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(54) Title: COATING COMPOSITIONS

(57) Abstract: The present invention relates to a composition, comprising A) a photo-curable component; B) a photo-initiator; and C) a polymer-containing coating, wherein the component A is physically mixed with component C, or is chemically bonded to the polymer of component C. The present invention further relates to a process for preparing the composition and a process for applying the composition, and the coating film obtained therefrom.

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Coating Compositions

FIELD OF THE INVENTION

The present invention relates to a coating composition, a preparation method for the same and a use of the same. In particular, the present invention relates to coating composition for interior and exterior application, especially for exterior application. Also the present invention relates to a preparation method for the same and a use of the same.

BACKGROUND OF THE INVENTION

Coating compositions are widely used for various substrates for such as decorating and /or protecting. In many applications, especially in exterior application, from the moment it is applied, a coating film is exposed to contamination from the atmosphere. This contamination is comprised of dirt and dust which are carried to the coating film surface by rain, airborne moisture droplets, wind currents or direct physical contact with people, animals or other objects. Also the microorganism on a coated wall may accelerate the accumulation of the dusts. It is desirable that the coating film remain clean and free of dirt, soil or other contaminants throughout the useful service life of the coating film. Therefore, it is desirable that the coating film formed from a coating composition will have excellent dirt pick-up resistance (DPUR), stain resistance, blocking resistance, etc.

On the other hand, generally a substrate on which a coating is applied may have defects, such as cracks and rough surfaces, which requires the coating film has bridging ability to cover those defects. In addition, new defects could be generated and/or the existing defects could further develop over the time as the substrate being aged, which may lead to cracks on the formed coating film if the flexibility of the coating is not sufficient. Therefore, it is desirable that the coating has excellent flexibility such that the coating film defects caused by the defects of the substrate or caused from being aged will be avoided.

In general, dirt pick-up resistance requires a hard coating on a substrate, while to avoid the coating film defects on a substrate, it is desirable that the coating film has excellent flexibility. They are usually a pair of contradicting properties.

WO 2010105938 A1 describes incorporation of surface modified silica particles into the coating to improve the hardness of the film, such that to obtain an improved DPUR. However the final coating doesn't have sufficient flexibility to bridge the cracks of the substrate.

CN1256295A describes a method to balance DPUR and flexibility by using dispersions of multi-staged emulsion polymers. It uses multi-staged emulsion polymerization to have both hard and soft polymer domains in the final film. However, CN1256295A obtains DPUR to certain extent at the cost of flexibility. The final coating film of CN1256295A has moderate DPUR and flexibility performance, neither of them is outstanding.

US 8993667 describes a redox polymerization to improve DPUR for elastomeric wall coatings.

In US 8993667, the glass transition temperature of the obtained polymer is low for obtaining good flexibility. In US 8993667, DPUR is still poor because the bulk polymer is too soft.

JP2007224084A discloses a photo-curable composition for coating film used for flooring of kitchen and passage. According to JP2007224084A, the photo-curable composition contains a photopolymerizable oligomer having two or more radically polymerizable double bonds, wherein the photopolymerizable oligomer (a) should contain specially selected photopolymerizable oligomer (a1) and photopolymerizable oligomer (a2) with defined ratio. Furthermore, the composition of JP2007224084A contains high level of volatile organic compounds, and needs additional UV-lamp to help curing. Due to high level of photo-initiator and bi-/multi-functional monomers dosage, the final film obtained from the composition of JP2007224084A is too rigid to provide sufficient flexibility.

Therefore, people are still searching for a coating film that has both good DPUR and good flexibility at the same time for various applications, while the preparation of the coating for the coating film is simple and cost-saving.

SUMMARY

An objective of this invention is to provide a composition, which will form a coating film having both good DPUR and good flexibility at the same time.

In one aspect, the invention relates to a composition comprising:

A. a photo-curable component;

B. a photo-initiator; and

C. a polymer-containing coating, not comprising component A;

wherein the component A is physically mixed with component C, or is chemically bonded to the polymer of component C to form a modified polymer having chemically bonded component A.

Another object of this invention is to provide a process for preparing the composition of the invention, comprising:

Step 1: forming a polymer-containing coating;

Step 2: incorporating a photo-curable component and a photo-initiator into the polymer-containing coating during step 1 or after the polymer-containing coating is formed,

wherein the photo-curable component is physically mixed with the polymer-containing coating, or is chemically bonded to the polymer of the polymer-containing coating.

In addition, the present invention relates to a process for applying the composition of the invention, comprising applying the composition of the invention to a substrate.

Also the present invention relates to a coating film formed from the composition of the invention.

The coating film formed from the composition of the invention has excellent dirt pick-up resistance (DPUR), stain resistance, blocking resistance, etc. At the same time, the coating film of the present invention has excellent flexibility.

DETAILED DESCRIPTION OF THE INVENTION

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

Expressions “a”, “an”, “the”, when used to define a term, include both the plural and singular forms of the term.

The term “polymer”, as used herein, includes both homopolymers, that is, polymers prepared from a single reactive compound, and copolymers, that is, polymers prepared by reaction of at least two polymer forming reactive, monomeric compounds.

In the first aspect of the invention, the present invention relates to a composition comprising:

A. a photo-curable component;

B. a photo-initiator; and

C. a polymer-containing coating not comprising component A.

In another aspect of the invention, the present invention relates to a composition comprising:

A. a photo-curable component;

B. a photo-initiator; and

C. a polymer-containing coating not comprising component A;

wherein the component A is physically mixed with component C, or is chemically bonded to the polymer of component C to form a modified polymer having chemically bonded component A.

The component A of the composition of the present invention is a photo-curable component. Said photo-curable component includes monomers, oligomers and/or polymers having two or more radically polymerizable double bonds. Any photo-curable material that can be used in a coating composition may be applicable in the composition of the present invention. For example, the component A may be photo-curable (meth)acrylates, photo-curable (poly)urethanes, photo-curable epoxide polymers and the like. Preferably, the component A of the inventive composition are monomers and/or oligomers of polyester acrylates, polyether acrylates, epoxy acrylates, polyurethane acrylates or mixtures thereof. More preferably, component A of the inventive composition can be selected from the group consisting of monomers and/or oligomers of polyurethane acrylates, Laromer® PE55WIN, Laromer® LR8765, Laromer® LR 8983, Laromer® LR 8889, Laromer® LR8949, and 1,4-butanediol diacrylate, all of them are available from BASF SE, Ludwigshafen, Germany. More preferably component A of the composition of the invention is Laromer® WA9057 or Laromer® LR8949.

Preferred components A of the composition of the present invention contain unsaturated double bonds with different polymerization reactivity. The component A comprises, monomers and/or oligomers and/or polymers of allyl ester, vinyl ester of (meth) acrylic acid, maleic acid, fumaric acid, itaconic acid; allyl, vinyl – vinyl ether or thioether; and the like. More preferably, component A comprises monomers and/or oligomers of allyl ester, vinyl ester of (meth) acrylic acid, maleic acid, fumaric acid, itaconic acid; allyl, vinyl – vinyl ether or thioether or mixtures thereof.

The amount of component A in the composition of the invention may be in the range of 0.01 to 9.9 wt%; preferably in the range of 0.05 to 8 wt%; more preferably in a range of 0.1 to 6 wt%; most preferable in a range of 0.5 to 5 wt%, based on the total weight of the solid components of the composition of the invention.

In a preferable embodiment wherein the component A is physically mixed with component C, the amount of component A in the composition of the invention may be in the range of 0.1 to 9.9 wt%; preferably in the range of 0.1 to 8 wt%; more preferably in a range of 0.1 to 6 wt%, such as in the range of 0.5 to 5 wt%, based on the total weight of the solid components of the composition of the invention.

In a preferable embodiment wherein the component A is chemically bonded to the polymer of component C, the amount of component A in the composition of the invention may be in the range of 0.01 to 9.9 wt%; preferably in the range of 0.05 to 8 wt%; more preferably in a range of 0.1 to 6 wt%, such as in the range of 0.5 to 5 wt%, based on the total weight of the solid components of the composition of the invention.

Any photo-initiator can be used as the component B of the composition for the purpose of the invention, provided that it can be used in a coating composition. For example, the photo-initiator can be selected without limitation from benzophenone or acetophenone or derivatives with benzophenone or acetophenone substructures, such as substituted benzophenones, for instance 4-methylbenzophenone, 2,4,6-trimethylbenzophenone, thioxanthones, such as isopropylthioxanthone, or olefinically unsaturated derivatives of benzophenone or of acetophenone, examples being those with a (meth)acrylic radical such as (meth)acryloxyethoxybenzophenone, or with a vinyl group such as 4-vinyloxybenzophenone, or mixtures of these active ingredients, such as 4-methylbenzophenone and 2,4,6-trimethylbenzophenone. Component B may either be added before, during or after the actual formulating of A and/or C.

Preferably, component B of the composition of the invention may be selected from the group consisting of Benzophenone, IRGACURE® 754, IRGACURE® 500 from BASF, and Esacure® TZM, Esacure® TZT from Lamberti SPA Company. More preferably, component B of the composition of the invention may be selected from the group consisting of Esacure® TZM, and IRGACURE® 500.

The amount of component B in the composition of the invention may be in the range of 0.01 to 5 wt%; preferably in the range of 0.01 to 1 wt%; more preferable in a range of 0.01 to 0.5 wt%;

most preferable in a range of 0.1 to 0.5 wt%, based on the total weight of the solid components of the composition of the invention.

The component A and component B of the composition of the present invention may be used in an appropriate ratio in a range of 1 to 990 by weight. Preferably, in the composition of the invention, the component A and component B may be used in a component A/component B ratio up to 200, more preferably up to 100. Preferably, in the composition of the invention, the component A and component B may be used in a component A/component B ratio equal to or more than 1.6, preferably equal to or more than 2, more preferably equal to or more than 5.

The component C of the composition of the invention may be any polymer-containing coating. The component C per se is a coating composition that can be used directly to a substrate to form a coating film. Preferably the component C is directly applicable for exterior application, such as for an exterior wall of a building. Any conventional polymer-containing coating composition in the art may be used as component C. The component C may be prepared by a skilled person according to a conventional procedure, or the component C may be commercially available. For example, the component C may be available from BASF under the trade name of Acronal® 290; Acronal® 7035; Acronal® 7079. In other embodiments of the invention, the component C may be obtained by the processes disclosed in US2014107249 or US2013079462 (each of these two documents is incorporated by reference in entirety).

The polymer of the component C of the composition of the invention may be any polymer applicable to be contained in a coating composition. For example, the polymer may be polyester, polyurethane, epoxy resin, poly(meth)acrylate, and the like. A skilled person will easily select an appropriate polymer of the component C, and will easily obtain it by common technology.

The glass transition temperatures (Tg) of the polymer of the component C is in the range of from -20°C to 60°C, preferred range of from -10 to 50°C; more preferred range of from -10 to 40°C, most preferred range of from 0 to 30°C.

The polymer of the component C has a Mw in the range of from 25,000 to 10,000,000 Dalton, preferred range of from 30,000 to 5,000,000 Dalton, more preferred range of from 100,000 to 2,000,000 Dalton, most preferred range of from 300,000 to 1,000,000 Dalton, and a Mn in the range of from 4,000 to 1,000,000 Dalton, preferred range of from 5,000 to 500,000 Dalton, more preferred range of from 10,000 to 200,000 Dalton, most preferred range of from 40,000 to 100,000 Dalton.

The component C constitutes the balance of the composition of the present invention. As in general, the component C may further contain additives. These additives may be pigment, such as TiO_2 CR828 from Kerr-McGee Corporation, Oklahoma, U.S.A; filler, such as $CaCO_3$ Omyacarb® 5 from Omya; film-forming aids, such as Texonal® from Eastman Chemical Company; thickener, such as Natrosol® 250HBR from Ashland; and antifreeze additive, such as propylene glycol from GuoYao Reagent Company; and the like. Any conventional additives for a coating composition may be contained in the component C. Generally, these additives are used in their conventional amount respectively.

In the second aspect of the invention, the present invention relates to a process for preparing the composition of the invention, comprising:

Step 1: forming a polymer-containing coating;

Step 2: incorporating a photo-curable component and a photo-initiator into the polymer-containing coating during step 1 or after the polymer-containing coating is formed,

wherein the photo-curable component is physically mixed with the polymer-containing coating, or is chemically bonded to the polymer of the polymer-containing coating.

The step 1 of the process for preparing the composition of the invention may be carried out under any conventional temperature and pressure conditions for forming a coating. A skilled person can select appropriate conditions for step 1. In one embodiment of this invention, the step 1 is achieved via free-radically initiated aqueous emulsion polymerization. This method has been widely described before now and is therefore sufficiently well known to the skilled person [cf., e.g., Encyclopedia of Polymer Science and Engineering, vol. 8, pages 659 to 677, John Wiley & Sons, Inc., 1987; D. C. Blackley, Emulsion Polymerisation, pages 155 to 465, Applied Science Publishers, Ltd., Essex, 1975; D. C. Blackley, Polymer Latices, 2nd Edition, vol. 1, pages 33 to 415, Chapman & Hall, 1997; H. Warson, The Applications of Synthetic Resin Emulsions, pages 49 to 244, Ernest Benn, Ltd., London, 1972; J. Piirma, Emulsion Polymerisation, pages 1 to 287, Academic Press, 1982; F. Hölscher, Dispersionen synthetischer Hochpolymerer, pages 1 to 160, Springer-Verlag, Berlin, 1969, and patent specification DE-A 40 03 422]. The free-radically initiated aqueous emulsion polymerization is typically accomplished by dispersing the ethylenically unsaturated monomers in the aqueous medium, generally using dispersing assistants, such as emulsifiers and/or protective colloids, and polymerizing them by means of at least one water-soluble free-radical polymerization initiator. Frequently, in the aqueous polymer dispersions obtained, the residual amounts of unreacted ethylenically unsaturated monomers are lowered by chemical and/or physical methods that are likewise known to the skilled person [see, for example, EP-A 771328, DE-A 19624299, DE-A 19621027, DE-A 19741184, DE-A 19741187, DE-A 19805122, DE-A 19828183, DE-A 19839199, DE-A 19840586 and 19847115], the polymer solids content is adjusted to a desired level by dilution or concentration, or other customary additives, such as bactericidal, foam-modifying or viscosity-modifying additives, are added to the aqueous polymer dispersion.

As for step 2 of the process, it may be carried out under any appropriate temperature and pressure. For convenience and cost-saving, the process for preparing the composition of the invention may be carried out at ambient temperature and ambient pressure, such as room temperature and normal pressure.

In the third aspect of the invention, the present invention relates to a process for applying the composition of the invention, comprising applying the composition of the invention to a substrate.

The composition of the invention may be applied by conventional application methods such as, for example, brush or roller, spray-coating such as air-atomized spray, air-assisted spray, airless spray, high volume low pressure spray, air-assisted airless spray, electrostatic spray, etc., spin coating, curtain-coating, and the like.

Any appropriate substrate may be used as a substrate for applying the composition of the invention, such as polymeric substrate, cement, concrete, ceramics, metals, woods, leather, and the like, provided that the coated substrate will be exposed to a light, such as sunlight.

After being applied to a substrate, the coating film formed from the composition of the invention may have any appropriate dry film thickness. Preferably, the dry film thickness of the coating film formed from the composition of the invention is up to 2000μm, preferably up to 1000μm, such as up to 500μm, more preferably up to 300μm, and especially up to 200μm, and no less than 10μm, preferably no less than 50μm, more preferably no less than 100μm.

More preferably, for an interior application, normally the dry film thickness of the coating film formed from the composition of the invention is in the range of 50μm to 500μm, more preferably in the range of 50μm to 300μm, such as in the range of 100μm to 300μm.

Preferably, for an exterior application, normally the dry film thickness of the coating film formed from the composition of the invention is in the range of 10μm to 2000μm, such as in the range of 30μm to 1000μm, more preferably in the range of 50μm to 1000μm, still preferably in the range of 50μm to 500μm such as in the range of 50μm to 300μm.

In some preferred embodiments of the invention for an exterior application, the substrate is wood and the dry film thickness of the coating film formed from the composition of the invention is in the range of 30μm to 200μm, more preferably in the range of 50μm to 150μm, still preferably in the range of 50μm to 100μm.

In the fourth aspect of the invention, the present invention relates to a coating film obtained from the composition of the invention.

To sum up, the present invention includes the following embodiments.

1. a composition, comprising

A. a photo-curable component;

B. a photo-initiator; and

C. a polymer-containing coating not comprising component A.

2. a composition, comprising

A. a photo-curable component;

B. a photo-initiator; and

C. a polymer-containing coating not comprising component A;

wherein the component A is physically mixed with component C.

3. a composition, comprising

A. a photo-curable component;

B. a photo-initiator; and

C. a polymer-containing coating not comprising component A;

wherein the component A is chemically bonded to the polymer of component C to form a modified polymer having chemically bonded component A.

4. the composition of any one of embodiments 1-3, wherein the amount of component A is in the range of 0.01 to 9.9 wt%; preferably in the range of 0.05 to 8 wt%; more preferable in a range of 0.1 to 6 wt%; most preferable in a range of 0.5 to 5 wt%, based on the total weight of the solid components of the composition of the invention.

5. the composition of any one of embodiments 1-3, the amount of component A in the composition of the invention may be in the range of 0.1 to 9.9 wt%; preferably in the range of 0.1 to 8 wt%; more preferably in a range of 0.1 to 6 wt%, such as in the range of 0.5 to 5 wt%, based on the total weight of the solid components of the composition of the invention.

6. the composition of any one of embodiments 1-3, wherein the Tg of the polymer of component C is in the range of from -20°C to 60°C, preferred range of from -10 to 50°C; more preferred range of from -10 to 40°C, most preferred range of from 0 to 30°C.

7. the composition of any one of embodiments 1-3, wherein the polymer of component C has a Mw in the range of from 25,000 to 10,000,000 Dalton, preferred range of from 30,000 to 5,000,000 Dalton, more preferred range of from 100,000 to 2,000,000 Dalton, most preferred range of from 300,000 to 1,000,000 Dalton, and a Mn in the range of from 4,000 to 1,000,000 Dalton, preferred range of from 5,000 to 500,000 Dalton, more preferred range of from 10,000 to 200,000 Dalton, most preferred range of from 40,000 to 100,000 Dalton, measured by gel permeation chromatography according to ISO 13885-1.

8. the composition of any one of embodiments 1-3, wherein the amount of component A in the composition of the invention may be in the range of 0.1 to 9.9 wt%; the Tg of the polymer of component C is in the range of -10 to 50°C, the polymer of component C has a Mw in the range of 30,000 to 5,000,000 Dalton, and a Mn in the range of from 5,000 to 500,000 Dalton measured by gel permeation chromatography according to ISO 13885-1.

9. the composition of any one of embodiments 1-3, wherein the amount of component A in the composition of the invention may be in the range of 0.1 to 9.9 wt%; the Tg of the polymer of component C is in the range of -10 to 40°C, the polymer of component C has a Mw in the range of 100,000 to 2,000,000 Dalton, and a Mn in the range of from 10,000 to 200,00 Dalton 0 measured by gel permeation chromatography according to ISO 13885-1.

10. the composition of any one of embodiments 1-9, wherein the amount of component B is in the range of 0.01 to 5 wt%; preferably in the range of 0.01 to 1 wt%; more preferable in a range of 0.01 to 0.5 wt%; most preferable in a range of 0.1 to 0.5 wt%, based on the total weight of the solid components of the composition of the invention.

11. the composition of any one of embodiments 1-10, wherein the ratio of component A and component B is in a range of 1 to 990 by weight, preferably the ratio of the component A and component B is up to 200, preferably up to 100, and the ratio of the component A and component B is no less than 1.6, preferably is no less than 2, more preferably is no less than 5.

12. the composition of any one of embodiments 1-11, wherein the component A is selected from the group consisting of monomers, oligomers and/or polymers of photo-curable (meth)acrylates, photo-curable (poly)urethanes, and photo-curable epoxides, allyl ester, vinyl ester of (meth) acrylic acid, maleic acid, fumaric acid, itaconic acid; allyl, vinyl – vinyl ether or thioether; and the like; preferably, the component A is selected from the group consisting of monomers, oligomers or polymers of polyester acrylates, polyether acrylates, epoxy acrylates, and 1,4-butanediol diacrylate; more preferably the component A is selected from the group consisting of monomers, oligomers or polymers of polyurethane acrylates and allyl (meth)acrylate .

13. the composition of any one of embodiments 1-12, wherein the component B is selected from benzophenone, acetophenone, derivatives with benzophenone or acetophenone substructures, such as substituted benzophenones, for instance 4-methylbenzophenone, 2,4,6-trimethylbenzophenone, thioxanthones, such as isopropylthioxanthone, olefinically unsaturated derivatives of benzophenone or of acetophenone, examples being those with a (meth)acrylic radical such as (meth)acryloxyethoxybenzophenone, or with a vinyl group such as 4-vinyloxybenzophenone, or mixtures of these active ingredients, such as 4-methylbenzophenone and 2,4,6-trimethylbenzophenone.

14. a process for preparing the composition of any one of embodiments 1-13, comprising:

Step 1: forming a polymer-containing coating;

Step 2: incorporating a photo-curable component and a photo-initiator into the polymer-containing coating during step 1 or after the polymer-containing coating is formed,

wherein the photo-curable component is physically mixed with the polymer-containing coating, or is chemically bonded to the polymer of the polymer-containing coating.

15. a process for applying the composition of any one of embodiments 1-13, comprising applying the composition of any one of embodiments 1-13 to a substrate.

16. a coating film obtained from the composition of any one of embodiments 1-13.

17. the coating film of embodiment 13, wherein the dry film thickness of the coating film is up to 1000μm, preferably up to 500μm, more preferably up to 300μm, and especially up to 200μm, and no less than 30μm, preferably no less than 50μm, more preferably no less than 30μm.

18. a coating film of embodiment 13, wherein for an interior application, the dry film thickness of the coating film is in the range of 50μm to 500μm, more preferably in the range of 50μm to 300μm, such as in the range of 100μm to 300μm.

19. a coating film of embodiment 13, wherein for an exterior application, the dry film thickness of the coating film is in the range of 30μm to 1000μm, more preferably in the range of 50μm to 1000μm, still preferably in the range of 50μm to 500μm such as in the range of 50μm to 300μm.

20. a coating film of embodiment 19, wherein for a wood substrate, the dry film thickness of the coating film is in the range of 30μm to 200μm, more preferably in the range of 50μm to 150μm, still preferably in the range of 50μm to 100μm.

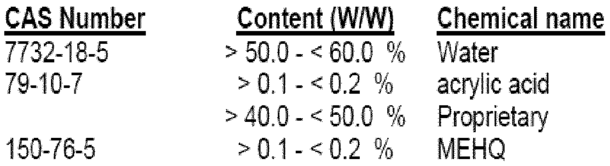
EXAMPLES

The present invention will be further illustrated hereinafter with the reference of the specific examples which are exemplary and explanatory only and are not restrictive.

Each part and percentage when used, if not defined otherwise, is provided on weight basis.

Materials that were used:

Trade name	**Description about the material**	**Supplier**
Esacure® TZM	benzophenone and 4-methylbenzophenone	From Lamberti SPA company
Laromer® LR 8765	2-Propenoic acid, 1,4-butanediylbis[oxy(2-hydroxy-3,1-propanediyl)] ester	from BASF
IRGACURE® 500	Benzophenone	from BASF
Esacure® TZT	mixture of 2,4,6-trimethylbenzophenone and 4-methylbenzophenone	From Lamberti SPA company
Texonal®	Propanoic acid, 2-methyl-, monoester with 2,2,4-trimethyl-1,3- pentanediol	Eastman
Natrosol® 250HBR	Hydroxyethylcellulose	Ashland
Laromer® WA9057	Sodium salt of modified acrylic copolymer	from BASF
IRGACURE® 754	2-(2-((oxo(phenyl)acetyl)oxy)ethoxy)ethyl oxo(phenyl)acetate;(2-(2-hydroxyethoxy)ethyl)	from BASF

	oxo(phenyl)acetate	
Laromer® LR 8983	Aqueous dispersion of a polymer based on: polyurethane, acrylic ester	from BASF
Laromer® LR 8949	Aqueous dispersion of a polymer based on: polyurethane, acrylic ester	from BASF
Laromer® PE55 WIN	 CAS Number / Content (W/W) / Chemical name 7732-18-5 / > 50.0 - < 60.0 % / Water 79-10-7 / > 0.1 - < 0.2 % / acrylic acid / > 40.0 - < 50.0 % / Proprietary 150-76-5 / > 0.1 - < 0.2 % / MEHQ	from BASF
Laromer® LR 8889	Polymer based on: polyetherpolyol, acrylic ester, modified	from BASF
Laromer® HDDA	Hexanediol diacrylate	from BASF

Example 1

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. Then the reactor containing the above charge was heated to 85°C for synthesis with stirring. Then 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed obtained by mixing 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 705 g of methyl methacrylate, 527 g of n-butyl acrylate, 23 g of methacrylic acid and 13g of Esacure® TZM, was fed into the reactor over 210 minutes. In parallel to the emulsion feed, an initiator feed of 95g of 7wt% sodium peroxosulfate aqueous solution was fed to the reactor over 240 min. After the addition of the initiator feed was finished, the obtained reaction mixture was cooled to 75°C. To the reaction mixture was then added 45 g of an 8% aqueous solution of sodium hydroxide within 5 min. After that 26 g of a 10% aqueous solution of tert-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min followed by adding 260g of Laromer® LR 8765. After the end of the feed the reaction mixture was cooled to room temperature. A latex was resulted. The glass transition temperature of the resulted polymer was 31°C. Molecular weight was measured by gel permeation chromatography according to ISO 13885-1. Mw was around 373,000 Dalton, Mn was around 86,000 Dalton.

Formulate 310g of the resulting latex with 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 45%.

In the resulting composition, the content of Laromer® LR 8765 is about 5.01%, and the content of Esacure® TZM is about 0.25%.

Comparative Example 1

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C for synthesis with stirring. Then 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed obtained by mixing 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 705 g of methyl methacrylate, 527 g of n-butyl acrylate, 23 g of methacrylic acid, was fed into the reactor over 210 minutes. In parallel to the emulsion feed, an initiator feed of 95g of 7wt% sodium peroxosulfate aqueous solution was fed to the reactor over 240 min. After the addition of the initiator feed was finished, the obtained reaction mixture was cooled to 75°C. To the reaction mixture was then added 45 g of a 8% aqueous solution of sodium hydroxide within 5 min. After that 26 g of a 10% aqueous solution of *tert*-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min then the reaction mixture was cooled to room temperature. A latex was resulted.

Formulate 310g of the resulting latex with 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the in the resulting composition is around 45%.

In the resulting composition, no photo-curable component and no photo-initiator were contained.

Example 2

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C for synthesis with stirring. Then 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed obtained by mixing 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 625 g of methyl methacrylate, 607 g of 2-ethylhexyl acrylate, 23 g of methacrylic acid and 13g of IRGACURE® 500, was fed into the reactor over 210 minutes. In parallel to the emulsion feed, an initiator feed of 95g of 7wt% sodium peroxosulfate aqueous solution was fed to the reactor over 240 min. After the addition of the initiator feed was finished, the obtained reaction mixture was cooled to 75°C. To the reaction mixture was then added 45 g of a 8% aqueous solution of sodium hydroxide within 5 min. After that 26 g of a 10% aqueous solution of *tert*-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min followed by adding 260g of Laromer® LR 8765. After the end of the feed the reaction mixture was cooled to room temperature. A latex was resulted. The glass transition temperature of the resulted polymer was 4°C. Molecular weight was measured by gel permeation chromatography according to ISO 13885-1. Mw was around 467,000 Dalton, Mn was around 91,000 Dalton.

Formulate 310g of the resulting latex with 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 45%.

In the resulting composition, the content of Laromer® LR 8765 is about 5.01%, and the content of IRGACURE® 500 is about 0.25%.

Comparative Example 2

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C for synthesis with stirring. Then 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed obtained by mixing 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 625 g of methyl methacrylate, 607 g of 2-ethylhexyl acrylate, 23 g of methacrylic acid, was fed into the reactor over 210 minutes. In parallel to the emulsion feed, an initiator feed of 95g of 7wt% sodium peroxosulfate aqueous solution was fed to the reactor over 240 min. After the addition of the initiator feed was finished, the obtained reaction mixture was cooled to 75°C. To the reaction mixture was then added 45 g of an 8% aqueous solution of sodium hydroxide within 5 min. After that 26 g of a 10% aqueous solution of *tert*-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min then the reaction mixture was cooled to room temperature. A latex was resulted.

Formulate 310g of the resulting latex with 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 45%.

In the resulting composition, no photo-curable component and no photo-initiator were contained.

Example 3

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 1000 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C for synthesis with stirring. Then 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed obtained by mixing 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 1000 g of allyl methacrylate, 25 g of n-dodecyl mercapten, was fed into the reactor over 180 minutes. In parallel to the emulsion feed, an initiator feed of 95g of 7wt% sodium peroxosulfate aqueous solution was fed to the reactor over 210 min. After the addition of the initiator feed was finished, the obtained reaction mixture was cooled to 75°C. To the reaction mixture 25 g of an 8% aqueous solution of sodium hydroxide was then added within 5 min. After that 26 g of a 10% aqueous solution of *tert*-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min. After the end of the feed the reaction mixture was cooled to room temperature. A latex was resulted for further use. The glass transition temperature of the polymer in the resulted latex was 19°C. Molecular weight was measured by gel permeation chromatography according to ISO 13885-1. Mw was around 98,000 Dalton, Mn was around 4,000 Dalton.

In this example, allyl methacrylate was chemically bonded to the polymers formed in the latex. FT-IR analysis showed that in the obtained latex, about 70 % by weight of allyl groups were remained, which is active photo-curable component.

Example 4

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C for synthesis with stirring. Then 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed obtained by mixing 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 594 g of methyl methacrylate, 577 g of 2-ethylhexyl acrylate, 23 g of methacrylic acid and 13g of IRGACURE® 500, was fed into the reactor over 210 minutes. In parallel to the emulsion feed, an initiator feed of 95g of 7wt% sodium peroxosulfate aqueous solution was fed to the reactor over 240 min. When the emulsion feed was fed for 190 minutes, 62g allyl methacrylate was fed into the rest of the emulsion feed and feeding was continued. After the end of the initiator feed the reaction mixture was cooled to 75°C. To the reaction mixture 45 g of an 8% aqueous solution of sodium hydroxide was then added within 5 min. After that 26 g of a 10% aqueous solution of *tert*-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min. After the end of the feed the reaction mixture was cooled to room temperature. A latex was resulted. The glass transition temperature of the resulted polymer was 11°C. Molecular weight was measured by gel permeation chromatography according to ISO 13885-1. Mw was around 1,453,000 Dalton, Mn was 108,000 Dalton.

Formulate the resulting latex same as described in Example 1.

In this example, allyl methacrylate was added during the preparation of the latex. FT-IR analysis showed that in the obtained latex, about 70 % by weight of allyl groups were remained, which is active photo-curable component. In the resulting composition, the content of allyl methacrylate is about 1.35%, and the content of IRGACURE® 500 is about 0.28%.

Comparative Example 3

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C for synthesis with stirring. Then 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed obtained by mixing 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 625 g of methyl methacrylate, 607 g of 2-ethylhexyl acrylate, 23 g of methacrylic acid and 13g of IRGACURE® 500, was fed into the reactor over 210 minutes. In parallel to the emulsion feed, an initiator feed of 95g of 7wt% sodium peroxosulfate aqueous solution was fed to the reactor over 240 min. After the addition of the initiator feed was finished, the obtained reaction mixture was cooled to 75°C. To the reaction mixture 45 g of an 8% aqueous solution of sodium hydroxide was then added within 5 min. After that 26 g of a 10% aqueous solution of *tert*-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min. After the end of the feed the reaction mixture was cooled to room temperature. A latex was resulted.

Formulate the resulting latex same as described in Example 1.

In the resulting composition, no photo-curable component was contained.

Example 5

Formulate 280g of a commercially available dispersion Acronal® 290, from BASF (Latex A) with 1.4g of Esacure® TZT, 29g of Laromer® WA9057, 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 45%. The glass transition temperature of the polymer in Latex A was 20°C. Molecular weight was measured by gel permeation chromatography according to ISO 13885-1. Mw was around 512,000 Dalton, Mn was around 77,000 Dalton.

In the resulting composition, the content of Laromer® WA9057 is about 5.30%, and the content of Esacure® TZT is about 0.26%.

Comparative Example 4

Formulate 309g of Latex A with 1.4g of Esacure® TZT, 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 45%.

In the resulting composition, no photo-curable component was contained.

Example 6

Formulate 303g of Latex A with 0.6g of IRGACURE® 754, 6.4g of Laromer® LR 8983, 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 45%.

In the resulting composition, the content of Laromer® LR 8983 is about 1.16%, and the content of IRGACURE® 754 is about 0.11%.

Comparative Example 5

Formulate 280g of Latex A with 29g of Laromer® WA9057, 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 45%.

In the resulting composition, no photo-initiator was contained.

Example 7

Formulate 280g of Latex A with 0.3g of Benzophenone, 29g of Laromer® LR 8949, 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 45%.

In the resulting composition, the content of Laromer® LR 8949 is about 5.15%, and the content of Benzophenone is about 0.05%.

Example 8

Formulate 284g of a commercially available dispersion Acronal® 7079, from BASF (Latex B) with 1g of Esacure® TZM, 25g of Laromer® PE55 WIN, 270g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 45%. The glass transition temperature of the polymer in Latex B was 10°C. Molecular weight was measured by gel permeation chromatography according to ISO 13885-1. Mw was around 917,000 Dalton, Mn was around 190,000 Dalton.

In the resulting composition, the content of Laromer® PE55 WIN is about 4.49%, and the content of Esacure® TZM is about 0.18%.

Example 9

Formulate 408g of Latex B with 1.3g of IRGACURE® 500, 35.7g of Laromer® LR 8889, 185g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 34%.

In the resulting composition, the content of Laromer® LR 8889 is about 6.15%, and the content of IRGACURE® 500 is about 0.22%.

Comparative Example 6

Formulate 445g of Latex B with 185g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 34%.

In the resulting composition, no photo-curable component and no photo-initiator were contained.

Example 10

Formulate 427g of Latex B with 1g of Esacure® TZT, 17g of Laromer® HDDA, 185g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 34%.

In the resulting composition, the content of Laromer® HDDA is about 2.98%, and the content of Esacure® TZT is about 0.18%.

Example 11

Formulate 400g of a commercially available dispersion Acronal® 7035, from BASF (Latex C) with 1g of IRGACURE® 754, 44g of Laromer® WA9057, 185g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 34%. The glass transition temperature of the polymer in Latex C was 23°C. Molecular weight was measured by gel permeation chromatography according to ISO 13885-1. Mw was around 394,000 Dalton, Mn was around 62,000 Dalton.

In the resulting composition, the content of Laromer® WA9057 is about 7.93%, and the content of IRGACURE® 754 is about0.18%.

Comparative Example 7

Formulate 445g of Latex C with 185g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 34%.

In the resulting composition, no photo-curable component and no photo-initiator were contained.

Example 12

Formulate 400g of Latex C with 1g of Benzophenone, 44g of resulting dispersion from Example 3, 185g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 35%.

In the resulting composition, the content of allyl methacrylate is about 2.89%, and the content of Benzophenone is about 0.18%.

Comparative Example 8

Formulate 444g of Latex C with 1g of Benzophenone, 185g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 34%.

In the resulting composition, no photo-curable component was contained.

Example 13

Formulate 408g of Latex A with 1.3g of Benzophenone, 36g of resulting dispersion from Example 3, 185g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 35%.

In the resulting composition, the content of allyl methacrylate is about 2.32%, and the content of Benzophenone is about 0.23%.

Comparative Example 9

Formulate 400g of Latex C with 45g of resulting dispersion from Example 3, 185g of demineralized water, 5g of dispersant DISPEX® AA4140 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company, to form a composition. The volume concentration of the total inorganic contents in the resulting composition is around 35%.

In the resulting composition, no photo-curable component was contained.

Comparatives Example 10

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C, and stirred over the complete time of synthesis. 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed, mixed by 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 705 g of methyl methacrylate, 527 g of n-butyl acrylate, 23 g of methacrylic acid and 13g of Esacure® TZM, was started and fed within 210 minutes. In parallel to the emulsion feed, 95g of 7wt% sodium peroxosulfate aqueous solution was started and fed to the reactor with 240 min. After the end of the initiator feed the reaction mixture was cooled to 75°C. To the reaction mixture was then added 45 g of a 8% aqueous solution of sodium hydroxide within 5 min. After that 26 g of a 10% aqueous solution of tert-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min followed by adding 870g of Laromer® 8765. After the end of the feed the reaction mixture was cooled to room temperature.

Formulate 310g of the resulting latex with 270g of demineralized water, 5g of dispersant N40 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company. The volume concentration of the total inorganic contents in the resulting composition of around 45%.

Comparatives Example 11

Formulate 408g of Latex B with 35g of IRGACURE® 500, 35.7g of Laromer® LR 8889, 185g of demineralized water, 5g of dispersant N40 from BASF, 1g of defoamer DC065 from Dow Corning, 196g of TiO_2 CR828 from Kerr-McGee, 139g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company. The volume concentration of the total inorganic contents in the resulting composition of around 34%.

Comparative Example 12

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C, and stirred over the complete time of synthesis. 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed, mixed by 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 998 g of methyl methacrylate, 304 g of n-butyl acrylate, 23 g of methacrylic acid and 13g of Esacure® TZM, was started and fed within 210 minutes. In parallel to the emulsion feed, 95g of 7wt% sodium peroxosulfate aqueous solution was started and fed to the reactor with 240 min. After the end of the initiator feed the reaction mixture was cooled to 75°C. To the reaction mixture was then added 45 g of a 8% aqueous solution of sodium hydroxide within 5 min. After that 26 g of a 10% aqueous solution of tert-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min followed by adding 260g of Laromer® 8765. After the end of the feed the reaction mixture was cooled to room temperature. Glass transition temperature of the obtained polymer is 59°C.

Formulate 310g of the resulting latex with 270g of demineralized water, 5g of dispersant N40 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company. The volume concentration of the total inorganic contents in the resulting composition of around 45%.

Comparatives Example 13

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C, and stirred over the complete time of synthesis. 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed, mixed by 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 247 g of methyl methacrylate, 1055 g of n-butyl acrylate, 23 g of methacrylic acid and 13g of Esacure® TZM, was started and fed within 210 minutes. In parallel to the emulsion feed, 95g of 7wt% sodium peroxosulfate aqueous solution was started and fed to the reactor with 240 min. After the end of the initiator feed the reaction mixture was cooled to 75°C. To the reaction mixture was then added 45 g of a 8% aqueous solution of sodium hydroxide within 5 min. After that 26 g of a 10% aqueous solution of tert-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min followed by adding 260g of Laromer® 8765. After the end of the feed the reaction mixture was cooled to room temperature. Glass transition temperature of the obtained polymer is -23°C.

Formulate 310g of the resulting latex with 270g of demineralized water, 5g of dispersant N40 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company. The volume concentration of the total inorganic contents in the resulting composition of around 45%.

Comparative Example 14

A 4L-reactor was inertized by passing nitrogen through for 10 min, then charged with 600 g of demineralized water, 25 g of a 33% seed latex of polystyrene with a particle size of 33 nm. The reactor containing the above charge was heated to 85°C, and stirred over the complete time of synthesis. 5 g of 7% sodium peroxosulfate aqueous solution was added at 85°C. After the addition, an emulsion feed, mixed by 450 g of demineralized water, 28 g of a sodium salt of a fatty alcohol polyglycol ether sulfate, 705g of methyl methacrylate, 527 g of n-butyl acrylate, 23 g of methacrylic acid, 52g of n-dodecyl mercaptan and 13g of Esacure® TZM, was started and fed within 210 minutes. In parallel to the emulsion feed, 95g of 7wt% sodium peroxosulfate aqueous solution was started and fed to the reactor with 240 min. After the end of the initiator feed the reaction mixture was cooled to 75°C. To the reaction mixture was then added 45 g of a 8% aqueous solution of sodium hydroxide within 5 min. After that 26 g of a 10% aqueous solution of tert-butyl hydroperoxide solution and 36 g of a 13 % solution of sodium sulfite were added within 60 min followed by adding 260g of Laromer® 8765. After the end of the feed the reaction mixture was cooled to room temperature. The molecular weight of the obtained polymer tested by gel permeation chromatography according to ISO 13885-1 is with Mw of 25421 Dalton and Mn of 4789 Dalton.

Formulate 310g of the resulting latex with 270g of demineralized water, 5g of dispersant N40 from BASF, 1g of defoamer DC065 from Dow Corning, 220g of TiO_2 CR828 from Kerr-McGee, 165g of $CaCO_3$ Omyacarb® 5 from Omya, 16g of Texonal® from Eastman, 3g of Natrosol® 250HBR from Ashland and 10g of propylene glycol from GuoYao Reagent Company. The volume concentration of the total inorganic contents in the resulting composition of around 45%.

Coating Film Preparation and Test Methods

All compositions samples from above examples and comparative examples are casted and cured into dry film according to the method described in SS500:2002, for mechanical test and outdoor exposure in BASF Advanced Chemicals Company, Shanghai Site. The mechanical test is in accordance with ASTM D412 using die C with the pulling rate of 50 mm/min.

For lab DPUR test, film preparation, ash specification and ash application are in accordance with JGT 172-2014, GB/T 9754, GB/T 9761 and GB/T 11186.2.

Tg is determined by Differential Scanning Calorimetrie (TA DSC Q100, Waters TA, -80 to 120°C, “midpoint temperature” of second heating curve, heating rate 10°C /min).

	Tensile Strength (MPa)	Elongation at Break (%)	Lab DPUR (ΔE)	3 Month Outdoor Exposure (ΔE)
Example 1	7.02	124	4.21	5.93
Example 2	3.52	412	6.63	9.12
Example 4	2.88	294	6.12	7.68
Example 5	6.67	157	6.21	8.31
Example 6	6.99	89	7.34	9.78
Example 7	6.14	212	6.79	7.65
Example 8	5.87	198	5.82	9.07
Example 9	4.64	234	6.36	8.11
Example 10	3.89	432	5.98	7.22
Example 11	5.09	206	4.60	6.78
Example 12	5.78	164	6.76	9.17
Example 13	5.59	98	6.04	7.96
Comparative Example 1	10.84	16	6.04	7.96
Comparative Example 2	2.24	456	13.61	14.11
Comparative Example 3	2.33	288	11.78	15.39
Comparative Example 4	7.17	66	9.12	12.27
Comparative Example 5	6.38	165	9.88	13.33
Comparative Example 6	4.78	145	8.84	12.88
Comparative Example 7	5.65	118	8.23	11.02
Comparative Example 8	5.39	102	7.98	9.97
Comparative Example 9	5.51	211	8.87	12.33
Comparative Example 10	7.61	43	4.35	5.67
Comparative Example 11	5.71	62	7.11	7.86
Comparative Example 12	12.14	7	3.12	4.22
Comparative Example 13	1.16	517	14.32	19.88
Comparative Example 14	2.12	177	13.36	17.12

According to the data shown in the table, the Elongation at Break values obtained by the inventive examples are around 100% or higher, which means a sufficient flexibility of the coating film obtained from the inventive composition.

As for the Lab DPUR, the highest Lab DPUR ΔE value obtained by the inventive examples is 7.34 (example 6), which is still lower than comparative examples 2-9. The lower value of the Lab DPUR ΔE value means the better the dirt pick-up resistance.

As for the 3 Month Outdoor Exposure, the highest value obtained by the inventive examples is 9.78 (example 6), which is still lower than comparative examples 2-9. The lower the ΔE value of the 3 Month Outdoor Exposure, the better the dirt pick-up resistance is.

Comparative example 1, though it obtains the low DPUR value of 6.04, the obtained film of comparative example 1 has Elongation at Break of 16%, which is too low to be applicable.

According to the data provided in the table, it can be seen that the coating films obtained from the composition of the invention achieve both excellent flexibility and dirt pick-up resistance.

Each of the documents referred to above is incorporated herein by reference.

Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, and the like, are to be understood as modified by the word “about”.

It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

The present invention is not to be limited in scope by the specific embodiments and examples described herein. Indeed, various modifications of the invention in addition to those described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are intended to fall within the scope of the appended claims.

CLAIMS

1. a composition, comprising

A. a photo-curable component;

B. a photo-initiator; and

C. a polymer-containing coating not comprising component A.

2. a composition, comprising

A. a photo-curable component;

B. a photo-initiator; and

C. a polymer-containing coating not comprising component A;

wherein the component A is physically mixed with component C.

3. a composition, comprising

A. a photo-curable component;

B. a photo-initiator; and

C. a polymer-containing coating not comprising component A;

wherein the component A is chemically bonded to the polymer of component C to form a modified polymer having chemically bonded component A.

4. the composition of any one of claims 1-3, wherein the amount of component A is in the range of 0.01 to 9.9 wt%; preferably in the range of 0.05 to 8 wt%; more preferable in a range of 0.1 to 6 wt%; most preferable in a range of 0.5 to 5 wt%, based on the total weight of the solid components of the composition of the invention.

5. the composition of any one of claims 1-3, the amount of component A in the composition of the invention may be in the range of 0.1 to 9.9 wt%; preferably in the range of 0.1 to 8 wt%; more preferably in a range of 0.1 to 6 wt%, such as in the range of 0.5 to 5 wt%, based on the total weight of the solid components of the composition of the invention.

6. the composition of any one of claims 1-3, the Tg of the polymer of component C is in the range of from -20°C to 60°C, preferred range of from -10 to 50°C; more preferred range of from -10 to 40°C, most preferred range of from 0 to 30°C.

7. the composition of any one of claims 1-3, the polymer of component C has a Mw in the range of from 25,000 to 10,000,000 Dalton, preferred range of from 30,000 to 5,000,000 Dalton, more preferred range of from 100,000 to 2,000,000 Dalton, most preferred range of from 300,000 to 1,000,000 Dalton, and a Mn in the range of from 4,000 to 1,000,000 Dalton, preferred range of from 5,000 to 500,000 Dalton, more preferred range of from 10,000 to 200,000 Dalton, most

preferred range of from 40,000 to 100,000 Dalton, measured by gel permeation chromatography according to ISO 13885-1.

8. the composition of any one of claims 1-3, wherein the amount of component A in the composition of the invention may be in the range of 0.1 to 9.9 wt%; the Tg of the polymer of component C is in the range of -10 to 50°C, the polymer of component C has a Mw in the range of 30,000 to 5,000,000 Dalton, and a Mn in the range of from 5,000 to 500,000 Dalton measured by gel permeation chromatography according to ISO 13885-1.

9. the composition of any one of claims 1-3, wherein the amount of component A in the composition of the invention may be in the range of 0.1 to 9.9 wt%; the Tg of the polymer of component C is in the range of -10 to 40°C, the polymer of component C has a Mw in the range of 100,000 to 2,000,000 Dalton, and a Mn in the range of from 10,000 to 200,000 Dalton measured by gel permeation chromatography according to ISO 13885-1.

10. the composition of any one of claims 1-9, wherein the amount of component B is in the range of 0.01 to 5 wt%; preferably in the range of 0.01 to 1 wt%; more preferable in a range of 0.01 to 0.5 wt%; most preferable in a range of 0.1 to 0.5 wt%, based on the total weight of the solid components of the composition of the invention.

11. the composition of any one of claims 1-10, wherein the ratio of component A and component B is in a range of 1 to 990 by weight, preferably the ratio of the component A and component B is up to 200, preferably up to 100, and the ratio of the component A and component B is no less than 1.6, preferably is no less than 2, more preferably is no less than 5.

12. the composition of any one of claims 1-11, wherein the component A is selected from the group consisting of monomers, oligomers and/or polymers of photo-curable (meth)acrylates, photo-curable (poly)urethanes, and photo-curable epoxides, allyl ester, vinyl ester of (meth) acrylic acid, maleic acid, fumaric acid, itaconic acid; allyl, vinyl – vinyl ether or thioether; and the like; preferably, the component A is selected from the group consisting of monomers, oligomers or polymers of polyester acrylates, polyether acrylates, epoxy acrylates, polyurethane acrylates and 1,4-butanediol diacrylate; more preferably the component A is selected from the group consisting of monomers, oligomers or polymers of polyurethane acrylate and allyl (meth)acrylate.

13. the composition of any one of claims 1-12, wherein the component B is selected from benzophenone, acetophenone, derivatives with benzophenone or acetophenone substructures, such as substituted benzophenones, for instance 4-methylbenzophenone, 2,4,6-trimethylbenzophenone, thioxanthones, such as isopropylthioxanthone, olefinically unsaturated derivatives of benzophenone or of acetophenone, examples being those with a (meth)acrylic radical such as (meth)acryloxyethoxybenzophenone, or with a vinyl group such as 4-vinyloxybenzophenone, or mixtures of these active ingredients, such as 4-methylbenzophenone and 2,4,6-trimethylbenzophenone.

14. a process for preparing the composition of any one of claims 1-13, comprising:

Step 1: forming a polymer-containing coating;

Step 2: incorporating a photo-curable component and a photo-initiator into the polymer-containing coating during step 1 or after the polymer-containing coating is formed,

wherein the photo-curable component is physically mixed with the polymer-containing coating, or is chemically bonded to the polymer of the polymer-containing coating.

15. a process for applying the composition of any one of claims 1-13, comprising applying the composition of any one of claims 1-13 to a substrate.

16. a coating film obtained from the composition of any one of claims 1-13.

17. the coating film of claim 16, wherein the dry film thickness of the coating film is up to 1000μm, preferably up to 500μm, more preferably up to 300μm, and especially up to 200μm, and no less than 30μm, preferably no less than 50μm, more preferably no less than 30μm.

18. a coating film of claim 16, wherein for an interior application, the dry film thickness of the coating film is in the range of 50μm to 500μm, more preferably in the range of 50μm to 300μm, such as in the range of 100μm to 300μm.

19. a coating film of claim 16, wherein for an exterior application, the dry film thickness of the coating film is in the range of 30μm to 1000μm, more preferably in the range of 50μm to 1000μm, still preferably in the range of 50μm to 500μm such as in the range of 50μm to 300μm.

20. a coating film of claim 19, wherein for a wood substrate, the dry film thickness of the coating film is in the range of 30μm to 200μm, more preferably in the range of 50μm to 150μm, still preferably in the range of 50μm to 100μm.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/067876

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D133/12 C09D4/06
ADD. C08F220/14

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)
C09D C08F

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

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X	EP 1 008 635 A1 (ROHM & HAAS [US]) 14 June 2000 (2000-06-14) examples 19,20 claim 1 paragraph [0027] -----	1,3-6, 10-17,19
X	WO 2012/160891 A1 (KANSAI PAINT CO LTD [JP]; INADA YUICHI [JP]; KONDOH MITSURU [JP]; ISHI) 29 November 2012 (2012-11-29) tables 1,2 paragraphs [0071], [0169] ----- -/--	1,2,6, 8-17,19, 20

☒ 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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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