soluble initiators for the emulsion polymerization include ammonium salts and alkali metal salts of peroxydisulfuric acid, e.g., sodium peroxodisulfate, hydrogen peroxide or organic peroxides, e.g., tert-butyl hydroperoxide. The initiator may be a thermal initiator. Suitable initiators include, but are not limited to 2,2'-azobis(2-methylpropionamidine)dihydrochloride, ammonium persulfate, sodium persulfate, and potassium persulfate. Also suitable are reduction-oxidation (redox) initiator systems. The redox initiator systems consist of at least one, usually inorganic, reducing agent and an organic or inorganic oxidizing agent. The oxidizing component comprises, for example, the emulsion polymerization initiators already identified above. The reducing components comprise, for example, alkali metal salts of sulfurous acid, such as, for example sodium sulfite, sodium hydrogensulfite, alkali metal salts of disulfurous acid such as sodium disulfite, bisulfite addition compounds with aliphatic aldehydes and ketones, such as acetone bisulfite, or reducing agents such as hydroxymethanesulfinic acid and its salts, or ascorbic acid. The redox initiator systems can be used along with soluble metal compounds whose metallic component is able to exist in a plurality of valence states. Typical redox initiator systems are, for example, ascorbic acid/iron(II) sulfate/sodium peroxydisulfate, tert-butyl hydroperoxide/sodium disulfite, tert-butyl hydroperoxide/Na hydroxymethanesulfinic acid. The individual components, the reducing component for example, may also be mixtures, an example being a mixture of the sodium salt of hydroxymethanesulfinic acid and sodium disulfite. The stated compounds are used usually in the form of aqueous solutions, with the lower concentration being determined by the amount of water that is acceptable in the dispersion, and the upper concentration by the solubility of the respective compound in water. Generally speaking, the concentration is 0.1% to 30% by weight, preferably 0.5% to 20% by weight, more preferably 1.0% to 10% by weight, based on the solution. The amount of the initiators is generally 0.1% to 10% by weight, preferably 0.5% to 5% by weight, based on the monomers to be polymerized. It is also possible for two or more different initiators to be used in the emulsion polymerization.

[0022] In some embodiments, an initiator may be ammonium persulfate and an oxidizer may be t-butyl hydroperoxide. In such case, a weight ratio between ammonium persulfate and t-butyl hydroperoxide may range from 40:1 to 2:1 or from 30:1 to 4:1 or any subrange or value within these ranges.

[0023] In some embodiments, the emulsion includes one or more chain transfer agents to control molecular weight, branching and/or gel formation. Exemplary chain transfer agents include, but are not limited to, isooctyl mercaptopropionate (IOMPA), butylmercaptopropionate, 2-ethyl hexylmercaptopropionate, tertiary dodecylmercaptan, and thioglycerol.

[0024] In general, the amounts of the chain transfer agents employed can be varied from 0.01% to 1% by weight, based on the total amount of the monomers to be polymerized.

[0025] The polymer emulsions described herein may also contain a surfactant. In some embodiments, the surfactant is anionic or non-ionic. In some embodiments, the surfactant contains one or more fatty alcohol alkoxylates. In further embodiments, the one or more fatty alcohol alkoxylates are fatty alcohol ethoxylates, fatty alcohol propoxylates, or any combination thereof. In some embodiments, the surfactant contains one or more ethylene oxide/propylene oxide block copolymers. In some embodiments, the surfactant contains one or more fatty alcohol ethoxylates. In some embodiments, the surfactant contains one or more alkylsulfosuccinate ethoxylates. In some embodiments, the surfactant contains one or more fatty alcohols having an alkyl chain length of about 12 to about 18 carbons; and a degree of ethoxylation of about 10 to about 80 molar ethylene oxide units. In some embodiments, the surfactant includes non-ionic surfactants. In some embodiments, the surfactant includes anionic surfactants. In some embodiments, the anionic surfactant includes one or more alkyl sulfonates, alkyl benzene sulfonates, alkyl sulfates, alkyl benzene sulfates, phosphates, phosphinates, fatty carboxylates, or any combination of two or more thereof.

[0026] In general, the amounts of the surfactants employed can be varied from 0.3% to 1% by weight, based on the total amount of the monomers to be polymerized.

[0027] The polymer compositions described herein may contain other materials such as, but not limited to, other aqueous resin solutions, rheology modifiers, wetting agents, defoamers, thickeners, stabilizers, buffering agents, salts, preservatives, fire retardants, biocides, corrosion inhibitors, cross-linkers, lubricants, colorants, dyes, waxes, perfumes, and fillers.

[0028] In some preferred embodiments, the polymer compositions described herein are substantially free of matting agents. "Substantially free of matting agents" as used herein indicates that the aqueous coating composition comprises less than 0.1% by weight of matting agents, based on the total weight of the aqueous coating composition. The term "matting agents" as used herein includes but is not limited to silica, polyurea, polyacrylate, polyethylene, polytetrafluoroethene, organic wax, aluminum stearate, calcium stearate, polymethyl methacrylate, and mixtures thereof. The matting agent may be a powder or emulsion.

[0029] In one particularly preferred embodiment, the polymer compositions described herein are entirely free of matting agents.

[0030] As described herein, the acrylic or styrene-acrylic emulsion dispersion particles may have a d(0.1) of 0.1 µm or greater, 0.5 µm or greater, or 1 µm or greater. The large and multimode particle size distribution is aided by flooding the reactor with monomer and seed polymer at the initial stage of polymerization thereby creating a scarcity for micelles. Additionally, the ramp-up and ramp-down power feeding of surfactants and monomers promotes large and multimode particle sizes.

[0031] As described herein, the polymer films of the present disclosure may have a low gloss as measured by a gloss meter. At an angle of 20° on a black background, the present films may have a gloss of 20 GU or less, 15 GU or less, 10 GU or less, or 5 GU or less. At an angle of 20° on a white background, the present films may have a gloss of 20 GU or less, 15 GU or less, 10 GU or less, or 5 GU or less. At an angle of 60° on a black background, the present films may have a gloss of 30 GU or less, 25 GU or less, 20 GU or less, or 15 GU or less. At an angle of 60° on a white background, the present films may have a gloss of 30 GU or less, 25 GU or less, 20 GU or less, or 15 GU or less. At an angle of 85° on a black background, the present films may have a gloss of 60 GU or less, 55 GU or less, 50 GU or less, or 45 GU or less. At an angle of 85° on a white background, the present films may have a gloss of 65 GU or less, 60 GU or less, 55 GU or less, or 50 GU or less as measured by the ASTM D523 test method for specular gloss.

[0032] II. Methods of Making Emulsions

[0033] The emulsions of the present disclosure may be formed through an emulsion polymerization, which relies on the use of small molecule surfactants containing a polar/hydrophilic group and a nonpolar/hydrophobic group. The amphiphilic nature of these materials allows them to effectively stabilize heterogenous solutions (i.e. polymer particles in water). The emulsion polymerization reactions of the present disclosure may be performed in a dual feed reactor such as the one depicted in FIG. 1. The reactor may be equipped with a water bath, mechanical stirrer, temperature control probes, feeding tubes for monomer addition, feeding tubes for initiator addition, and reflux condensers. In general, each tank is charged with the contents listed below in Table 1

[0034] Table 1. Charges for different vessels in dual feed reactor depicted in FIG. 1.

Vessel	**Charge**
Tank 12	Pre emulsion (DI-Water + Surfactant + Monomer A+ Optionally Chain Transfer Agent
Tank 16	Neat monomer (Monomer B) or Pre emulsion (DI-Water + Surfactant + Monomer B)
Tank 10	Initiator (DI-Water + Initiator + Optionally Buffer)
Reactor 14	Reactor Charge (DI-Water + Surfactant + Seed + Acid Monomer

[0035] Initially, reactor 14 is charged with DI-water which is then heated to 85°C. Acid monomer at 80°C is added to reactor 14 at one shot followed by an initial initiator shot from tank 10 which is pumped into reactor 14 via pump 20. Then, the pre-emulsion feed in tank 12 comprising DI-water, surfactant, Monomer A, and optionally a chain transfer reagent is pumped through pump 18 to feed into reactor 14. Simultaneously, the neat monomer feed in tank 16 comprising Monomer A is pumped through pump 22 into reactor 14. After 15 minutes of pre-emulsion, a second charge of initiator feed from tank 10 is pumped into reactor 14. The total feeding time is three hours. At the end of pre-emulsion, the neat monomer and initiator feeds hold the reactor at 85°C for 30 minutes and then flush water is added to reduce the temperature to 70°C. After completion of the chemical stripping process, reactor 14 is cooled to room temperature before the polymer finished polymer is filtered into a storage container.

[0036] As described herein, the free radical initiators can be water-soluble initiators. Examples of such water-soluble initiators can include but are not limited to, persulfates such as sodium persulfate ($Na_2S_2O_8$), ammonium persulfate and potassium persulfate; peroxides such as hydrogen peroxide and tert-butyl hydroperoxide (t-BHP); and azo compounds such as VAZO™ initiators, commercially available from The Chemours Company. They can be used alone or in combination with one or more reducing agents or activators, for example, bisulfites, metabisulfites, ascorbic acid, erythorbic acid, sodium formaldehyde sulfoxylate, ferrous sulfate, ferrous ammonium sulfate, and ferric ethylenediamine tetraacetic acid.

[0037] In general, the amounts of the free-radical initiators employed can be varied from 0.1% to 1% by weight, based on the total amount of the monomers to be polymerized.

[0038] The examples below are intended to further illustrate certain aspects of the methods and compositions described herein and are not intended to limit the scope of the claims.

EXAMPLES

[0039] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compositions and/or methods claimed herein are made and evaluated and are intended to be purely exemplary and are not intended to limit the scope of the disclosure. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

[0040] The particle size distribution percentiles are denoted by the letter "d" followed by the % value. Thus, d(0.1) or d10 = 1.107 uM, d(0.5) or d(50) =3.79uM & d(0.9) 0r d(90) = 7.094uM means that 10% of the sample is smaller 1.107uM, 50% of sample is smaller than 3.79uM and 90% of sample is smaller than 7.094uM.

[0041] <u>Example 1: Synthesis of Acrylic Emulsions</u>

[0042] Initially, the polymerization reactor was charged with a required amount of DI-water, about 25% of the total surfactant amount and seed polymer. The reactor was heated to 85°C and at 80°C acid monomer was added at one shot. Then at 85°C an initial initiator shot (about 25% of total initiator solution) was instantly added. After the initiator shot, pre-emulsion neat monomer feeds were started simultaneously. After 15 minutes of pre-emulsion and neat monomer feeds, the second charge of initiator feed was started. The total feeding (Neat Monomer+Pre-emulsion+Initiator) time was 3 hours. At the end of pre-emulsion, the neat monomer and initiator feed held the reactor at 85°C for 30 minutes and then flush water was added to reduce the reactor temperature to 70°C. At 70°C, delayed oxidizer and reducer feeds were started to reduce the residual monomers. After the completion of chemical strip process, the reaction was cooled to room temperature. Finally post addition solution was added and the reactor mixed the contents for 15 minutes before filtering the polymer in storage container.

[0043] Table 2. List of acrylic emulsion formulations.

Formulaiton	Surfactant	Acid Monomer	Tank-1	Tank-2
1	Polystep LAS40	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ t-Dodecylmercaptan	Methylmethacrylate
2	Polystep LAS40	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate	Styrene
3	Polystep LAS40	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Ethyldiglycol Acrylate + t-Dodecylmercaptan	Styrene
4	Polystep LAS40	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Diacetoneacrylamide + t-Dodecylmercaptan	Methylmethacrylate
5	Polystep LAS40	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Methylmethacrylate+ Glycidylmethacrylate + t-Dodecylmercaptan	Methylmethacrylate
6	Polystep LAS40	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Methylmethacrylate+ Glycidylmethacrylate + t-Dodecylmercaptan	Methylmethacrylate + Triethoxyvinyl Silane
7	Polystep LAS40	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Diacetoneacrylamide + Isooctyl-3-mercaptopropianate	Methylmethacrylate
8	Polystep LAS40	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Butylmethacryalte +t-Dodecylmercaptan	Methylmethacrylate
9	Polystep LAS40 + Polystep A-16-22 + Lutensol XP-80	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Tert-Butylacrylate + t-Dodecylmercaptan	DI-Water +Surfactant +Methylmethacrylate
10	Polystep LAS40 + Polystep A-16-22 + Lutensol XP-80	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Ureidomethacrylate+ t-Dodecylmercaptan	DI-Water +Surfactant +Methylmethacrylate
11	Polystep LAS40 + Polystep A-16-22 + Lutensol XP-80	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Cyclohexyl methacrylate+ t-Dodecylmercaptan	DI-Water +Surfactant +Methylmethacrylate
12	Polystep LAS40 + Polystep A-16-22 + Lutensol XP-80	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ 2-Ethylhexyl Acrylate+ t-Dodecylmercaptan	DI-Water +Surfactant +Methylmethacrylate
13	Polystep LAS40 + Polystep A-16-22 + Lutensol XP-80	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Styrene + t-Dodecylmercaptan	DI-Water + Surfactant + Methylmethacrylate + Isobornylmethacrylate
14	Polystep LAS40 + Polystep A-16-22 + Lutensol XP-81	Methacrylic Acid	DI-Water+Surfactant+ Butylacrylate+ Isobornylmethacrylate+ t-Dodecylmercaptan	DI-Water + Surfactant + Methylmethacrylate

[0044] Table 3. Particle size distribution of formulations 1-14.

Formulation #	**Particle Size Distribution**		
	d(0.1)	**d(0.5)**	**d(0.9)**
1	1.107	3.79	7.094
2	*0.925*	*1.773*	*9.042*
3	*0.888*	*1.314*	*2.005*
4	1.131	1.834	3.146
5	0.576	1.005	1.714
6	0.627	1.207	2.035
7	1.103	1.666	2.512
8	1.13	1.742	2.648
9	1.273	2.422	4.084
10	1.145	2.114	3.896
11	0.136	0.221	5.79
12	1.367	2.515	4.205
13	1.8	3.1	6.88
14	0.12	1.96	4.49

[0045] Table 4. Gloss measurements of formulations 1-14.

Formulation #	Gloss on Black/White Background			
		20°	60°	85°
1	Black	2.1	17.8	47
	White	3.9	22.2	58.3
2	Black	0.6	2	23
	White	1.3	3	23
3	Black	1.1	16.2	51.9
	White	2.2	16.8	49.4
4	Black	0.5	9.8	47.6
	White	1.4	5.3	45
5	Black	11.6	24.8	58.6
	White	12.3	29.5	60.1
6	Black	0.6	9.3	46.6
	White	1.5	7.4	49.2
7	Black	11.2	24.8	44.3
	White	12.1	26.1	45.6
8	Black	16.1	28.1	55.2
	White	15.2	25.2	59.3
9	Black	1.8	17.9	69.1
	White	3	20.5	73.6
10	Black	3	19	68.3
	White	3.2	19.8	69
11	Black	2.1	15.5	50.7
	White	2.6	16.2	42.1
12	Black	0.4	7.2	66.3
	White	1.6	9.3	66.7
13	Black	1.3	14.6	70.8
	White	2.6	17.6	72.1
14	Black	0.9	11.6	2
	White	2	13.3	70.3

CLAIMS

WHAT IS CLAIMED IS

1. A polymer emulsion composition comprising
at least one block copolymer;
at least one chain transfer agent
at least one surfactant
wherein, the polymer emulsion is substantially free of organic or inorganic matting agents.

2. The polymer emulsion composition of claim 1, wherein the organic or inorganic matting agents comprise silica, polyurea, polyacrylate, polyethylene, polytetrafluoroethene, organic wax, aluminum stearate, calcium stearate, polymethyl methacrylate, and/or mixtures thereof.

3. The polymer emulsion composition of claim 1, wherein the emulsion inherently diffuses rays of incident light to provide a matte effect.

4. The polymer emulsion composition of claim 1, wherein the particles of the acrylic polymer have a measured d(0.5) value of 1μm or more.

5. The polymer emulsion of claim 1, wherein the emulsion composition has a glass transition temperature from -60°C to 130°C.

6. The polymer emulsion of claim 1, wherein the copolymer is an acrylic or styrene-acrylic copolymer.

7. The polymer emulsion composition of claim 1 wherein the polymer comprises the functional monomers acrylic acid, methacrylic acid, styrene, alpha-methylstyrene, hydroxyethylmethacrylate. esters of acrylic acid, or methacrylic acid

8. The polymer emulsion of claim 1, wherein the chain transfer agent is present in an amount of from 0.01 wt. % to 1 wt. % based on the total weight of the composition.

9. The polymer emulsion of claim 1, wherein the chain transfer agent is selected from the group consisting of isooctyl mercaptopropionate (IOMPA), butylmercaptopropionate, 2-ethyl hexylmercaptopropionate, tertiary dodecylmercaptan, and thioglycerol.

10. The polymer emulsion of claim 1, wherein the surfactant is present in an amount of from 0.3 wt. % to 1 wt. % based on the total weight of the composition

11. The polymer emulsion of claim 1, wherein the surfactant is selected from the group consisting of fatty alcohol alkoxylates, fatty alcohol ethoxylates, ethylene oxide block copolymers, propylene oxide block copolymers, alkyl sulfonates, alkyl benzene sulfonates, alkyl

sulfates, alkyl benzene sulfates, phosphates, phosphinates, or fatty carboxylates.

12. The polymer emulsion of claim 1, wherein the emulsion further comprises an aqueous resin solution, rheology modifier, wetting agent, defoamer, thickener, stabilizer, buffering agent, salt, preservative, fire retardant, biocide, corrosion inhibitor, cross-linker, lubricant, colorant, dye, wax, perfume, or filler.

13. A method for producing the polymer emulsion of claim 1 in dual feed reactor comprising

(i) charging a polymerization reactor with DI-water, surfactant, and seed polymer;

(ii) adding an initiator to the reactor;

(iii) feeding monomers into the reactor from two separate tanks to form a polymer composition;

(iv) adding flush water to the reactor;

(v) chemically stripping the polymer composition; and

(vi) filtering the polymer composition into a storage container.

14. The method of claim 13, wherein the monomer feeding is ramped-up and ramped-down gradually.

15. The method of claim 13, wherein the dual power feed synthesis process produces gradient molecular weight polymeric chains.

16. The method of claim 13, wherein the dual power feed synthesis process produces a wide Tg of the resulting polymer dispersion

17. The method of claim 13, wherein the dual power feed synthesis process produces a gradient Tg.

18. A substrate coated with the composition of claim 1.

19. The coated substrate of claim 18, wherein the substrate has a gloss value of 20 GU or less as measured by a gloss meter at an angle of 20° on a black background.

20. The coated substrate of claim 18, wherein the substrate has a gloss value of 30 GU or less as measured by a gloss meter at an angle of 60° on a black background.

21. The coated substrate of claim 18, wherein the substrate has a gloss value of 60 GU or less as measured by a gloss meter at an angle of 85° on a black background.

22. The coated substrate of claim 18, wherein the substrate has a gloss value of 20 GU or less as measured by a gloss meter at an angle of 20° on a white background.

23. The coated substrate of claim 18, wherein the substrate has a gloss value of 30 GU or less as measured by a gloss meter at an angle of 60° on a white background.

24. The coated substrate of claim 18, wherein the substrate has a gloss value of 65 GU or less as measured by a gloss meter at an angle of 85° on a white background.

FIGURE 1

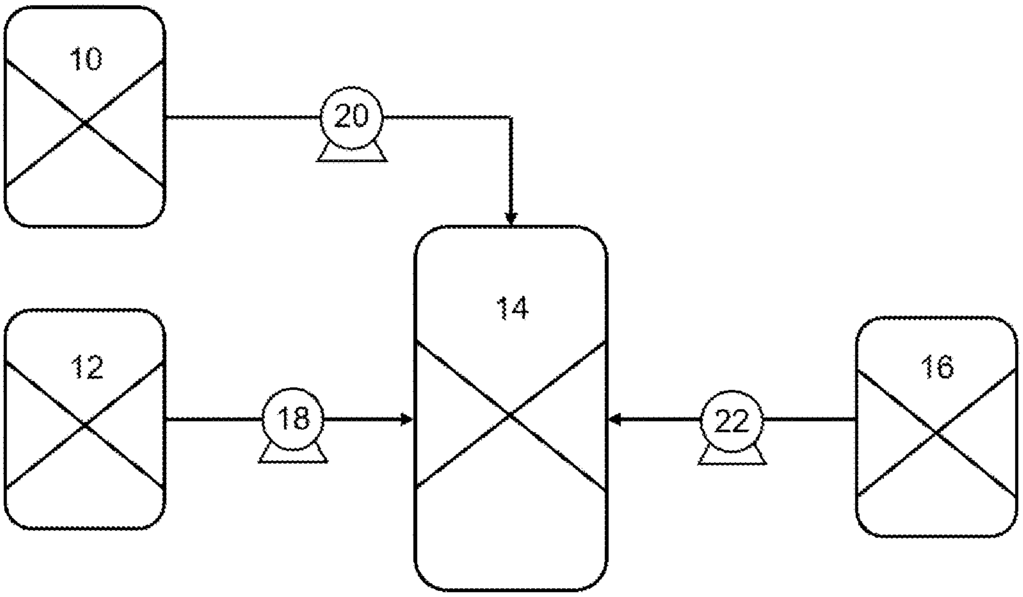
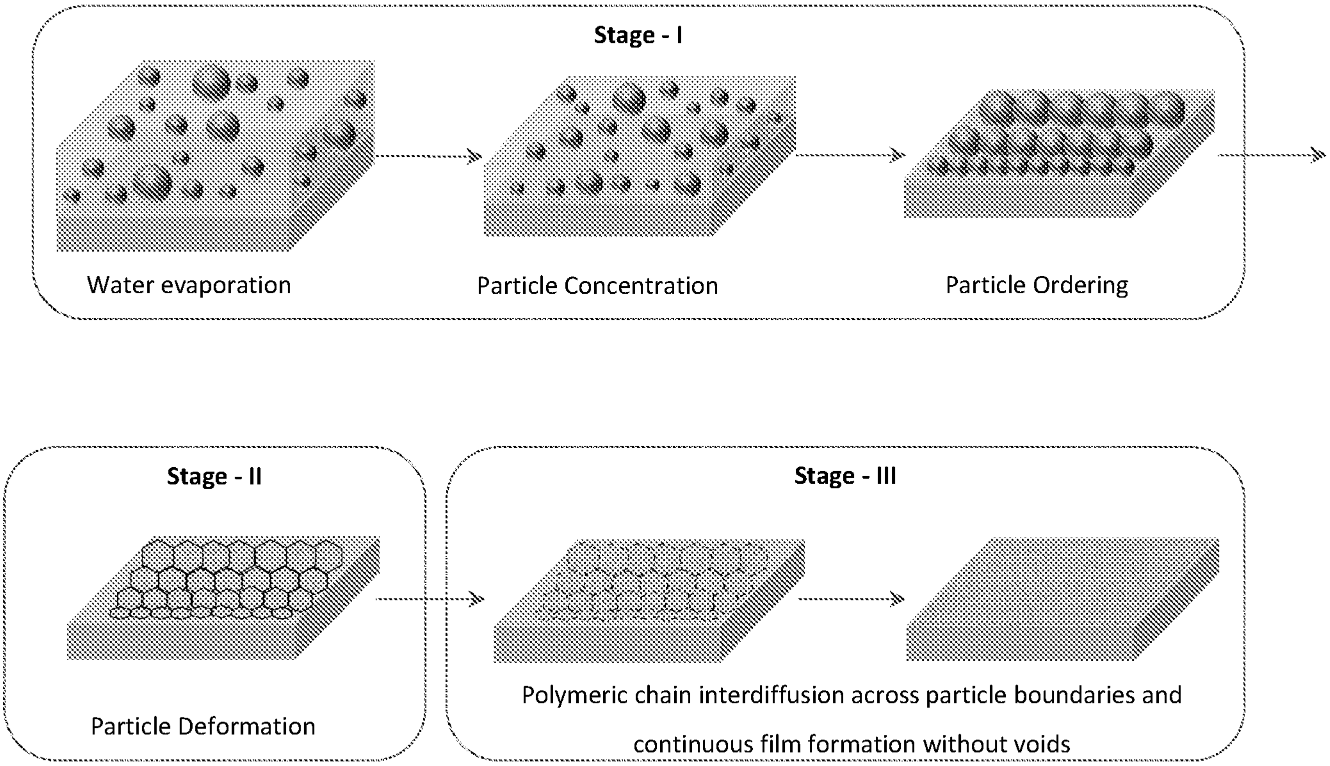


FIGURE 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/020931

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J133/08 C08F2/24 C08F2/38 C08F265/06 C09J125/06
ADD.

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)
C08F B32B C09J

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Wikipedia: "gradient copolymer", , 16 November 2021 (2021-11-16), XP093054018, Retrieved from the Internet: URL:https://en.wikipedia.org/wiki/Gradient_copolymer [retrieved on 2023-06-13] page 1, paragraph 1 -----	1-24
X	CN 114 085 632 A (UNIV MINNAN NORMAL; FUJIAN CHANGXIN PAPER IND PACKAGING CO LTD) 25 February 2022 (2022-02-25) embodiment 2 -----	1,5-8,10
X	EP 3 224 283 A1 (CELANESE INT CORP [US]) 4 October 2017 (2017-10-04) example 1 -----	1,2,5-7, 10,13-18

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search 14 June 2023	Date of mailing of the international search report 22/06/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Jegou, Gwénaëlle

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2023/020931

C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2018/066166 A1 (ZORN MATTHIAS [DE] ET AL) 8 March 2018 (2018-03-08) example 2 -----	1,2,5-7, 9,10, 13-15,18
X	WO 2022/008456 A1 (COVESTRO NETHERLANDS B V [NL]) 13 January 2022 (2022-01-13) examples 2B, 3B, 3C; table 8 -----	1-7,9, 11-15, 18-24

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2023/020931

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			JP	6789967	B6	16-12-2020
			JP	2018514605	A	07-06-2018
			KR	20170129216	A	24-11-2017
			US	2018066166	A1	08-03-2018
			WO	2016146427	A1	22-09-2016
WO 2022008456	A1	13-01-2022	NONE			