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- (71) Applicant: PPG INDUSTRIES OHIO, INC. [US/US];
3800 West 143rd Street, Cleveland, OH 44111 (US).
- (72) Inventors: SWARUP, Shanti; 4918 Meadow Crest Drive,
Allison Park, PA 15101 (US). PAGAC, Edward, S.; 1113
West Portersville Road, Portersville, PA 16051 (US).
RAGUNATHAN, Kaliappa, G.; 1100-3 Nineteen North
Drive, Pittsburgh, PA 15237 (US).
- (74) Agents: ALTMAN, Deborah, M.; PPG Industries, Inc.,
One PPG Place, Pittsburgh, PA 15272 et al. (US).
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(54) Title: AQUEOUS DISPERSIONS OF POLYMERIC MICROPARTICLES AND COATING COMPOSITIONS CONTAINING SAME

(57) Abstract: An aqueous dispersion including polymeric microparticles having a functionality adapted to react with a crosslinking agent is provided. The microparticles are prepared in two or more stages by emulsion polymerization and include a first stage uncrosslinked polymerization reaction product and a final stage crosslinked polymerization reaction product having a glass transition temperature greater than 25 °C. The first stage uncrosslinked reaction product is formed from reactants at least one of which is an acid functional group-containing polymerizable, ethylenically unsaturated monomer. The second stage crosslinked reaction product is formed from reactants which include at least one polymerizable, ethylenically unsaturated monomer having two or more sites of reactive unsaturation, and/or at least one ethylenically unsaturated monomer having at least one self-reactive site. Curable compositions which contain the aqueous dispersions as well as multi-component composite coating compositions are also provided. Further provided are substrates coated with the aforementioned compositions.

Over the past decade, there has been a concerted effort to reduce atmospheric pollution caused by volatile solvents that are emitted during the painting process. One approach to volatile emission control has been the use of water as an organic solvent replacement in automotive coating compositions (i.e., waterborne or aqueous coating compositions).

Many application problems can be encountered with the use of such waterborne coating compositions. For example, such coatings can be particularly susceptible to "sagging" or "flooding" during application in high humidity environments. Also, at higher film-builds, or when subsequently top coated, these cured waterborne coatings can exhibit "popping" or pinholing, i.e., surface defects which can result from water escaping from the surface area upon thermal curing. Moreover, application of an organic solvent-based clear coat to an aqueous metallic base coat can result in a decreased "flip-flop" effect. The decreased "flip-flop" is the result of "strike in"; that is, a softening of the base coat by the organic solvent present in the clear coating composition. As the organic solvent contacts the base coat, metallic pigment flakes contained therein can move resulting in random orientation.

U.S. Patent Nos. 4,539,363 and 4,403,003, describe the use of a polymeric particulate dispersion in base coat/clearcoat applications which are less sensitive to humidity during application and more resistant to popping during thermal curing. However, the aqueous coating compositions disclosed in these references are notably low in solids. Such low solids systems often necessitate multiple applications to achieve cured coatings with desired film-builds. Also, a significant amount of organic solvent is required for acceptable flow and coalescence of the applied aqueous coating compositions.

U.S. Patent Nos. 4,046,729 and 4,489,135 disclose waterborne coating compositions which employ polyurethane polymers in aqueous media. These compositions are flexible and contain low levels of organic solvent. However, due to the presence of high levels of water-soluble polymers, these coatings can exhibit poor humidity resistance and "popping" upon thermal curing.

U.S. Patent No. 4,973,621 discloses aqueous dispersion of uncrosslinked polymeric particles dispersed in aqueous media. The uncrosslinked polymeric

particles are prepared from addition polymers which are obtained in two or more steps by emulsion polymerization. The aqueous coating compositions based upon the aqueous dispersions provide base coats having excellent "flip-flop" effect. Such compositions, however, can exhibit increased viscosity over time
5 due to particle swelling resulting in poor storage stability

U.S. Patent No. 5,356,956 discloses an aqueous dispersion of acrylic polymer particles. The polymeric particles are composite particles composed of a core layer and a skin (i.e., shell) layer of acrylic polymers having mutually different glass transition temperatures (" T_g "). The core layer acrylic polymer has
10 a T_g ranging from 130°C to 10°C and the shell layer acrylic polymer has a T_g less than or equal to -10°C. This T_g differential is disclosed as being critical to provide chip-resistant coatings (see column 7, lines 6-18). Although such core/shell acrylic dispersions provide flexible and chip resistant coatings, when employed as a reflective pigment-containing base coat, these coatings can have
15 a decreased "flip/flop" effect and/or poor humidity resistance due to the presence of the low T_g acrylic polymer in the shell layer.

Thus, there remains a need in the automotive coating industry for a storage stable aqueous coating composition suitable for use as a reflective pigment-containing base coat in a multi-component composite coating which will
20 provide excellent "flip-flop" effect while maintaining excellent humidity resistance and appearance properties.

SUMMARY OF THE INVENTION

In accordance with the present invention, provided is an aqueous
25 dispersion comprising polymeric microparticles having a functionality adapted to react with a crosslinking agent. The microparticles are prepared in two or more stages by emulsion polymerization and comprise (a) a first stage uncrosslinked polymerization reaction product formed from reactants comprising at least one acid functional group-containing polymerizable, ethylenically unsaturated
30 monomer; and (b) a final stage crosslinked polymerization reaction product having a glass transition temperature greater than 25°C and formed from reactants comprising at least one polymerizable, ethylenically unsaturated

monomer having two or more sites of reactive unsaturation, and/or at least one ethylenically unsaturated monomer having at least one self-reactive site.

Curable compositions which contain the aqueous dispersions described above are also provided. Further provided are multi-component composite coating
5 compositions composed of a base coat deposited from an aqueous, pigmented film-forming composition comprising the aqueous dispersion and a top coat deposited from a substantially pigment-free film-forming composition. Coated substrates are also provided.

Other than in the operating examples, or where otherwise indicated, all
10 numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Also, as used herein, the term "polymer" is meant to refer to oligomers, and both homopolymers and copolymers.

15 DETAILED DESCRIPTION OF THE INVENTION

As discussed above, the aqueous dispersion of the present invention is comprised of polymeric microparticles which have a functionality adapted to react with a crosslinking agent. As used herein, the term "dispersion" means that the microparticles are capable of being distributed throughout water as finely
20 divided particles, such as a latex. See Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 435, which is hereby incorporated by reference.

The microparticles, which are prepared in two or more stages by emulsion polymerization, comprise, as a core component, component (a), a first stage
25 uncrosslinked polymerization reaction product formed from reactants which comprise at least one acid functional group-containing polymerizable, ethylenically unsaturated monomer, and component (b), a final stage crosslinked polymerization reaction product having a glass transition temperature greater than 25°C which is formed from at least one polymerizable, ethylenically
30 unsaturated monomer having two or more sites of reactive unsaturation, and/or at least one ethylenically unsaturated monomer having at least one self-reactive site.

The first stage uncrosslinked polymerization reaction product (a) comprises at least one acid functional group-containing, ethylenically unsaturated monomer. Suitable acid functional group-containing ethylenically unsaturated monomers include α,β -unsaturated mono- or di-
5 carboxylic acids having 3 to 5 carbon atoms, for example acrylic acid, methacrylic acid, crotonic acid, citraconic acid, itaconic acid, maleic acid, maleic anhydride, fumaric acid and the like. Preferred acid functional group-containing monomers are those selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

10 The amount of acid functional group-containing monomer present in the first stage polymerization reaction product (a) typically can range up to 7 weight percent, preferably 0.5 to 5 weight percent and more preferably 1 to 3 weight percent of the monomers used to form the first stage polymerization reaction product (a).

15 In a preferred embodiment of the invention, the first stage polymerization reaction product further comprises at least one polymerizable, ethylenically unsaturated monomer free from acid functional groups. Non-limiting examples of polymerizable, ethylenically unsaturated monomers free of acid functional
20 groups include vinyl monomers such as alkyl esters of acrylic and methacrylic acids, for example, ethyl (meth)acrylate, methyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isobornyl methacrylate and lauryl methacrylate; vinyl aromatics such as styrene, alpha-methyl styrene and vinyl toluene; acrylamides such as N-butoxymethyl acrylamide; acrylonitriles; dialkyl esters of maleic and fumaric acids; vinyl and vinylidene halides; vinyl acetate;
25 vinyl ethers; allyl ethers; allyl alcohols; derivatives thereof and mixtures thereof. As used herein the term "(meth)acrylic" and like terms are intended to include both acrylic and methacrylic.

Functional group-containing monomers, such as hydroxyl and/or carbamate functional group-containing ethylenically unsaturated monomers may
30 also be used to form the first stage uncrosslinked polymerization reaction product (a). Non-limiting examples of suitable hydroxyl group-containing

monomers include hydroxyalkyl esters, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and hydroxybutyl (meth)acrylate.

Non-limiting examples of suitable carbamate functional, ethylenically unsaturated monomers include carbamate functional alkyl esters of (meth)acrylic acid. These carbamate functional alkyl esters are prepared by reacting, for example, a hydroxyalkyl carbamate, such as the reaction product of ammonia and ethylene carbonate or propylene carbonate, with (meth)acrylic anhydride. Other carbamate functional, ethylenically unsaturated monomers include the reaction product of hydroxyethyl methacrylate, isophorone diisocyanate, and hydroxypropyl carbamate. Still other carbamate functional, ethylenically unsaturated monomers can be used, such as the reaction product of isocyanic acid (HNCO) with a hydroxyl functional acrylic or methacrylic monomer such as hydroxyethyl acrylate, and those carbamate functional, ethylenically unsaturated monomers described in U.S. Patent 3,479,328.

The ethylenically unsaturated monomers free of acid functional groups used to form reaction product (a) can also include ethylenically unsaturated, beta-hydroxy ester functional monomers, for example, those derived from the reaction of an ethylenically unsaturated acid functional monomer, such as a monocarboxylic acid, for example, acrylic acid, and an epoxy compound which does not participate in the free radical initiated polymerization with the unsaturated acid monomer. Examples of such epoxy compounds are glycidyl ethers and esters. Suitable glycidyl ethers include glycidyl ethers of alcohols and phenols such as butyl glycidyl ether, octyl glycidyl ether, phenyl glycidyl ether and the like. Suitable glycidyl esters include those that are commercially available from Shell Chemical Company under the tradename CARDURA E and from Exxon Chemical Company under the tradename GLYDEXX-10.

Alternatively, suitable beta-hydroxy ester functional monomers can be prepared from an ethylenically unsaturated, epoxy functional monomer, for example glycidyl (meth)acrylate and allyl glycidyl ether, and a saturated carboxylic acid such as a saturated monocarboxylic acid, for example, isostearic acid.

Since the first stage polymerization reaction product (a) is uncrosslinked, the reaction product is formed from monomers which do not contain neither self-crosslinking sites nor more than one site of reactive unsaturation. Preferably, the reaction product (a) also is essentially free of crosslinking agents.

5 In a preferred embodiment of the invention, the reaction product (a) is prepared from one or more acid functional monomers, such as (meth)acrylic acid, and one or more ethylenically unsaturated monomers free of acid functional groups is selected from the group consisting of methyl (meth)acrylate, butyl (meth)acrylate and mixtures thereof.

10 If present, the amount of ethylenically unsaturated monomer free of acid functional groups typically can comprise at least 93 weight percent, preferably 95 to 99.5 weight percent, and more preferably 97 to 99 weight percent of the monomers used to form the first stage polymerization reaction product (a), the balance being acid functional group-containing ethylenically unsaturated
15 monomers.

The first stage polymerization reaction product (a) typically is present in the aqueous dispersion of the present invention in an amount less than 90 weight percent, preferably less than 85 weight percent, and more preferably less than 75 weight percent, based on the weight of total resin solids in the
20 dispersion. Also, the first stage polymerization reaction product (a) is typically present in the aqueous dispersion of the present invention in an amount of at least 45 weight percent, preferably at least 55 weight percent and more preferably at least 60 weight percent, based on the weight of total resin solids in the dispersion. The amount of the first stage polymerization reaction product (a)
25 present in the dispersion can range between any combination of these values inclusive of the recited ranges.

The final stage crosslinked polymerization reaction product (b) has a glass transition temperature (T_g) of greater than 25°C. Preferably the final stage polymerization reaction product (b) has a T_g greater than 30°C and ranging up to
30 120°C, more preferably ranging from 35°C to 80°C, and even more preferably from 40°C to 60°C. It has been found that if the T_g of the final stage polymerization reaction product (b) is less than 25°C, the "flip-flop" effect of

resultant reflective pigment-containing base coat is diminished. The T_g of the polymer can be calculated as described by Fox in *Bull. Amer. Physics. Soc.*, 1,3 page 123 (1956). The T_g can also be measured experimentally and differential scanning calorimetry can be used (rate of heating 10°C° per minute, T_g taken at the first inflection point). Unless otherwise indicated, the stated T_g as used
5 herein refers to the calculated T_g .

As aforementioned, the final stage polymerization reaction product (b) comprises (i) at least one polymerizable, ethylenically unsaturated monomer having two or more sites of reactive unsaturation and/or (ii) at least one
10 ethylenically unsaturated monomer having at least one self-reactive site.

Non-limiting examples of ethylenically unsaturated monomers having two or more sites of reactive unsaturation suitable for use in the present invention include ethylene glycol di(meth)acrylate, allyl (meth)acrylate, diallyl phthalate, triallyl cyanurate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol
15 di(meth)acrylate, (meth)acrylic anhydride, tetraethylene glycol diacrylate, tripropylene glycol diacrylate and divinyl benzene. Ethylene glycol di(meth)acrylate is preferred.

Non-limiting examples of ethylenically unsaturated monomers having at least one self-reactive site (ii) include (meth)acrylamides, such as acrylamide
20 and methacrylamide, and N-alkoxymethyl(meth)acrylamides, such as those having 1 to 6, preferably 1 to 4 carbon atoms, in the alkoxy group, for example, N-ethoxy methyl (meth)acrylamide and N-butoxy methyl(meth)acrylamide, and isobutoxy (meth)acrylamide, and diacetone acrylamide. In a preferred embodiment of the invention, the ethylenically unsaturated monomer having at
25 least one self-reactive site is selected from the group consisting of N-butoxy (meth)acrylamide, isobutoxy (meth)acrylamide and mixtures thereof.

The amount of the above-described ethylenically unsaturated monomers having two or more sites of reactive unsaturation and/or the ethylenically unsaturated monomers having at least one self-reactive site typically used to
30 form the final stage polymerization reaction product (b) typically can range from 5 to 40 weight percent, preferably from 10 to 30 weight percent and more

preferably from 15 to 25 weight percent of the ethylenically unsaturated used to form the final stage reaction product (b).

The final stage polymerization reaction product (b) is "crosslinked" due to the presence of (i) and/or (ii) described immediately above. The final stage
5 reaction product (b) can be crosslinked through radical polymerization of the ethylenically unsaturated monomers having two or more sites of reactive unsaturation, and/or via the self-condensation reaction between the ethylenically unsaturated monomers having at least one self-reactive site.

In a preferred embodiment of the invention, to provide sites reactive with a
10 crosslinking agent, the final stage crosslinked polymerization reaction product (b) further comprises at least one functional group-containing ethylenically unsaturated monomer, exclusive of the above-mentioned acid functional ethylenically unsaturated monomers, preferably a hydroxyl functional group-containing monomer. Non-limiting examples of functional group-containing
15 monomers suitable for use in forming the final stage polymerization reaction product include the hydroxyl, beta-hydroxy ester and/or carbamate functional group-containing monomers described above.

When present, the amount of the functionally group-containing ethylenically unsaturated monomers used to form the final stage reaction product
20 (b) typically can range from 5 to 40 weight percent, preferably from 10 to 30 weight percent and more preferably from 15 to 25 weight percent of the monomers used to form the final-stage polymerization reaction product (b).

In yet another preferred embodiment of the present invention, the final
25 stage crosslinked polymerization reaction product (b) further comprises at least one polymerizable, ethylenically unsaturated monomer containing acid functional groups. Suitable examples of such ethylenically unsaturated acid functional group-containing monomers include those described above with reference to the first stage polymerization reaction product (a).

Typically, the amount of ethylenically unsaturated monomer containing
30 acid functional groups present in the final stage crosslinked polymerization reaction product (b) ranges from 2 to 40 weight percent, preferably from 5 to 30 weight percent, and more preferably from 7 to 20 weight percent, based on total

weight of the monomers used to form the final stage polymerization reaction product (b).

In a preferred embodiment of the invention, the final stage polymerization reaction product (b) further includes one or more of the ethylenically unsaturated monomers free of acid functional groups (exclusive of the above-described
5 ethylenically unsaturated monomers which contain two or more sites or reactive unsaturation and/or self reactive sites, and those which containing functional groups, such as hydroxyl groups) which are described above with reference to the first stage polymerization product (a).

10 When employed, the amount of the ethylenically unsaturated monomers free of acid functional groups used to form the final-stage reaction product (b) typically can range from 5 to 40 weight percent, preferably from 10 to 30 weight percent and more preferably from 15 to 25 weight percent of the monomers used to form the final-stage polymerization reaction product (b).

15 The final stage polymerization reaction product (b) typically is present in the aqueous dispersion of the present invention in an amount less than 55 weight percent, preferably less than 45 weight percent, and more preferably less than 40 weight percent, based on the weight of total resin solids in the dispersion. Also, the final stage polymerization reaction product (b) is typically
20 present in the aqueous dispersion of the present invention in an amount of at least 10 weight percent, preferably at least 15 weight percent and more preferably at least 25 weight percent, based on the weight of total resin solids in the dispersion. The amount of the final stage polymerization reaction product (b) present in the dispersion can range between any combination of these values
25 inclusive of the recited ranges.

It should be understood that for purposes of the aqueous dispersion of the present invention, the microparticles can further comprise one or more
intervening stage polymerization reaction products formed from any of the polymerizable ethylenically unsaturated monomers described above. That is,
30 the microparticles are formed in more than two stages and the one or more intervening stage reaction products are each separately formed by emulsion polymerization in the presence of the previously formed reaction product(s)

(which includes the first stage polymerization product (a)), followed by emulsion polymerization of the final stage polymerization reaction product (b).

The ratio of the first stage polymerization reaction product (a), the final stage polymerization reaction product (b) and any of the optional intervening stage reaction product(s) can be varied in accordance with the characteristics
5 desired for the final aqueous dispersion.

As mentioned above, the aqueous dispersion of the present invention comprises polymeric microparticles which are prepared in two or more stages by emulsion polymerization. As used herein, by "emulsion polymerization" is
10 meant the polymerization of one or more ethylenically unsaturated monomers in water in the presence of one or more radical polymerization initiators and one or more emulsifying agents (i.e., surfactants), which are discussed in more detail below.

The polymeric microparticles have a "core/shell" morphology. That is the
15 first stage uncrosslinked polymerization reaction product (a) is incorporated into the interior or "core" of the microparticle and the final stage crosslinked polymerization reaction product (b) is incorporated onto the exterior or "shell" of the microparticle. The one or more intervening stage reaction products, if employed, are incorporated into the microparticle between the core
20 polymerization reaction product (a) and the shell polymerization reaction product (b).

Generally, the aqueous dispersion of polymeric microparticles is prepared as follows. A first stage polymerization reaction product is formed by emulsion polymerization by adding to an admixture of water and an emulsifying agent, (i)
25 an ethylenically unsaturated monomer, or mixture of such monomers, comprising at least one acid functional group-containing monomer, and (ii) a radical polymerization initiator. The monomers are added to the reaction vessel over a two to three hour period under agitation as the reaction temperature is maintained at 70°C to 85°C. Agitation is continued at the reaction temperature
30 for an additional period of time to ensure complete reaction prior to formation of any intervening stage reaction product(s), if employed, and/or the final stage polymerization reaction product (b).

A final stage polymerization reaction product is then formed by emulsion polymerization by further adding under agitation, in the presence of (a), an admixture of an ethylenically unsaturated monomer, or mixture of such monomers, comprising at least one ethylenically unsaturated monomer having two or more sites of reactive unsaturation and/or at least one ethylenically unsaturated monomer having at least one self-reactive site, and one or more emulsifying agents; and an aqueous radical polymerization initiator. The resulting reaction mixture is maintained at a temperature of 70°C to 85°C for 0.5 to 1.0 hours to ensure complete reaction, at which time the reaction mixture is cooled to ambient temperature.

To form the aqueous dispersion of polymeric microparticles, the acid functional groups derived from the acid functional group-containing monomers used to prepare the polymeric microparticles are neutralized with a neutralizing agent as discussed below.

Any of a variety of nonionic, anionic, cationic and amphoteric surfactants, which are well known in the art, can be used as the emulsifying agent in the above-described emulsion polymerization process. Anionic emulsifying agents are preferred. Examples of suitable anionic emulsifying agents include fatty acid salts such as sodium stearate, sodium oleate and sodium laurate; alkarylsulfonic acid salts such as sodium dodecylbenzenesulfonate; alkyl sulfate ester salts such as sodium lauryl sulfate; alkyl sulfosuccinate ester salts such as sodium mono-octyl sulfosuccinate, sodium dioctyl sulfosuccinate and sodium polyoxyethylenelauryl sulfosuccinate; polyoxyalkylene alkyl ether sulfate ester salts such as sodium polyoxyethylene lauryl ether sulfate; and polyoxyalkylene alkyaryl ether sulfate ester salts such as sodium polyoxyalkylene nonylphenol ether sulfate.

Reactive anionic emulsifying agents can also be used to prepare the aqueous dispersions of the present invention. Suitable examples of such reactive anionic emulsifying agents include the sulfosuccinic acid salt-type and the alkenylsuccinic acid salt-type surfactants which are described in detail in U.S. Patent No. 5,356,956 at column 8, line 19 to column 9, line 31.

If desired, the above-described anionic emulsifying agents can be combined with a small amount of nonionic surfactant. Examples of nonionic surfactants suitable for use as an emulsifying agent in the aqueous dispersions of the present invention include polyoxyalkylene alkyl ethers, such as
5 polyoxyethylene lauryl ether and polyoxyethylene stearyl ether; polyoxyalkylene alkylphenol ethers, such as polyoxyethylene octylphenol ether and polyoxyethylene nonylphenol ether; sorbitan fatty acid esters such as sorbitan monolaurate, sorbitan monostearate and sorbitan trioleate; polyoxyalkylene sorbitan fatty acid esters, such as polyoxyethylene sorbitan monolaurate;
10 polyoxyalkylene fatty acid esters such as polyoxyethylene monolaurate and polyoxyethylene monostearate; glycerol fatty acid esters, such as oleic acid monoglyceride and stearic acid monoglyceride; and polyoxyethylene-polypropylene block copolymers.

The above-described emulsifying agents can be used alone or in
15 combination. The emulsifying agent is typically present in the aqueous dispersion of the present invention in an amount ranging from 0.1 to 10 percent by weight, preferably from 0.3 to 7 percent by weight, and more preferably from 0.5 to 5 percent by weight, based on total resin solids present in the dispersion.

As described above, the polymeric microparticles are prepared by
20 emulsion polymerization in the presence of radical polymerization initiator. Both water-soluble and water-insoluble initiators can be used. Any of the radical initiators commonly used in the art can be used. Non-limiting examples of suitable polymerization initiators include ammonium persulfate, potassium persulfate, sodium persulfate, t-butyl hydroperoxide, hydrogen peroxide, cumene
25 hydroperoxide, dibenzoyl peroxide, dilauroyl peroxide, bis(2-ethylhexyl) peroxydicarbonate, di-n-butyl peroxydicarbonate, 2,2'-azobisisobutyronitrile and 2,2'-azobis-2-methylbutyronitrile. Ammonium persulfate is preferred.

The amount of polymerization initiator used in the aqueous dispersions of the present invention can vary depending on the various monomers used to form
30 the polymerization reaction products and desired reaction conditions. Typically, however, the polymerization initiator is present in the aqueous dispersion of the present invention in an amount ranging from 0.05 to 1.5 weight percent,

preferably from 0.1 to 1.0 weight percent, and more preferably from 0.1 to 0.5 weight percent, based on total weight of resins solids present in the dispersion.

If desired, a reducing agent also can be used in the above-described emulsion polymerization process. Non-limiting examples of suitable reducing agents include organic reducing agents such as ascorbic acid, tartaric acid, citric acid and glucose, inorganic reducing agents such as sodium thiosulfate, sodium sulfite, sodium bisulfite, and sodium metabisulfite and water-soluble amines such as diethylene triamine, triethylene tetraamine, N,N' -diethyl ethanolamine.

Also, if desired, a chain transfer agent can be used in the above-described emulsion polymerization, for example, n-octyl mercaptan, dodecyl mercaptan, and 3-mercaptopropionic acid.

The polymeric microparticles are formed by emulsion polymerization, as described above, which typically is carried out at temperature ranging from 30°C to 100°C, preferably from 50°C to 90°C, and more preferably from 70°C to 85°C.

To facilitate a stable dispersion in aqueous media, the polymeric microparticles are contacted with a neutralizing agent to neutralize acid functional groups derived from the acid functional group-containing monomers used to prepare the microparticles. Typically, 40 percent to 100 percent of the acid groups are neutralized by the addition of 0.5 to 1.5, preferably 0.8 to 1.3 equivalents of neutralizing agent per equivalent of acid. Any neutralizing agent commonly known in the art of emulsion polymerization can be used for this purpose. Non-limiting examples of neutralizing agents suitable for use in the aqueous dispersions of the present invention include ammonia and amines such as N,N' -dimethyl ethanolamine, N,N' -diethyl ethanolamine, diisopropanolamine, triethyl amine, and morpholine. Mixtures of amines can be used.

Once the polymerization is complete, the resultant product is a stable dispersion of polymer microparticles in an aqueous medium, wherein the first stage polymerization reaction product (a), the final stage polymerization reaction product (b) and, if employed, any intervening stage polymerization reaction product(s) are contained within each microparticle. The aqueous medium, therefore, is substantially free of water-soluble polymer. The resultant polymeric microparticles are insoluble in the aqueous medium. As used herein,

"substantially free" means that the aqueous medium contains less than 30 percent by weight of dissolved polymer, preferably less than 15 percent.

By "stably dispersed" is meant that the polymer microparticles do not settle upon standing and do not coagulate or flocculate upon standing.

5 The aqueous medium provides the continuous phase of dispersion in which the microparticles are uniformly suspended or dispersed. The aqueous medium is almost exclusively water. However, for some polymer systems it may be desirable to include a minor amount of inert organic solvent, for example, to reduce viscosity of the polymer to be dispersed. For some applications, for
10 example where the aqueous dispersion of polymeric microparticles is used as a resinous binder component in coating compositions, it may be desirable to include a coalescing solvent during the emulsion polymerization process. Examples of organic solvents suitable for this purpose can include butyl acetate, methyl isobutyl ketone, ethylene glycol monohexyl ether and ethylene glycol monobutyl
15 ether.

 The aqueous dispersions of the present invention comprise polymeric microparticles which have a functionality adapted to react with a crosslinking agent. Thus, the dispersions are useful as the resinous binder component in curable compositions which comprise (I) the aqueous dispersion of polymeric
20 microparticles as described above, and (II) a crosslinking agent having functional groups reactive with the functionality of the microparticles.

 The aqueous dispersion of polymeric microparticles (I) typically is present in the curable composition of the present invention in an amount less than 85 weight percent, preferably less than 75 weight percent, and more preferably less
25 than 50 weight percent, based on the weight of total resin solids in the composition. Also, the aqueous dispersion of polymeric microparticles (I) is typically present in the curable composition of the present invention in an amount of at least 10 weight percent, preferably at least 15 weight percent and more preferably at least 20 weight percent, based on the weight of total resin solids in
30 the composition. The amount of the aqueous dispersion of polymeric microparticles (I) present in the curable composition can range between any combination of these values inclusive of the recited ranges.

As discussed above, the curable composition also comprises at least one crosslinking agent (II) having functional groups which are reactive with the functional groups of the polymeric microparticles. Preferred crosslinking agents are or have been adapted to be water dispersible or water-soluble.

5 Suitable hydrophobic crosslinking agents for crosslinking hydroxyl and/or carbamate functional group-containing materials include aminoplast resins. Aminoplast resins are based on the condensation products of formaldehyde, with an amino- or amido-group carrying substance. Condensation products obtained from the reaction of alcohols and formaldehyde with melamine, urea or
10 benzoguanamine are most common and preferred herein. However, condensation products of other amines and amides can also be employed, for example, aldehyde condensates of triazines, diazines, triazoles, guanadines, guanamines and alkyl- and aryl-substituted derivatives of such compounds, including alkyl- and aryl-substituted ureas and alkyl- and aryl-substituted
15 melamines. Some examples of such compounds are N,N'-dimethyl urea, benzourea, dicyandiamide, formaguanamine, acetoguanamine, glycoluril, ammeline, 2-chloro-4,6-diamino-1,3,5-triazine, 6-methyl-2,4-diamino-1,3,5-triazine, 3,5-diaminotriazole, triaminopyrimidine, 2-mercapto-4,6-diaminopyrimidine, 3,4,6-tris(ethylamino)-1,3,5 triazine, and the
20 like.

While the aldehyde employed is most often formaldehyde, other similar condensation products can be made from other aldehydes, such as acetaldehyde, crotonaldehyde, acrolein, benzaldehyde, furfural, glyoxal and the like.

The aminoplast resins preferably contain methylol or other alkylol groups,
25 and in most instances, at least a portion of these alkylol groups are etherified by a reaction with an alcohol to provide organic solvent-soluble resins. Any monohydric alcohol can be employed for this purpose, including such alcohols as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol and others, as well as, benzyl alcohol and other aromatic alcohols, cyclic alcohols such as
30 cyclohexanol, monoethers of glycols, and halogen-substituted or other substituted alcohols, such as 3-chloropropanol and butoxyethanol. Commonly employed aminoplast resins are substantially alkylated with methanol or butanol. Preferred

aminoplast resins for use as the hydrophobic crosslinking agent (3) in the thermosettable dispersion of the present invention include those which are fully alkylated with butanol, such as CYMEL 1156 and the partially methylated melamine resin, CYMEL 327, both of which are commercially available from Cytec Industries, Inc.

Other useful crosslinking agents include polyisocyanates which are useful for crosslinking hydroxyl and/or amine functional group-containing materials. Preferred polyisocyanates for use as the crosslinking agent (II) in the curable composition of the present invention are blocked diisocyanates. Examples of suitable diisocyanates which can be utilized herein include toluene diisocyanate, 4,4'-methylene-bis(cyclohexyl isocyanate), isophorone diisocyanate, an isomeric mixture of 2,2,4- and 2,4,4-trimethyl hexamethylene diisocyanate, 1,6-hexamethylene diisocyanate, tetramethyl xylylene diisocyanate and 4,4'-diphenylmethylenediisocyanate. In addition, blocked polyisocyanate prepolymers of various polyols, such as polyester polyols, can also be used. Examples of suitable blocking agents include those materials which would unblock at elevated temperatures including lower aliphatic alcohols, such as methanol, oximes, such as methyl ethyl ketoxime, and lactams, such as caprolactam.

Also known in the art for crosslinking hydroxyl functional group-containing materials are triazine compounds, such as the tricarbamoyl triazine compounds which are described in detail in U.S. Patent No. 5,084,541, incorporated herein by reference.

If desired, mixtures of the above crosslinking agents can be used.

The crosslinking agent or mixture of crosslinking agents used in the curable composition is dependent upon the functionality associated with the polymer microparticles, such as hydroxyl and/or carbamate functionality. Preferably, the functionality is hydroxyl and the crosslinking agent is a hydrophilic aminoplast or polyisocyanate.

As aforementioned, the crosslinking agents which are useful as a component in the topcoat film-forming composition of the invention must be hydrophilic, that is, they must be adapted to be water soluble or water dispersible. For example, aminoplast resins suitable for use as the hydrophilic

crosslinking agent can include those which contain methylol or similar alkylol groups, a portion of which have been etherified by reaction with a lower alcohol, preferably methanol, to provide a water soluble/dispersible aminoplast resin. Exemplary of the preferred aminoplast resins. An example of a hydrophilic
5 blocked isocyanate suitable for use as the hydrophilic crosslinking agent is dimethyl pyrazole blocked hexamethylene diisocyanate trimer commercially available as BI 7986 from Baxenden Chemicals, Ltd. in Lancashire, England.

Preferred crosslinking agents include aminoplast resins and/or blocked polyisocyanates.

10 The crosslinking agent is typically present in the film-forming composition in an amount ranging from 0 to at least 10 weight percent, preferably at least 10 to at least 20 weight percent, and more preferably from at least 20 to at least 30 weight percent based on total resin solids weight in the film-forming composition. The crosslinking agent also typically is present in the film-forming composition in
15 an amount ranging from less than 70 to less than 60 weight percent, preferably from less than 60 to less than 50 weight percent, and more preferably from less than 50 to less than 40 weight percent based on total resin solids weight of the film-forming composition. The crosslinking agent can be present in the film-forming composition in an amount ranging between any combination of these
20 values inclusive of the recited ranges.

The curable composition typically contains, in addition to the components described above, a variety of materials as are well known in the art. For example, other resinous materials can be utilized in conjunction with the dispersion of polymeric microparticles so long as the resultant coating composition is not
25 detrimentally affected in terms of application, physical performance and properties.

The curable compositions of the present invention can be useful as primers and pigmented base coats and/or clear coats in color-clear composite coatings. The compositions in the pigmented form can be applied directly to a
30 substrate to form a color coat. The color coat may be in the form of a primer for subsequent application of a top coat or may be a pigmented top coat (i.e., a monocoat). Alternately, the curable composition of the present invention can be

unpigmented, in the form of a clear coat for application over a color coat (either a primer or a color top coat).

In a preferred embodiment, the curable coating compositions of the present invention are particularly useful as an aqueous pigmented film-forming composition, i.e., a base coat, in a multi-component composite coating composition.

The multi-component composite coating compositions of the present invention comprise a base coat deposited from the aqueous pigmented film-forming composition and a film-forming composition which is substantially free of pigment. As aforementioned, the pigmented film-forming composition comprises the curable composition described above.

These multi-component composite coating compositions are particularly useful in automotive color-plus-clear applications. For this application, pigment is a principle component in the aqueous base coat film-forming composition.

Any of a variety of pigments well known in the coatings art can be used. In a preferred embodiment of the present invention, the aqueous film-forming composition comprises a reflective pigment to provide a multi-component composite coating having a "flip-flop" effect. Non-limiting examples of reflective pigments include metallic pigments such as aluminum flake pigments, for example, ALPATE MIRAGLOW 7670 NS-A, available from Toyo Aluminum Co., SPARKLE SILVER 5000 AR, available from Silberline, TOYO 8260 from Toyo Aluminum Co. and OBT 8767 STAPA M available from Obron.

Other metallic pigments suitable for use in pigmented film-forming compositions include bronze flakes, mica and coated mica, nickel flakes, tin flakes, silver flakes, copper flakes and combinations thereof. Besides the metallic pigments, the base coat compositions can contain non-metallic color pigments conventionally used in surface coatings including inorganic pigments such as titanium dioxide, iron oxide, chromium oxide, lead chromate, and carbon black, and organic pigments such as phthalocyanine blue and phthalocyanine green. The specific pigment to binder ratio can vary widely, so long as it provides the requisite hiding at the desired film thickness and application solids.

The pigmented film-forming composition preferably also contains a catalyst to accelerate the cure reaction, for example, between the aminoplast curing agent and the reactive hydroxyl and/or carbamate functional groups present in the polymeric microparticles of the dispersion. Examples of suitable catalysts include acidic materials, for example, acid phosphates, such as phenyl acid phosphate, and substituted or unsubstituted sulfonic acids, such as dodecylbenzene sulfonic acid or paratoluene sulfonic acid. The catalyst usually is present in an amount ranging from 0.1 to 5.0 percent by weight, preferably 0.5 to 1.5 percent by weight, based on the total weight of resin solids.

Other additive ingredients, for example, plasticizers, surfactants, thixotropic agents, anti-gassing agents, flow controllers, anti-oxidants, UV light absorbers and similar additives conventional in the art, can be included in the composition. These ingredients typically are present in an amount of up to 40 percent by weight based on the total weight of resin solids.

The above-described pigmented film-forming compositions are storage stable compositions which provide multi-component composite coating compositions suitable for automotive color-plus-clear applications. The reflective pigment-containing base coats exhibit excellent "flip-flop" effect and excellent humidity resistance and appearance properties.

The pigmented film-forming compositions from which the base coat is deposited can be applied to the substrate by any conventional coating technique such as brushing, spraying, dipping or flowing, but they are most often applied by spraying. The usual spray techniques and equipment for air spraying, airless spray and electrostatic spraying in either manual or automatic methods can be used.

During application of the base coat to the substrate, the film thickness of the base coat formed on the substrate is typically 0.1 to 5 mils (2.54 to 127 micrometers), preferably 0.1 to 2 mils (2.54 to 50.4 micrometers).

After forming a film of the base coat on the substrate, the base coat can be cured or alternately given a drying step in which solvent is driven out of the base coat film by heating or an air drying period before application of the substantially pigment-free film-forming composition from which the clear coat is

deposited. Preferably, the heating will only be for a short period of time, sufficient to ensure that the clear coat can be applied to the base coat without dissolving the base coat composition. Suitable drying conditions will depend on the ambient humidity, but preferably, a drying time of from 1 to 15 minutes at a
5 temperature of 75° to 200°F (21° to 93°C) will be adequate.

Also, more than one coat of the aqueous pigmented coating composition (the base coat) and multiple coats of substantially pigment-free coating composition (the clear coat) can be applied to develop optimum appearance. Usually between coats, the previously applied coat is "flashed"; that is, exposed
10 to ambient conditions for about 1 to 20 minutes.

The solids content of the pigmented film-forming composition generally ranges from 15 to 60 weight percent, and preferably 20 to 50 weight percent.

The curable compositions of the present invention also can be advantageously formulated as an aqueous film-forming composition which is
15 substantially free of pigment. These unpigmented film-forming compositions also are suitable for use in automotive multi-component composite coating compositions as the clear coating composition. It should be understood, that either or both the base coating composition and the clear coating composition can be based on the curable compositions of the invention.

20 The substantially unpigmented film-forming composition from which the clear coat is deposited can be any of the clear coating compositions known in the art. The clear coating composition can be solvent-based or water-based. Alternatively, the substantially unpigmented film-forming composition can be in solid particulate form, that is, a powder coating. Preferably, the clear coat is
25 deposited from a solvent-based film-forming composition. The unpigmented film-forming composition. may be applied to the base coated substrate by any of the conventional coating techniques described above, but spray applications are preferred because of superior gloss. Any of the known spraying techniques may be employed such as compressed air spraying, electrostatic spraying and either
30 manual or automatic methods.

The substantially pigment-free film-forming composition can be applied to a cured base coat or to a dried base coat before the base coat has been cured.

In the latter instance, the two coatings typically are then heated to thermally cure both coating layers simultaneously. In the curing operation, solvents and/or water are driven off and the film-forming materials of the clear coat and the base coat are each crosslinked. The heating or curing operation is usually carried out at a temperature in the range of from 160°F to 350 °F (71°C to 177 °C) but if needed, lower or higher temperatures may be used as necessary to activate crosslinking mechanisms. Alternatively, the two coatings can be cured at ambient conditions (that is, approximately 22°C to 28°C at 1 atmosphere pressure). The thickness of the clear coat usually ranges from 0.10 to 5 mils (12.7 to 127 microns), preferably 1.2 to 3 mils (30.5 to 76.2 microns).

In an alternative embodiment, after the base coat is applied (and cured, if desired), multiple layers of substantially unpigmented film-forming compositions can be applied over the base coat. This is generally referred to as a "clear-on-clear" application. Each of the clears can be the same as or different from the previously applied clear coat.

The multi-component composite coating compositions can be applied over virtually any substrate including wood, metals, glass, cloth, plastic, foam, including elastomeric substrates and the like. They are particularly useful in applications over metals and elastomeric substrates that are found on motor vehicles. The pigmented aqueous film-forming compositions of the present invention provide multi-component composite coating systems that have appearance and performance properties commensurate with those provided by solvent-based counterparts with appreciably less volatile organic emissions during application.

Illustrating the invention are the following examples which, however, are not to be considered as limiting the invention to their details. Unless otherwise indicated, all parts and percentages in the following examples, as well as throughout the specification, are by weight.

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EXAMPLES

Example A describes the preparation of an aqueous dispersion of the present invention prepared in three stages. That is, the dispersion is prepared

from a first-stage polymerization reaction product and a final-stage polymerization reaction product with an intervening polymerization reaction product. Example B describes the preparation of an aqueous dispersion of the present inventions prepared in two stages. Comparative Example C describes the preparation of a comparative aqueous dispersion wherein the Final Stage reaction product is not crosslinked and has T_g of -30°C .

Example AA describes the preparation of an aluminum pigment slurry which is employed in the following base coating compositions described in Examples 1-6. Examples 1 and 2 describe the preparation of base coating compositions of the present invention. Comparative Examples 3 and 4 describe the preparation of base coating compositions which contain commercially available aqueous dispersions; Comparative Example 5 contains no aqueous dispersion; and Comparative Example 6 contains the comparative aqueous dispersion of Comparative Example C.

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EXAMPLE A

The following example describes the preparation of an aqueous dispersion of the present invention. The aqueous dispersion was prepared in three stages from the following ingredients:

STAGE I	Weight (grams)
CHARGE 1:	
Deionized water	884.2
AOT-75 ¹	17.0
FEED A:	
Methyl methacrylate	441.6
Butyl acrylate	147.2
Methacrylic acid	11.9
Deionized water	423.3
AOT-75	13.6
FEED B:	
Deionized water	339.6
Ammonium persulfate	2.5
STAGE II	
FEED C:	
Methyl methacrylate	71.0
Butyl acrylate	35.0
Hydroxyethyl acrylate	6.9
AOT-75	2.4
Deionized water	75.2
FEED D:	
Deionized water	319.8
Ammonium persulfate	0.42
STAGE III	
FEED E:	
Methyl methacrylate	12.3
Butyl acrylate	30.8
Hydroxyethyl methacrylate	40.2
Methacrylic acid	22.7
Ethylene glycol dimethacrylate	34.5
AOT-75	2.4
Deionized water	97.5
FEED F:	
Deionized water	319.8
Ammonium persulfate	0.54
Sodium bicarbonate	1.3
FEED G:	
Dimethylethanolamine	10.9
Deionized water	176.0

¹ Aerosil OT-75, sodium dioctylsulfosuccinate, commercially available from Cytec Industries, Inc.

The aqueous dispersion was prepared as follows. Charge 1 was added to a suitably equipped reaction vessel and heated to a temperature of 80°C. The ingredients of STAGE I were simultaneously added as separate feeds A and B to the reaction vessel under agitation over a period of three hours and heated to a temperature of 80°C. The ingredients of STAGE II were added simultaneously as feeds C and D over a period of 30 minutes, then stirred for an additional 30 minutes at a temperature of 80°C. The ingredients of STAGE III were then added simultaneously under agitation as feeds E and F over a period of 30 minutes. The reaction mixture was stirred for one hour, then cooled to ambient temperature. Feed G was then added over a period of 5 minutes and stirred for 10 minutes.

The procedure generally described above was used in the preparation of the aqueous dispersions of the following examples:

EXAMPLE B

The following example describes the preparation of an aqueous dispersion of the present invention. The aqueous dispersion was prepared in two stages from the following ingredients:

STAGE I	Weight (grams)
CHARGE 1:	
Deionized water	546.2
AOT-75 ¹	10.5
FEED A:	
Styrene	136.4
Methyl methacrylate	136.4
Butyl acrylate	90.0
Methacrylic acid	7.34
AOT-75	8.4
Deionized water	261.5
FEED B:	
Deionized water	209.8
Ammonium persulfate	1.53
STAGE II	
FEED C:	
Styrene	7.0
Methyl methacrylate	7.0
Butyl acrylate	35.0
Hydroxyethyl methacrylate	45.6
Methacrylic acid	25.8
Ethyleneglycol dimethacrylate	39.2
AOT-75	2.72
Deionized water	110.7
FEED D:	
Deionized water	363.0
Ammonium persulfate	0.61
Sodium bicarbonate	1.48
FEED E:	
Dimethyl ethanolamine	10.4
Deionized water	142.8

COMPARATIVE EXAMPLE C

This example describes the preparation of a comparative aqueous dispersion prepared in two stages. Unlike the Stage II polymer in the aqueous dispersion of the present invention, the Stage II reaction product of aqueous dispersion of this comparative example is not crosslinked and has a T_g of -30°C .

STAGE I	Weight (grams)
Charge 1:	
Deionized water	479.2
Sodium bicarbonate	2.5
FEED A:	
Methyl methacrylate	134.8
Butyl acrylate	204.7
Acrylic acid	10.5
ALIPAL CO-436 ¹	8.33
TRITON-N 101 ²	5.0
Deionized water	150.0
FEED B:	
Deionized water	210.0
Ammonium persulfate	1.5
STAGE II	
FEED C:	
2-Ethylhexyl acrylate	120.0
Styrene	25.5
Acrylic acid	4.5
FEED D:	
Deionized water	100.0
Ammonium persulfate	0.5
FEED E:	
Deionized water	7.95
Dimethyl ethanolamine	7.95

¹ Anionic surfactant (60% in water), now commercially available from Rhodia as RHODAPEX CO-436.

² Nonionic surfactant (100% solids), now commercially available from Union Carbide as TREGITOL NP-9.

EXAMPLE AA

This example describes the preparation of an aluminum pigment slurry premix to which the above-described aqueous dispersions were subsequently added to form base coats of the present invention. The aluminum pigment slurry premix was prepared from a mixture of the following ingredients:

COMPONENT	Weight (grams)
Ethylene Glycol Monohexyl ether	46
Ethylene Glycol Monobutyl ether	15
Byk 031 ¹	2
Aluminum paste ²	42
Tinuvin 1130 ³	4
Phosphatized Epoxy ⁴	1
CYMEL® 327 ⁵	31
Aluminum Passivator ⁶	7
50% Aqueous DMEA	2

¹ Mineral oil defoamer available from Byk-Chemie.

² ALPATE MIRAGLOW 7670 NS-A, a non-chromated aluminum paste available from Toyo Aluminum.

³ Substituted benzotriazole UV light absorber available from Ciba Additives, Inc.

⁴ Phosphatized epoxy prepared from EPON® 828, a polyglycidyl ether of Bisphenol A, available from Shell Oil and Chemical Co., reacted with phosphoric acid at an 83:17 weight ratio.

⁵ Partially methylated melamine resin available from CYTEC Industries, Inc.

⁶ Prepared according to Example 6 of U.S. Patent No. 5,429,674.

The components were blended under agitation and the admixture was allowed to stir for 20 minutes until well dispersed.

The aluminum pigment slurry premix was then added under agitation to the aqueous dispersions described above in Examples A-C to produce the base coating compositions which follow.

COMPARATIVE EXAMPLE 5

This comparative base coating composition example was prepared as described above in Example 1 except that no aqueous dispersion of the present invention was incorporated into the composition.

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COMPARATIVE EXAMPLE 6

This comparative base coating composition example was prepared as described in Example 1 above except that the aqueous dispersion of Example A was replaced with the aqueous polyacrylate dispersion of Comparative Example C.

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PANEL PREPARATION AND EVALUATION:

The base coating compositions of Examples 1-10 were spray applied over 30 x 57 cm coil coated brass panels available from Herberts GmbH using a Herberts Spray Robot, available from Herberts GmbH, to produce a wedge of base coat varying from 0.1 to 1.0 mils (2.5 to 25 micrometers). The wedge was created using a two coat process with a 30 second ambient flash period between coats (60% relative humidity and 70°F (21.1°C)). After application of the second coat, the coated panels received a 5 minute ambient flash period and were then heat dried for 10 minutes at 80°C (176°F).

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A commercially available one-component acrylic/melamine clearcoat (available from DuPont as RKG-64102) was spray applied to the base coated panels to give a dry film thickness of approximately 1.5 mils (37.5 micrometers). The panels were allowed to flash at ambient conditions for 10 minutes and were then thermally cured at 140°C for 30 minutes.

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The test panels were evaluated for appearance properties at a base coat dry film thickness of 12 microns (0.5 mils). Test results are presented in Table 1 below.

TABLE 1

EXAMPLE	1	2	3**	4**	5**
Flip/Flop	1.58	1.56	1.58	1.24	1.28

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* Flip/Flop as measured using an Alcope LMR-200 Laser Multiple Reflectometer. Flip/Flop is a measure of the change in brightness as a function of viewing angle. The larger the number the greater the color change with angle. A higher Flip/Flop is more desirable for silver

metallic base coats. It should be noted that a variation in flip/flop values of 0.03 to 0.05 represents a significant difference in appearance.

** Comparative examples.

- 5 Storage stability properties of the base coating compositions of Example 1 and Comparative Example 3 were evaluated by measuring an initial viscosity (as measured by # 4 DIN Cup in presence of 4% octanol) and comparing with the viscosity of the same sample after hot room exposure (7 days @ 120°F (48.9°C)). Storage stability data is presented in the following Table 2.

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TABLE 2

BASE COATING COMPOSITION	INITIAL VISCOSITY	VISCOSITY (7 days @ 120°F)
Example 1	34.6 seconds	51.2 second
Comparative Example 3	35.8 seconds	> 120 second

- 15 The storage stability data presented above in Table 2 illustrate that the aqueous dispersion of the present invention (Example 1) provides a base coating composition having storage stability superior to that provided by the commercial aqueous polyacrylate dispersion, SETALUX 6802 (Comparative Example 3).

- 20 To compare the effect of T_g of the Final Stage reaction product (i.e., the shell polymer) of the respective aqueous dispersions employed in the base coating compositions, the base coating compositions of Example 1, Comparative Example 3 and Comparative Example 6 were evaluated for appearance properties (flip/flop). Test results are presented in the following Table 3.

TABLE 3

EXAMPLE	T_g (Final Stage)	Flip/Flop*
Example 1	53°	1.58
Example 3**	---	1.58
Example 6**	-30°C	1.50

- 25 * Flip/Flop as measured using an Alcope LMR-200 Laser Multiple Reflectometer. Flip/Flop is a measure of the change in brightness as a function of viewing angle. The larger the number the greater the color change with angle. It should be noted that a variation in flip/flop values of 0.03 to 0.05 represents a significant difference in appearance.

** Comparative examples.

The data presented above in Table 3 illustrate that an aqueous dispersion of microparticles with a Final Stage (i.e., "shell") polymer having a T_g of -30°C , has an undesirable effect on the appearance properties (as measured by "flip/flop") of the base coating composition into which it is incorporated. By contrast, the aqueous dispersion of the present invention (Example 1), having a Final Stage polymer with a T_g of 53°C , provides a base coating composition having flip/flop values equivalent to that of the commercial control (Example 3).

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications which are within the spirit and scope of the invention, as defined by the appended claims.

15

THEREFORE, WE CLAIM:

1. An aqueous dispersion comprising polymeric microparticles having a functionality adapted to react with a crosslinking agent, said microparticles being prepared in two or more stages by emulsion polymerization and comprising the following components:
 - (a) a first stage uncrosslinked polymerization reaction product formed from reactants comprising at least one acid functional group-containing polymerizable, ethylenically unsaturated monomer; and
 - (b) a final stage crosslinked polymerization reaction product having a glass transition temperature greater than 25°C and formed from reactants comprising:
 - (i) at least one polymerizable, ethylenically unsaturated monomer having two or more sites of reactive unsaturation, and/or
 - (ii) at least one ethylenically unsaturated monomer having at least one self-reactive site.
2. The aqueous dispersion of claim 1, wherein the acid functional group-containing polymerizable, ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.
3. The aqueous dispersion of claim 1, wherein the first stage uncrosslinked reaction product (a) is formed from reactants further comprising at least one polymerizable, ethylenically unsaturated monomer free of acid functional groups.
4. The aqueous dispersion of claim 3, wherein the ethylenically unsaturated monomer free of acid functional groups is selected from the group consisting of methyl (meth)acrylate, butyl (meth)acrylate and mixtures thereof.
5. The aqueous dispersion of claim 1, wherein the first stage uncrosslinked polymerization reaction product (a) is present in an amount

ranging from 45 to 90 weight percent based on the weight of total resin solids in the dispersion.

6. The aqueous dispersion of claim 1, wherein the final stage
5 crosslinked polymerization reaction product (b) is formed from reactants comprising at least one ethylenically unsaturated monomer having more than one site of unsaturation which is selected from the group consisting of ethylene glycol dimethacrylate, allyl methacrylate, triallyl cyanurate, hexanediol diacrylate, methacrylic anhydride, tetraethylene glycol diacrylate, tripropylene glycol
10 diacrylate, divinyl benzene and mixtures thereof.

7. The aqueous dispersion of claim 1, wherein the final stage
crosslinked polymerization reaction product (b) is formed from reactants comprising at least one ethylenically unsaturated monomer having at least one
15 self-reactive, said monomer selected from the group consisting of N-butoxy methacrylamide, isobutoxy methacrylamide and mixtures thereof.

8. The aqueous dispersion of claim 1, wherein the final stage
crosslinked polymerization reaction product (b) is formed from reactants further
20 comprising at least one hydroxyl group-containing polymerizable, ethylenically unsaturated monomer.

9. The aqueous dispersion of claim 8, wherein the hydroxyl group-
containing monomer is selected from the group consisting of hydroxyethyl
25 acrylate, hydroxyethyl methacrylate, hydroxyl propyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate and mixtures thereof.

10. The aqueous dispersion of claim 1, wherein the final stage
30 crosslinked polymerization reaction product (b) is formed from reactants comprising ethylene glycol dimethacrylate and hydroxyethyl methacrylate.

11. The aqueous dispersion of claim 1, wherein the final stage polymerization reaction product (b) is formed from reactants further comprising at least one polymerizable, ethylenically unsaturated monomer containing acid functional groups.

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12. The aqueous dispersion of claim 1, wherein the glass transition temperature of the final stage polymerization reaction product (b) ranges from 25°C to 80°C.

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13. The aqueous dispersion of claim 1, wherein the final stage crosslinked polymerization reaction product (b) is present in an amount ranging from 10 to 55 weight percent, based on the weight of total resin solids in the dispersion.

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14. The aqueous dispersion of claim 1, wherein said microparticles are prepared in three or more stages such that said microparticles further comprise one or more intervening-stage polymerization reaction products which are separately formed sequentially by emulsion polymerization in the presence of the first-stage polymerization reaction product (a) and followed by formation by emulsion polymerization of final-stage polymerization reaction product (b).

20

15. The aqueous dispersion of claim 1, wherein said microparticles comprise the following components:

25

(a) 45 to 90 weight percent based on weight of total resin solids in the dispersion of a first-stage uncrosslinked polymerization reaction product formed from reactants comprising:

(i) 0.5 to 7.0 weight percent based on total weight of monomer solids in (a) of at least one acid functional group-containing polymerizable, ethylenically unsaturated monomer; and

30

(ii) 93 to 99.5 weight percent based on total weight of monomer solids in (a) of at least one polymerizable, ethylenically unsaturated monomer free of acid functional groups; and

(b) 10 to 55 weight percent based on weight of total resin solids in the dispersion of a final-stage crosslinked polymerization reaction product having a glass transition temperature greater than 25°C and formed from reactants comprising:

5 (i) 5 to 40 weight percent based on total weight of monomer solids in (b) of at least one polymerizable, ethylenically unsaturated monomer having two or more sites of reactive unsaturation, and/or at least one ethylenically unsaturated monomer having at least one self-reactive site;

10 (ii) 5 to 40 weight percent based on total weight of monomer solids in (b) of at least one ethylenically unsaturated hydroxyl group-containing monomer

(iii) 2 to 40 weight percent based on total weight of monomer solids in (b) of at least one ethylenically unsaturated acid functional group-containing monomer.

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16. A curable composition comprising:

(I) an aqueous dispersion comprising polymeric microparticles having a functionality adapted to react with a crosslinking agent, said microparticles being prepared in two or more stages by emulsion polymerization and comprising the following components:

20 (a) a first stage uncrosslinked polymerization reaction product formed from reactants comprising at least one acid functional group-containing polymerizable, ethylenically unsaturated monomer; and

25 (b) a final stage crosslinked polymerization reaction product having a glass transition temperature greater than 25°C and formed from reactants comprising:

(i) at least one polymerizable, ethylenically unsaturated monomer having two or more sites of reactive unsaturation, and/or
30 (ii) at least one ethylenically unsaturated monomer having at least one self-reactive site; and

(II) at least one crosslinking agent having functional groups reactive with the functionality of said microparticles.

17. The curable composition of claim 16, wherein the acid functional group-containing polymerizable, ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

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18. The curable composition of claim 16, wherein the first stage uncrosslinked reaction product (a) is formed from reactants further comprising at least one polymerizable, ethylenically unsaturated monomer free of acid functional groups.

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19. The curable composition of claim 18, wherein the ethylenically unsaturated monomer free of acid functional groups is selected from the group consisting of methyl (meth)acrylate, butyl (meth)acrylate and mixtures thereof.

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20. The curable composition of claim 16, wherein the first stage uncrosslinked polymerization reaction product (a) is present in an amount ranging from 45 to 90 weight percent based on the weight of total resin solids in the dispersion.

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21. The curable composition of claim 16, wherein the final stage crosslinked polymerization reaction product (b) is formed from reactants comprising at least one ethylenically unsaturated monomer having more than one site of unsaturation which is selected from the group consisting of ethylene glycol dimethacrylate, allyl methacrylate, triallyl cyanurate, hexanediol diacrylate, methacrylic anhydride, tetraethylene glycol diacrylate, tripropylene glycol diacrylate, divinyl benzene and mixtures thereof.

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22. The curable composition of claim 16, wherein the final stage crosslinked polymerization reaction product (b) is formed from reactants comprising at least one ethylenically unsaturated monomer having at least one self-reactive, said monomer selected from the group consisting of N-butoxy methacrylamide, isobutoxy methacrylamide and mixtures thereof.

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23. The curable composition of claim 16, wherein the final stage crosslinked polymerization reaction product (b) is formed from reactants further comprising at least one hydroxyl group-containing polymerizable, ethylenically
5 unsaturated monomer.

24. The curable composition of claim 23, wherein the hydroxyl group-containing monomer is selected from the group consisting of hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxyl propyl acrylate, hydroxypropyl
10 methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate and mixtures thereof.

25. The curable composition of claim 16, wherein the final-stage crosslinked polymerization reaction product (b) is formed from reactants
15 comprising ethylene glycol dimethacrylate and hydroxyethyl methacrylate.

26. The curable composition of claim 16, wherein the final-stage polymerization reaction product (b) is formed from reactants further comprising at least one polymerizable, ethylenically unsaturated monomer containing acid
20 functional groups.

27. The curable composition of claim 16, wherein the glass transition temperature of the final stage polymerization reaction product (b) ranges from 25°C to 80°C.
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28. The curable composition of claim 16, wherein the final-stage crosslinked polymerization reaction product (b) is present in an amount ranging from 10 to 55 weight percent, based on the weight of total resin solids in the dispersion.
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29. The curable composition of claim 16, wherein said microparticles are prepared in three or more stages such that said microparticles further comprise one or more intervening-stage polymerization reaction products which

are separately formed sequentially by emulsion polymerization in the presence of the first-stage polymerization reaction product (a) and followed by formation by emulsion polymerization of final-stage polymerization reaction product (b).

5 30. The curable composition of claim 16, wherein said microparticles comprise the following components:

(a) 45 to 90 weight percent based on weight of total resin solids in the dispersion of a first-stage uncrosslinked polymerization reaction product formed from reactants comprising:

10 (i) 0.5 to 7.0 weight percent based on total weight of monomer solids in (a) of at least one acid functional group-containing polymerizable, ethylenically unsaturated monomer; and

(ii) 93 to 99.5 weight percent based on total weight of monomer solids in (a) of at least one polymerizable, ethylenically unsaturated monomer free of acid functional groups; and

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(b) 10 to 55 weight percent based on weight of total resin solids in the dispersion of a final-stage crosslinked polymerization reaction product having a glass transition temperature greater than 25°C and formed from reactants comprising:

20 (i) 5 to 40 weight percent based on total weight of monomer solids in (b) of at least one polymerizable, ethylenically unsaturated monomer having two or more sites of reactive unsaturation, and/or at least one ethylenically unsaturated monomer having at least one self-reactive site;

(ii) 5 to 40 weight percent based on total weight of monomer solids in (b) of at least one ethylenically unsaturated hydroxyl group-containing monomer; and

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(iii) 2 to 40 weight percent based on total weight of monomer solids in (b) of at least one ethylenically unsaturated acid functional group-containing monomer.

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31. The curable composition of claim 16, wherein the aqueous dispersion (I) is present in an amount ranging from 10 to 85 weight percent based on total weight of resin solids present in the composition.

5 32. The curable composition of claim 16, wherein the crosslinking agent (II) is selected from the group consisting of aminoplast resins, polyisocyanates, blocked isocyanates, triazine compounds and mixtures thereof.

10 33. The curable composition of claim 16, wherein the crosslinking agent (II) is present in an amount ranging from 10 to 70 weight percent based on total weight of resin solids in the composition.

15 34. The curable composition of claim 16, further comprising at least one pigment.

35. The curable composition of claim 1, wherein the composition is curable at ambient conditions.

20 36. The curable compositions of claim 1 wherein the composition is thermally curable.

25 37. A multi-component composite coating composition comprising a base coat deposited from an aqueous pigmented film-forming composition and a transparent top coat composition applied over the base coat deposited from a film-forming composition which is substantially free of pigment, said pigmented film-forming composition comprising the following components:

30 (I) an aqueous dispersion comprising polymeric microparticles having a functionality adapted to react with a crosslinking agent, said microparticles being prepared in two or more stages by emulsion polymerization and comprising the following components:

(a) a first stage uncrosslinked polymerization reaction product formed from reactants comprising at least one acid functional group-containing polymerizable, ethylenically unsaturated monomer; and

5 (b) a final stage crosslinked polymerization reaction product having a glass transition temperature greater than 25°C and formed from reactants comprising:

(i) at least one polymerizable, ethylenically unsaturated monomer having two or more sites of reactive unsaturation, and/or

10 (ii) at least one ethylenically unsaturated monomer having at least one self-reactive site; and

(II) at least one crosslinking agent having functional groups reactive with the functionality of said microparticles.

38. The multi-component composite coating composition of claim 37,
15 wherein the acid functional group-containing polymerizable, ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

39. The multi-component composite coating composition of claim 37,
20 wherein the first stage uncrosslinked reaction product (a) is formed from reactants further comprising at least one polymerizable, ethylenically unsaturated monomer free of acid functional groups.

40. The multi-component composite coating composition of claim 39,
25 wherein the ethylenically unsaturated monomer free of acid functional groups is selected from the group consisting of methyl (meth)acrylate, butyl (meth)acrylate and mixtures thereof.

41. The multi-component composite coating composition of claim 37,
30 wherein the first stage uncrosslinked polymerization reaction product (a) is present in the dispersion in an amount ranging from 45 to 90 weight percent based on the weight of total resin solids in the dispersion.

42. The multi-component composite coating composition of claim 37, wherein the final stage crosslinked polymerization reaction product (b) is formed from reactants comprising at least one ethylenically unsaturated monomer
5 having more than one site of unsaturation which is selected from the group consisting of ethylene glycol dimethacrylate, allyl methacrylate, triallyl cyanurate, hexanediol diacrylate, methacrylic anhydride, tetraethylene glycol diacrylate, tripropylene glycol diacrylate, divinyl benzene and mixtures thereof.

10 43. The multi-component composite coating composition of claim 37, wherein the final stage crosslinked polymerization reaction product (b) is formed from reactants comprising at least one ethylenically unsaturated monomer having at least one self-reactive, said monomer selected from the group consisting of N-butoxy methacrylamide, isobutoxy methacrylamide and mixtures
15 thereof.

44. The multi-component composite coating composition of claim 37, wherein the final stage crosslinked polymerization reaction product (b) is formed from reactants further comprising at least one hydroxyl group-containing
20 polymerizable, ethylenically unsaturated monomer.

45. The multi-component composite coating composition of claim 44, wherein the hydroxyl group-containing monomer is selected from the group consisting of hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxyl propyl
25 acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate and mixtures thereof.

46. The multi-component composite coating composition of claim 37, wherein the final-stage crosslinked polymerization reaction product (b) is formed
30 from reactants comprising ethylene glycol dimethacrylate and hydroxyethyl methacrylate.

47. The multi-component composite coating composition of claim 37, wherein the final-stage polymerization reaction product (b) is formed from reactants further comprising at least one polymerizable, ethylenically unsaturated monomer containing acid functional groups.

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48. The multi-component composite coating composition of claim 37, wherein the glass transition temperature of the final stage polymerization reaction product (b) ranges from 25°C to 80°C.

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49. The multi-component composite coating composition of claim 37, wherein the final-stage crosslinked polymerization reaction product (b) is present in the dispersion in an amount ranging from 10 to 55 weight percent, based on the weight of total resin solids in the dispersion.

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50. The multi-component composite coating composition of claim 37, wherein said microparticles are prepared in three or more stages such that said microparticles further comprise one or more intervening-stage polymerization reaction products which are separately formed sequentially by emulsion polymerization in the presence of the first-stage polymerization reaction product (a) and followed by formation by emulsion polymerization of final-stage polymerization reaction product (b).

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51. The multi-component composite coating composition of claim 37, wherein said microparticles comprise the following components:

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(a) 45 to 90 weight percent based on weight of total resin solids in the dispersion of a first-stage uncrosslinked polymerization reaction product formed from reactants comprising:

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(i) 0.5 to 7.0 weight percent based on total weight of monomer solids in (a) of at least one acid functional group-containing polymerizable, ethylenically unsaturated monomer; and

(ii) 93 to 99.5 weight percent based on total weight of monomer solids in (a) of at least one polymerizable, ethylenically unsaturated monomer free of acid functional groups; and

5 (b) 10 to 55 weight percent based on weight of total resin solids in the dispersion of a final-stage crosslinked polymerization reaction product having a glass transition temperature greater than 25°C and formed from reactants comprising:

10 (i) 5 to 40 weight percent based on total weight of monomer solids in (b) of at least one polymerizable, ethylenically unsaturated monomer having two or more sites of reactive unsaturation, and/or at least one ethylenically unsaturated monomer having at least one self-reactive site;

(ii) 5 to 40 weight percent based on total weight of monomer solids in (b) of at least one ethylenically unsaturated hydroxyl group-containing monomer; and

15 (iii) 2 to 40 weight percent based on total weight of monomer solids in (b) of at least one ethylenically unsaturated acid functional group-containing monomer.

20 52. The multi-component composite coating composition of claim 37, wherein the aqueous dispersion (I) is present in the pigmented film-forming composition in an amount ranging from 10 to 85 weight percent based on total weight of resin solids present in the pigmented film-forming composition.

25 53. The multi-component composite coating composition of claim 37, wherein the crosslinking agent (II) is selected from the group consisting of aminoplast resins, isocyanates, blocked isocyanates, triazine compounds and mixtures thereof.

30 54. The multi-component composite coating composition of claim 37, wherein the crosslinking agent (II) is present in the pigmented film-forming composition in an amount ranging from 10 to 70 weight percent based on total weight of resin solids in the pigmented film-forming composition.

55. The multi-component composite coating composition of claim 37, wherein the pigmented film-forming composition further comprises at least one reflective pigment.

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56. The multi-component composite coating composition of claim 37, wherein said composite coating composition is curable at ambient conditions.

57. The multi-component composite coating composition of claim 37, wherein said composite coating composition is thermally curable.

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58. A substrate coated with the curable composition of claim 16.

59. A substrate coated with the multi-component composite coating composition of claim 35.

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