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- (71) Applicant (for all designated States except US): **KROHN INDUSTRIES, INC.** [US/US]; 3540 Orvall Drive, Fort Gratiot, MI 48059 (US).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): **KROHN, Roy, C.** [US/US]; 3540 Orvall Drive, Fort Gratiot, MI 48059 (US).
- (74) Agents: **PROSCIA, James, W.** et al.; Brooks & Kushman, 1000 Town Center, Twenty-Second Floor, Southfield, MI 48075 (US).
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(54) Title: UV CURABLE COMPOSITIONS FOR PRODUCING MULTILAYER PAINT COATINGS

(57) Abstract: The present invention discloses ultraviolet light curable paint compositions to be used in a multilayer paint coating and method for applying such a compositions to a substrate. Suitable substrates include glass, metals, and various plastics such as polycarbonates. The disclosed compositions do not contain any significant amount of volatile organic solvents that do not become incorporated in the coating or released to ambient after curing.

UV CURABLE COMPOSITIONS FOR PRODUCING MULTILAYER PAINT COATINGS

TECHNICAL FIELD

5 The present invention relates to ultraviolet light (UV) curable compositions capable of producing a multilayer paint coating.

BACKGROUND OF THE INVENTION

10 UV curable multilayer paint coatings are applied to a substrate through spraying, screen printing, dipping or brushing for the protection and decoration of the substrate. In the usual application, a substrate, such as metal, glass or plastic is successively coated to form at least three distinct layers, commonly referred to as the primer, base and top coat layers. As each layer is applied to the substrate, ultraviolet light is introduced to cure the layer. Multilayer paint coatings using UV curing processes offer many advantages over typical heat curable compositions.

15 Heat curable compositions require the use of organic solvents that contain a significant amount of volatile organic compounds (VOCs). These VOCs escape into the atmosphere while the heat curable composition dries. Such solvent based systems are undesirable because of the hazards and expense associated with VOCs. The hazards include water and air pollution and the expenses include the cost of complying with strict government regulation on solvent emission levels. In contrast, UV curable compositions contain reactive monomers instead of solvents; thus eliminating the detrimental effects of the VOCs.

20

25 Additionally, the process of heat curing typically results in coatings which suffer from poor physical properties. In the typical heat curing process, the base coat must be inordinately thick in order to hide the primer coat. Additionally, the thick base coat must be dried for a significant time to eliminate intermixing between the base coat and top coat. Due to the thickness and significant drying time

of the base coat, the resulting multilayer coating suffers from low resistance to chipping and a lack of surface smoothness.

Although UV curable compositions exhibit superior properties and performance over their heat curable counterparts, UV curable compositions themselves suffer from certain disadvantages. Generally, UV curable compositions have high molecular weights and a substantial degree of cross linkage due to the highly reactive nature of the composition. As a result, many of these compositions suffer from low durability and resin shrinkage. With the use of many such compositions, an inordinately high amount of UV light is required to cure. New formulations that lessen these problems typically suffer from diminished abrasion, chemical, and scratch resistance as well as low thermal stability and adhesion.

Accordingly, there exists a need to provide environmentally safe UV curable multilayer coating paint compositions which exhibit improved appearance, weatherability, corrosion resistance and workability. Additionally, there is a need to provide a method of applying an improved composition which furthers the goal of improved performance.

SUMMARY OF INVENTION

It is an object of the present invention to provide an improved composition that upon curing by ultraviolet light produces an improved topcoat paint coating.

It is another object of the present invention to provide an improved composition that upon curing by ultraviolet light produce an improved basecoat paint coating.

It is another object of the present invention to provide an improved composition that upon curing by ultraviolet light produce an improved primer paint coating.

It is another object of the present invention to provide an improved topcoat paint composition that can be applied by spraying, screen printing, dipping, and brushing.

5 It is another object of the present invention to provide an improved basecoat paint composition that can be applied by spraying, screen printing, dipping, and brushing.

It is another object of the present invention to provide an improved primer paint composition that can be applied by spraying, screen printing, dipping, and brushing.

10 The present invention discloses ultraviolet light curable paint compositions and methods for making such compositions that may be used to produce each layer of a multilayer paint coating. The disclosed compositions do not contain any significant amount of volatile organic solvents that do not become incorporated in the layers after curing. Specifically, the paint compositions contains
15 5% or less volatile organic solvents by weight.

In accordance with one aspect of the invention, ultraviolet light curable paint compositions is provided. The topcoat paint composition comprises a mixture of one or more aliphatic acrylated oligomers, wherein the aliphatic acrylated oligomer mixture is present in an amount of about 20% to 30% of the topcoat
20 composition. All percentages of each paint layer composition as expressed in this document refer to the weight percentage of the stated component to the total weight of the paint composition in its fluid state at standard temperature and pressure.

The topcoat composition preferably further comprises an acrylated epoxy oligomer in an amount of about 8% to 16%, an isobornyl acrylate monomer
25 in an amount of about 40% to 60% of the topcoat composition, a photoinitiator in an amount of about 2% to 8% of the topcoat composition, a flow promoting agent in an amount of 0% to 6%, a UV absorber (UVA) in an amount of 1% to 3%, and a Hindered Amine Light Stabilizer (HAL) in an amount of 0.5% to 3.0%.

In accordance with another aspect of the invention, ultraviolet light curable basecoat paint compositions is provided. The basecoat paint composition comprises an aliphatic acrylated oligomer, wherein the aliphatic acrylated oligomer is present in an amount of about 3% to 25% of the basecoat paint composition. The
5 basecoat composition preferably further comprises an acrylated epoxy oligomer in an amount of about 1% to 6%, an isobornyl acrylate monomer in an amount of about 10% to 70% of the basecoat composition, a photoinitiator in an amount of about 2% to 8% of the basecoat composition, a polyacrylic oligomer/acrylate monomer blend in an amount of 3% to 25%, a flow promoting agent in an amount of 0% to 6%, an
10 adhesion promoter in an amount of 1% to 7%, and pigments in an amount of 7% to 30% of the basecoat composition.

In accordance with another aspect of the invention, ultraviolet light curable primer compositions is provided. The primer paint composition comprises an aliphatic acrylated oligomer, wherein the aliphatic acrylated oligomer is present
15 in an amount of about 6% to 12% of the primer composition. The primer composition preferably further comprises an acrylated epoxy oligomer in an amount of about 2% to 10%, an isobornyl acrylate monomer in an amount of about 40% to 70% of the primer composition, a photoinitiator in an amount of about 4% to 12% of the primer composition, a polyacrylic oligomer/acrylate monomer blend in an
20 amount of 6% to 12%, a flow promoting agent in an amount of 0% to 8%, an adhesion promoter in an amount of 2% to 8%, a UV absorber (UVA) in an amount of 1% to 3%, and a Hindered Amine Light Stabilizer (HAL) in an amount of 0.5% to 3% of the basecoat composition.

In accordance with yet another aspect of the invention, a method is
25 provided for depositing each layer of a multilayer paint coating on a substrate. The method comprises a first step of applying to the substrate a primer composition ("primer composition"). The primer composition comprises the composition disclosed above. After the primer composition is applied to a substrate, the primer composition on the substrate is illuminated with an ultraviolet light to cause the
30 primer composition to cure into the primer coating. The method comprises a third step of applying to the substrate a basecoat composition ("basecoat composition").

The basecoat composition comprises the composition disclosed above. After the primer composition is applied to a substrate, the basecoat composition on the substrate is illuminated with an ultraviolet light to cause the basecoat composition to cure into the basecoat coating. The method comprises a fifth step of applying to the substrate a topcoat composition ("topcoat composition"). The topcoat composition comprises the composition disclosed above. After the topcoat composition is applied to a substrate, the topcoat composition on the substrate is illuminated with an ultraviolet light to cause the topcoat composition to cure into the primer coating.

10 In accordance with this method, each paint layer composition can be selectively deposited on the substrate at specific locations where the paint layer plating is desired. It need not be applied to the entire substrate.

BEST MODE FOR CARRYING OUT THE INVENTION

Topcoat Compositions

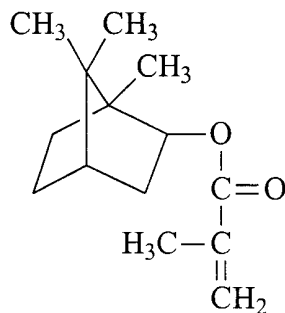
15 Reference will now be made in detail to presently preferred compositions or embodiments and methods of the invention, which constitute the best modes of practicing the invention presently known to the inventor.

In accordance with one aspect of the invention, a presently preferred ultraviolet light curable topcoat composition ("topcoat composition") is provided. In this preferred embodiment, the topcoat composition includes an aliphatic acrylated oligomer. The aliphatic acrylated oligomer is present in an amount of about 20% to 30% of the topcoat composition. The aliphatic acrylated oligomer mixture is more preferably present in an amount of about 23% to 27%, and most preferably about 25%. The aliphatic acrylated oligomer preferably comprises one or more urethane oligomers. Suitable aliphatic acrylated oligomers include Radcure Ebecryl 244 (aliphatic urethane diacrylate diluted 10% with 1,6-hexanediol diacrylate), Ebecryl 264 (aliphatic urethane triacrylate diluted 15% with 1,6-hexanediol diacrylate), Ebecryl 284 (aliphatic urethane diacrylate diluted 12 % by weight with 1,6-

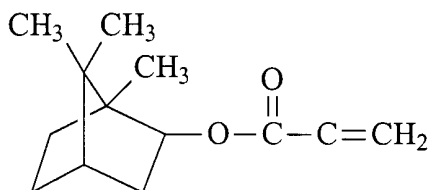
hexanediol diacrylate) urethanes, commercially available from Radcure UCB Corp. of Smyrna, Georgia; Sartomer CN-961E75 (aliphatic urethane diacrylate blended with 25% ethoxylated trimethylol propane triacrylate), CN-961H81 (aliphatic urethane diacrylate blended with 19% 2(2-ethoxyethoxy)ethyl acrylate), CN-963A80 (aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate), CN-964 (aliphatic urethane diacrylate), CN-966A80 (aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate), CN-982A75 (aliphatic urethane diacrylate blended with 25% tripropylene glycol diacrylate) and CN-983 (aliphatic urethane diacrylate), commercially available from Sartomer Corp. of Exton, Pennsylvania; TAB FAIRAD 8010, 8179, 8205, 8210, 8216, 8264, M-E-15, UVU-316, commercially available from TAB Chemicals of Chicago, Illinois; and Echo Resin ALU-303, commercially available from Echo Resins of Versaille, Missouri; and Genomer 4652, commercially available from Rahn Radiation Curing of Aurora, IL. The preferred aliphatic acrylated oligomers include Ebecryl 264 and Ebecryl 284. Ebecryl 264 is an aliphatic urethane triacrylate of 1200 molecular weight supplied as an 85% solution in hexanediol diacrylate. Ebecryl 284 is aliphatic urethane diacrylate of 1200 molecular weight diluted 10% with 1,6-hexanediol diacrylate. Combinations of these materials may also be employed herein.

This preferred topcoat composition further includes an acrylated epoxy oligomer. The acrylated epoxy oligomer is present in an amount of about 8% to 16%. The acrylated epoxy oligomer is more preferably present in an amount of about 11% to 14%, and most preferably about 13%. Suitable acrylated epoxy oligomers include Radcure Ebecryl 3603 (novolac epoxy acrylate diluted 20% by weight with tripropylene glycol diacrylate), commercially available from Radcure UCB Corp.; Sartomer CN-120 (difunctional bisphenol based epoxy acrylate) and CN-124 (difunctional bisphenol based epoxy acrylate), commercially available from Sartomer Corp.; and Echo Resin TME 9310 and 9345, commercially available from Echo Resins. The preferred acrylated epoxy oligomer is Ebecryl 3603, which is a tri-functional acrylated epoxy novolac. Combinations of these materials may also be employed herein.

The preferred topcoat composition also includes an isobornyl acrylate monomer in an amount of about 40% to 60%. The isobornyl acrylate monomer is more preferably present in an amount of about 45% to 55%, and most preferably about 50%. Suitable isobornyl acrylate monomers include Sartomer SR-423 (isobornyl methacrylate):



and SR-506 (isobornyl acrylate):



available from Sartomer Corp.; Radcure IBOA (isobornyl acrylate), commercially available from Radcure Corp.; IBOA and IBOMA, commercially available from CPS Chemical of Bradford, England; and Genomer 1121, commercially available from Rahn Radiation Curing. The preferred isobornyl acrylate monomer is Radcure IBOA, commercially available from Radcure Corp. Radcure IBOA is a high purity, low color monomer. Combinations of these materials may also be employed herein.

This preferred coat composition also includes a photoinitiator in an amount of about 2% to 8% of the topcoat composition. The photoinitiator is more preferably present in an amount of about 3% to 7%, and most preferably about 5%. If the coat composition is applied by flexographic techniques, the photoinitiator is more preferably present in an amount of about 2% to 6%, and most preferably about 4%. Suitable photoinitiators include Irgacure 184 (1-hydroxycyclohexyl phenyl

ketone), Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), Irgacure 369 (2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), Irgacure 500 (the combination of 50% 1-hydroxy cyclohexyl phenyl ketone and 50% benzophenone), Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1-one), Irgacure 1700 (the combination of 25% bis(2,6-dimethoxybenzoyl-2,4,4-trimethyl pentyl) phosphine oxide and 75% 2-hydroxy-2-methyl-1-phenyl-propan-1-one) DAROCUR 1173 (2-hydroxy-2-methyl-1-phenyl-1-propane) and DAROCUR 4265 (the combination of 50% 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide and 50% 2-hydroxy 2-methyl-1-phenyl-propan-1-one) available commercially from Ciba-Geigy Corp., Tarrytown, N.Y.; CYRACURE UVI-6974 (mixed triaryl sulfonium hexafluoroantimonate salts) and CYRACURE UVI-6990 (mixed triaryl sulfonium hexafluorophosphate salts) available commercially from Union Carbide Chemicals and Plastics Co. Inc., Danbury, Conn.; and Genocure CQ, Genocure BOK, and Genocure M.F., commercially available from Rahn Radiation Curing. The preferred photoinitiator is Irgacure 1700 commercially available from Ciba-Geigy of Tarrytown, New York. Combinations of these materials may also be employed herein.

The composition still further includes a flow promoting agent in an amount of about 0.0% to 6%, and preferably about 4.0%, of the topcoat composition. Suitable flow promoting agents include Genorad 17, commercially available from Rahn Radiation Curing; and Modaflow, commercially available from Monsanto Chemical Co., St. Louis, Missouri. The preferred flow promoting agent is Modaflow which is an ethyl acrylate and 2-ethylhexyl acrylate copolymer that improves the flow of the composition. Combinations of these materials may also be employed herein.

This preferred composition further comprises a UV absorber (UVA) in an amount of 1% to 3%, and preferably in a amount of 2%. Suitable UV absorbers include Tinuvin 328, Tinuvin 384, Tinuvin 900, Tinuvin 928, Tinuvin 1130, and Tinuvin 400 which are commercially available from Ciba-Geigy Corp., Tarrytown, N.Y.

This preferred composition further comprises a light stabilizer in an amount of 0.5% to 3%, and preferably in a amount of 1%. Suitable light stabilizers are Hindered Amine Light Stabilizers (HAL) such are Tinuvin 11 FD, Tinuvin 123, Tinuvin 144, and Tinuvin 292. These light stabilizers are commercially available
5 from Ciba-Geigy Corp., Tarrytown, N.Y.

To illustrate, the following example sets forth a presently preferred topcoat composition according to this aspect of the invention.

Example 1

This example provides a preferred topcoat composition according to
10 the invention. The topcoat composition was made from the following components:

15

Component	Approximate Weight %
Ebecryl 264	12.6
Ebecryl 284	12.6
IBOA	50.0
Irgacure 1700	4.9
Modaflow	4.4
Ebecryl 3603	12.6
UVA Tinuvin	1.9
HAL Tinuvin	1.0
Total	100.00

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In this example the IBOA and Irgacure 1700 are mixed in a pan with a propeller blade mixer for 30 seconds at a speed of 500 to 1000 rpm. In the next step, the Ebecryl 264, the Ebecryl 284, and the Ebecryl 3603 are introduced into the pan and mixed for 1 to 2 minutes at a speed of 3000 rpm. In the final step, the
25 Tinuvin 400 and the Tinuvin 292 are introduced into the pan and mixed for 1 to 2

minutes at a speed of 5000 rpm. The temperature during mixing is monitored. The mixing is temporarily suspended if the temperature exceed 100°F.

Basecoat Compositions

In accordance with one aspect of the invention, a presently preferred
5 ultraviolet light curable basecoat composition ("basecoat composition") is provided. In this preferred embodiment, the basecoat composition includes an aliphatic acrylated oligomers. The aliphatic acrylated oligomer is present in an amount of about 3% to 25% of the basecoat composition. In one preferred embodiment, the aliphatic acrylated oligomer mixture is more preferably present in an amount of
10 about 4% to 7%, and most preferably about 6%. Suitable aliphatic acrylated oligomers include Radcure Ebecryl 244 (aliphatic urethane diacrylate diluted 10% with 1,6-hexanediol diacrylate), Ebecryl 264 (aliphatic urethane triacrylate diluted 15% with 1,6-hexanediol diacrylate), Ebecryl 284 (aliphatic urethane diacrylate diluted 12 % by weight with 1,6-hexanediol diacrylate) urethanes, commercially
15 available from Radcure UCB Corp. of Smyrna, Georgia; Sartomer CN-961E75 (aliphatic urethane diacrylate blended with 25% ethoxylated trimethylol propane triacrylate), CN-961H81 (aliphatic urethane diacrylate blended with 19% 2(2-ethoxyethoxy)ethyl acrylate), CN-963A80 (aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate), CN-964 (aliphatic urethane diacrylate), CN-
20 966A80 (aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate), CN-982A75 (aliphatic urethane diacrylate blended with 25% tripropylene glycol diacrylate) and CN-983 (aliphatic urethane diacrylate), commercially available from Sartomer Corp. of Exton, Pennsylvania; TAB FAIRAD 8010, 8179, 8205, 8210, 8216, 8264, M-E-15, UVU-316, commercially available from TAB Chemicals
25 of Chicago, Illinois; and Echo Resin ALU-303, commercially available from Echo Resins of Versaille, Missouri; and Genomer 4652, commercially available from Rahn Radiation Curing of Aurora, IL. The preferred aliphatic acrylated oligomers include Ebecryl 264 and Ebecryl 284. Ebecryl 264 is an aliphatic urethane triacrylate of 1200 molecular weight supplied as an 85% solution in hexanediol diacrylate. Ebecryl 284 is aliphatic urethane diacrylate of 1200 molecular weight
30

diluted 10% with 1,6-hexanediol diacrylate. Combinations of these materials may also be employed herein.

5 This preferred basecoat composition further includes a polyacrylic/acrylate monomer blend. The polyacrylic blend is present in an amount of about 3 to 25%, and in one preferred embodiment, is more preferably about 9% of the basecoat composition. The preferred blend is Ebecryl 754 commercially available from Radcure UCB Corp. of Smyrna, Georgia.

10 This preferred basecoat composition further includes an acrylated epoxy oligomer. The acrylated epoxy oligomer is present in an amount of about 1% to 6%. In one preferred embodiment, the acrylated epoxy oligomer is more preferably present in an amount of about 3% to 5%, and most preferably about 4%. Suitable acrylated epoxy oligomers include Radcure Ebecryl 3603 (novolac epoxy acrylate diluted 20% by weight with tripropylene glycol diacrylate), commercially available from Radcure UCB Corp.; Sartomer CN-120 (difunctional bisphenol based epoxy acrylate) and CN-124 (difunctional bisphenol based epoxy acrylate),
15 commercially available from Sartomer Corp.; and Echo Resin TME 9310 and 9345, commercially available from Echo Resins. The preferred acrylated epoxy oligomer is Ebecryl 3603, which is a tri-functional acrylated epoxy novolac. Combinations of these materials may also be employed herein.

20 The preferred basecoat composition also includes an isobornyl acrylate monomer in an amount of about 10% to 70%. In one preferred embodiment, the isobornyl acrylate monomer is more preferably present in an amount of about 55% to 65%, and most preferably about 60%. Suitable isobornyl acrylate monomers include Sartomer SR-423 (isobornyl methacrylate) and SR-506 (isobornyl acrylate)
25 available from Sartomer Corp.; Radcure IBOA (isobornyl acrylate), commercially available from Radcure Corp.; IBOA and IBOMA, commercially available from CPS Chemical of Bradford, England; and Genomer 1121, commercially available from Rahn Radiation Curing. The preferred isobornyl acrylate monomer is Radcure IBOA, commercially available from Radcure Corp. Radcure IBOA is a high purity,
30 low color monomer. Combinations of these materials may also be employed herein.

This preferred basecoat composition also includes a photoinitiator in an amount of about 2% to 8% of the basecoat composition. The photoinitiator is more preferably present in an amount of about 3% to 7%, and most preferably about 5%. Suitable photoinitiators include Irgacure 184 (1-hydroxycyclohexyl phenyl ketone), Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), Irgacure 369 (2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), Irgacure 500 (the combination of 50% 1-hydroxy cyclohexyl phenyl ketone and 50% benzophenone), Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1-one), Irgacure 1700 (the combination of 25% bis(2,6-dimethoxybenzoyl-2,4,4-trimethyl pentyl) phosphine oxide, and 75% 2-hydroxy-2-methyl-1-phenyl-propan-1-one), DAROCUR 1173 (2-hydroxy-2-methyl-1-phenyl-1-propane) and DAROCUR 4265 (the combination of 50% 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, and 50% 2-hydroxy 2-methyl-1-phenyl-propan-1-one), available commercially from Ciba-Geigy Corp., Tarrytown, N.Y.; CYRACURE UVI-6974 (mixed triaryl sulfonium hexafluoroantimonate salts) and CYRACURE UVI-6990 (mixed triaryl sulfonium hexafluorophosphate salts) available commercially from Union Carbide Chemicals and Plastics Co. Inc., Danbury, Conn.; and Genocure CQ, Genocure BOK, and Genocure M.F., commercially available from Rahn Radiation Curing. The preferred photoinitiator is Irgacure 1700 commercially available from Ciba-Geigy of Tarrytown, New York. Combinations of these materials may also be employed herein.

The composition still further includes a flow promoting agent in an amount of about 0.0% to 6%, and preferably in one particular embodiment about 4.0%, of the topcoat composition. Suitable flow promoting agents include Genorad 17, commercially available from Rahn Radiation Curing; and Modaflow, commercially available from Monsanto Chemical Co., St. Louis, Missouri. The preferred flow promoting agent is Modaflow which is an ethyl acrylate and 2-ethylhexyl acrylate copolymer that improves the flow of the composition. Combinations of these materials may also be employed herein.

The preferred composition still further comprises an adhesion promoter in an amount of 1% to 7%, and preferably in one particular embodiment

in an amount of 4%. Suitable adhesion promoters include Ebecryl 168, commercially available from Radcure Corp.; and Sartomer CN 704 (acrylated polyester adhesion promoter) and CD 9052 (trifunctional acid ester), commercially available from Sartomer Corp. The preferred adhesion promoter is Ebecryl 168
5 which is a methacrylated acidic adhesion promoter. Combinations of these materials may also be employed herein.

The preferred composition still further comprises pigments in an amount of 7% to 30%, and preferably in one particular embodiment in an amount of 12%. Suitable pigments include metallic and flatbase pigments commercially
10 available from EM Industries, Inc., Hawthorne, N.Y. Representative examples include Red ST8673, Black BB 1355, BON Maroon ST 8684, and Carbazole Violet ST8119. Suitable pigments the Afflair line of pigments commercially available from EM Industries located in Hawthorne, New York. Representative examples include Afflair 100, Afflair 103, Afflair 300, Afflair 507, Afflair 600, and Afflair
15 504.

To illustrate, the following example sets forth a presently preferred basecoat composition according to this aspect of the invention.

Example 2

This example provides a preferred basecoat composition according to
20 the invention. The basecoat composition was made from the following components:

Component	Approximate Weight %
Ebecryl 284	6.2
Ebecryl 754	6.2
IBOA	59.2
Ebecryl 168	3.8
Irgacure 1700	5.4

25

Component	Approximate Weight %
Modaflow	3.8
Ebecryl 3603	3.8
Afflair 100	11.6
Total	100.00

5 In this example the IBOA and Irgacure 1700 are mixed in a pan with a propeller blade mixer for 30 seconds at a speed of 500 to 1000 rpm. In the next step, the Ebecryl 754, the Ebecryl 284, the Ebecryl 3603, and Modaflow are introduced into the pan and mixed for 1 to 2 minutes at a speed of 2000 rpm. The Afflair 100 is added and mixed for 1 to 2 minutes at 2000 rpm. In the final step, the
10 Ebecryl 168 is introduced into the pan and mixed for 1 to 2 minutes at a speed of 2000 rpm. The temperature during mixing is monitored. The mixing is temporarily suspended if the temperature exceed 100°F.

Example 3

15 This example provides a preferred basecoat composition according to the invention. The basecoat composition was made from the following components:

Component	Approximate Weight %
Ebecryl 284	22.0
Ebecryl 754	22.0
IBOA	12.4
Ebecryl 168	4.4
Irgacure 1700	6.1
Modaflow	4.0
Ebecryl 3603	4.0

20

Component	Approximate Weight %
Red ST8673	25.1
<i>Total</i>	100.00

In this example the IBOA and Irgacure 1700 are mixed in a pan with a propeller blade mixer for 30 seconds at a speed of 500 to 1000 rpm. In the next step, the Ebecryl 754, the Ebecryl 284, the Ebecryl 3603, and Modaflow are introduced into the pan and mixed for 1 to 2 minutes at a speed of 2000 rpm. The Red ST8673 is added and mixed for 1 to 2 minutes at 2000 rpm. In the final step, the Ebecryl 168 is introduced into the pan and mixed for 1 to 2 minutes at a speed of 2000 rpm. The temperature during mixing is monitored. The mixing is temporarily suspended if the temperature exceed 100°F.

Example 4

This example provides a preferred basecoat composition according to the invention. The basecoat composition was made from the following components:

Component	Approximate Weight %
Ebecryl 284	22.0
Ebecryl 754	22.0
IBOA	17.4
Ebecryl 168	4.4
Irgacure 1700	6.1
Modaflow	4.0
Ebecryl 3603	4.0
Black BB 1355	20.1
<i>Total</i>	100.00

In this example the IBOA and Irgacure 1700 are mixed in a pan with a propeller blade mixer for 30 seconds at a speed of 500 to 1000 rpm. In the next step, the Ebecryl 754, the Ebecryl 284, the Ebecryl 3603, and Modaflow are introduced into the pan and mixed for 1 to 2 minutes at a speed of 2000 rpm. The
5 Black B 1355 is added and mixed for 1 to 2 minutes at 2000 rpm. In the final step, the Ebecryl 168 is introduced into the pan and mixed for 1 to 2 minutes at a speed of 2000 rpm. The temperature during mixing is monitored. The mixing is temporarily suspended if the temperature exceed 100°F.

Primer Compositions

10 In accordance with one aspect of the invention, a presently preferred ultraviolet light curable primer composition ("primer composition") is provided. In this preferred embodiment, the primer composition includes an aliphatic acrylated oligomer. The aliphatic acrylated oligomer is present in an amount of about 6% to 12% of the primer composition. The aliphatic acrylated oligomer mixture is more
15 preferably present in an amount of about 7% to 10%, and most preferably about 9%. Suitable aliphatic acrylated oligomers include Radcure Ebecryl 244 (aliphatic urethane diacrylate diluted 10% with 1,6-hexanediol diacrylate), Ebecryl 264 (aliphatic urethane triacrylate diluted 15% with 1,6-hexanediol diacrylate), Ebecryl 284 (aliphatic urethane diacrylate diluted 12 % by weight with 1,6-hexanediol
20 diacrylate) urethanes, commercially available from Radcure UCB Corp. of Smyrna, Georgia; Sartomer CN-961E75 (aliphatic urethane diacrylate blended with 25% ethoxylated trimethylol propane triacrylate), CN-961H81 (aliphatic urethane diacrylate blended with 19% 2(2-ethoxyethoxy)ethyl acrylate), CN-963A80 (aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate), CN-964
25 (aliphatic urethane diacrylate), CN-966A80 (aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate), CN-982A75 (aliphatic urethane diacrylate blended with 25% tripropylene glycol diacrylate) and CN-983 (aliphatic urethane diacrylate), commercially available from Sartomer Corp. of Exton, Pennsylvania; TAB FAIRAD 8010, 8179, 8205, 8210, 8216, 8264, M-E-15, UVU-316,
30 commercially available from TAB Chemicals of Chicago, Illinois; and Echo Resin ALU-303, commercially available from Echo Resins of Versaille, Missouri; and

Genomer 4652, commercially available from Rahn Radiation Curing of Aurora, IL. The preferred aliphatic acrylated oligomers include Ebecryl 264 and Ebecryl 284. Ebecryl 264 is an aliphatic urethane triacrylate of 1200 molecular weight supplied as an 85% solution in hexanediol diacrylate. Ebecryl 284 is aliphatic urethane diacrylate of 1200 molecular weight diluted 10% with 1,6-hexanediol diacrylate. Combinations of these materials may also be employed herein.

This preferred basecoat composition further includes a polyacrylic/acrylate monomer blend. The polyacrylic blend is present in an amount of about 6 to 12%, and is more preferably about 9% of the basecoat composition. The preferred blend is Ebecryl 754 commercially available from Radcure UCB Corp. of Smyrna, Georgia.

This preferred primer composition further includes an acrylated epoxy oligomer. The acrylated epoxy oligomer is present in an amount of about 2% to 10%. The acrylated epoxy oligomer is more preferably present in an amount of about 4% to 8%, and most preferably about 6%. Suitable acrylated epoxy oligomers include Radcure Ebecryl 3603 (novolac epoxy acrylate diluted 20% by weight with tripropylene glycol diacrylate), commercially available from Radcure UCB Corp.; Sartomer CN-120 (difunctional bisphenol based epoxy acrylate) and CN-124 (difunctional bisphenol based epoxy acrylate), commercially available from Sartomer Corp.; and Echo Resin TME 9310 and 9345, commercially available from Echo Resins. The preferred acrylated epoxy oligomer is Ebecryl 3603, which is a tri-functional acrylated epoxy novolac. Combinations of these materials may also be employed herein.

The preferred primer composition also includes an isobornyl acrylate monomer in an amount of about 40% to 70%. The isobornyl acrylate monomer is more preferably present in an amount of about 45% to 60%, and most preferably about 55%. Suitable isobornyl acrylate monomers include Sartomer SR-423 (isobornyl methacrylate) and SR-506 (isobornyl acrylate) available from Sartomer Corp.; Radcure IBOA (isobornyl acrylate), commercially available from Radcure Corp.; IBOA and IBOMA, commercially available from CPS Chemical of Bradford,

England; and Genomer 1121, commercially available from Rahn Radiation Curing. The preferred isobornyl acrylate monomer is Radcure IBOA, commercially available from Radcure Corp. Radcure IBOA is a high purity, low color monomer. Combinations of these materials may also be employed herein.

5 This preferred primer composition also includes a photoinitiator in an amount of about 4% to 12% of the primer composition. The photoinitiator is more preferably present in an amount of about 6% to 10%, and most preferably about 8%. Suitable photoinitiators include Irgacure 184 (1-hydroxycyclohexyl phenyl ketone), Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one),
10 Irgacure 369 (2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), Irgacure 500 (the combination of 50% 1-hydroxy cyclohexyl phenyl ketone and 50% benzophenone), Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1-one), Irgacure 1700 (the combination of 25% bis(2,6-dimethoxybenzoyl-2,4,4-trimethyl pentyl) phosphine oxide, and 75% 2-hydroxy-2-methyl-1-phenyl-propan-1-one), DAROCUR
15 1173 (2-hydroxy-2-methyl-1-phenyl-1-propane) and DAROCUR 4265 (the combination of 50% 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, and 50% 2-hydroxy 2-methyl-1-phenyl-propan-1-one), available commercially from Ciba-Geigy Corp., Tarrytown, N.Y.; CYRACURE UVI-6974 (mixed triaryl sulfonium hexafluoroantimonate salts) and CYRACURE UVI-6990 (mixed triaryl sulfonium
20 hexafluorophosphate salts) available commercially from Union Carbide Chemicals and Plastics Co. Inc., Danbury, Conn.; and Genocure CQ, Genocure BOK, and Genocure M.F., commercially available from Rahn Radiation Curing. The preferred photoinitiator is Irgacure 1700 commercially available from Ciba-Geigy of Tarrytown, New York. Combinations of these materials may also be employed
25 herein.

 The composition still further includes a flow promoting agent in an amount of about 0.0% to 8%, and preferably about 6.0%, of the topcoat composition. Suitable flow promoting agents include Genorad 17, commercially available from Rahn Radiation Curing; and Modaflow, commercially available from
30 Monsanto Chemical Co., St. Louis, Missouri. The preferred flow promoting agent is Modaflow which is an ethyl acrylate and 2-ethylhexyl acrylate copolymer that

improves the flow of the composition. Combinations of these materials may also be employed herein.

5 The preferred composition still further comprises an adhesion promoter in an amount of 2% to 8%, and preferably in an amount of 6%. Suitable adhesion promoters include Ebecryl 168, commercially available from Radcure Corp.; and Sartomer CN 704 (acrylated polyester adhesion promoter) and CD 9052 (trifunctional acid ester), commercially available from Sartomer Corp. The preferred adhesion promoter is Ebecryl 168 which is a methacrylated acidic adhesion promoter. Combinations of these materials may also be employed herein.

10 This preferred composition further comprises a UV absorber (UVA) in an amount of 1% to 3%, and preferably in a amount of 2%. Suitable UVA is commercially available from Ciba-Geigy Corp., Tarrytown, N.Y.

15 This preferred composition further comprises a Hindered Amine Light Stabilizer (HAL) in an amount of 0.5% to 3%, and preferably in a amount of 1%. Suitable HAL is commercially available from Ciba-Geigy Corp., Tarrytown, N.Y.

To illustrate, the following example sets forth a presently preferred primer composition according to this aspect of the invention.

Example 5

20 This example provides a preferred primer composition according to the invention. The primer composition was made from the following components:

Component	Approximate Weight %
Ebecryl 284	9.1
Ebecryl 754	9.1

5

Component	Approximate Weight %
IBOA	54.0
Ebecryl 168	5.7
Irgacure 1700	7.8
Modaflow	5.7
Ebecryl 3603	5.7
Tiruin 400	1.9
Tinuvin 292	1.0
Total	100.00

10 In this example the IBOA and Irgacure 1700 are mixed in a pan with a propeller blade mixer for 30 seconds at a speed of 500 to 1000 rpm. In the next step, the Ebecryl 754, the Ebecryl 284, the Ebecryl 3603, and the Modaflow are introduced into the pan and mixed for 1 to 2 minutes at a speed of 2000 rpm. In the final step, Ebecryl 168, the Tinuvin 400, and the Tinuvin 292 are introduced into the pan and mixed for 1 to 2 minutes at a speed of 2000 rpm. The temperature during mixing is monitored. The mixing is temporarily suspended if the temperature exceed 15 100°F.

Method for Depositing a Multilayer Paint Coating on a Substrate

20 In accordance with still another aspect of the invention, a method is provided for depositing a multilayer coating on a suitable substrate. The method comprises a first step of applying a primer composition ("primer composition") to the substrate.

25 The primer composition comprises the compositions described above. The preferred primer compositions according to this method are those described herein, for example, including the compositions described in example 1. The method includes a second step of illuminating the primer composition on the

substrate with an ultraviolet light to cause the primer composition to cure into the primer coating. The method comprises a third step of applying to the substrate a basecoat composition ("basecoat composition"). The basecoat composition comprises the composition disclosed above. After the primer composition is applied to a substrate, the basecoat composition on the substrate is illuminated with an ultraviolet light to cause the basecoat composition to cure into the basecoat coating. The method comprises a fifth step of applying to the substrate a topcoat composition ("topcoat composition"). The topcoat composition comprises the composition disclosed above. After the topcoat composition is applied to a substrate, the topcoat composition on the substrate is illuminated with an ultraviolet light to cause the topcoat composition to cure into the primer coating.

This illumination for each layer may be carried out in any number of ways, provided the ultraviolet light or radiation impinges upon the paint composition so that the paint composition is caused to polymerize to form the coating, layer, film, etc., and thereby cures. Curing preferably takes place by free radical polymerization, which is initiated by an ultraviolet radiation source. The photoinitiator preferably comprises a photoinitiator, as described above. Various ultraviolet light sources may be used, depending on the application. Preferred ultraviolet radiation sources for a number of applications include known ultraviolet lighting equipment with energy intensity settings of, for example, 125 watts, 200 watts, and 300 watts per square inch.

Each paint composition may be applied to the substrate using a number of different techniques. The paint compositions may be applied, for example, by direct brush application, or it may be sprayed onto the substrate surface. It also may be applied using a screen printing technique. In such screen printing technique, a "screen" as the term is used in the screen printing industry is used to regulate the flow of liquid composition onto the substrate surface. The paint compositions typically would be applied to the screen as the latter contacts the substrate. The paint composition flows through the silk screen to the substrate, whereupon it adheres to the substrate at the desired film thickness. Screen printing techniques suitable for this purpose include known techniques, but wherein the

process is adjusted in ways known to persons of ordinary skill in the art to accommodate the viscosity, flowability, and other properties of the liquid-phase composition, the substrate and its surface properties, etc. Flexographic techniques, for example, using pinch rollers to contact the paint composition with a rolling substrate, also may be used.

While embodiments of the invention have been illustrated and described, it is not intended that these embodiments illustrate and describe all possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A photocurable topcoat paint composition comprising:
at least one aliphatic acrylated oligomers;
an acrylated epoxy oligomer;
5 an isobornyl acrylate monomer;
a UV absorber;
a light stabilizer; and
a photoinitiator.
- 10 2. The photocurable topcoat paint composition of claim 1,
wherein:
the at least one aliphatic acrylated oligomers is present in an amount
of about 20% to 30% by weight of the topcoat paint composition;
the acrylated epoxy oligomer is present in an amount of about 8% to
15 16% by weight of the topcoat paint composition;
the isobornyl acrylate monomer is present in an amount of about 40%
to 60% by weight of the topcoat paint composition;
the UV absorber is present in an amount of about 1% to 3% by
weight of the topcoat paint composition;
20 the light stabilizer is present in an amount of about 0.5% to 3% by
weight of the topcoat paint composition; and
the photoinitiator is present in an amount of about 2% to 8% by
weight of the topcoat paint composition.
- 25 3. The photocurable topcoat paint composition of claim 2,
wherein:
the at least one aliphatic acrylated oligomers is present in an amount
of about 23% to 27% by weight of the topcoat paint composition;
the acrylated epoxy oligomer is present in an amount of about 11%
30 to 14% by weight of the topcoat paint composition;
the isobornyl acrylate monomer is present in an amount of about 45%
to 55% by weight of the topcoat paint composition; and

the photoinitiator is present in an amount of about 3% to 7% by weight of the topcoat paint composition.

4. The photocurable topcoat paint composition of claim 3,
5 wherein:

the at least one aliphatic acrylated oligomers is present in an amount of about 25% by weight of the topcoat paint composition;

the acrylated epoxy oligomer is present in an amount of about 13% by weight of the topcoat paint composition;

10 the isobornyl acrylate monomer is present in an amount of about 50% by weight of the topcoat paint composition;

the UV absorber is present in an amount of about 2% by weight of the topcoat paint composition;

15 the light stabilizer is present in an amount of about 1% by weight of the topcoat paint composition; and

the photoinitiator is present in an amount of about 5% by weight of the topcoat paint composition.

5. The photocurable topcoat paint composition as set forth in
20 claim 1, further comprising a flow promoting agent.

6. The topcoat paint composition as set forth in claim 1 wherein the at least one aliphatic acrylate oligomer is selected from the group consisting of:

aliphatic urethane diacrylate diluted 10% with 1,6-hexanediol diacrylate;

25 aliphatic urethane triacrylate diluted 15% with 1,6-hexanediol diacrylate;

aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate;

30 aliphatic urethane diacrylate blended with 25% ethoxylated trimethylol propane triacrylate;

aliphatic urethane diacrylate blended with 19% 2(2-ethoxyethoxy)ethyl acrylate;

aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate;

aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate;

5 7. The topcoat paint composition as set forth in claim 1 wherein the photoinitiator is selected from the group consisting of:

1-hydroxycyclohexyl phenyl ketone;

2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-;

10 the combination of 50% 1-hydroxy cyclohexyl phenyl ketone and 50% benzophenone;

2,2-dimethoxy-1,2-diphenylethan-1-one;

the combination of 25% bis(2,6-dimethoxybenzoyl-2,4-, 4-trimethyl pentyl phosphine oxide and 75% 2-hydroxy-2-methyl-1-phenyl-propan-1-one;

2-hydroxy-2-methyl-1-phenyl-1-propane;

15 the combination of 50% 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide and 50% 2-hydroxy 2-methyl-1-phenyl-propan-1-one;

mixed triaryl sulfonium hexafluoroantimonate salts;

mixed triaryl sulfonium hexafluorophosphate salts; and

mixtures thereof.

20

8. A photocurable basecoat paint composition comprising:

an aliphatic acrylated oligomers;

an acrylated epoxy oligomer;

an isobornyl acrylate monomer;

25 a blend consisting of a polyacrylic monomer and an acrylate monomer;

at least one pigment; and

a photoinitiator.

9. The photocurable basecoat paint composition of claim 8, wherein:

the at least one aliphatic acrylated oligomers is present in an amount of about 3% to 25% by weight of the basecoat paint composition;

5 the acrylated epoxy oligomer is present in an amount of about 1% to 6% by weight of the basecoat paint composition;

the isobornyl acrylate monomer is present in an amount of about 10% to 70% by weight of the basecoat paint composition;

10 the pigment is present in an amount of about 7% to 26% by weight of the basecoat composition; and

the photoinitiator is present in an amount of about 2% to 8% by weight of the basecoat paint composition.

10. The photocurable basecoat paint composition of claim 9, wherein:

15 the at least one aliphatic acrylated oligomers is present in an amount of about 4% to 7% by weight of the basecoat paint composition;

the acrylated epoxy oligomer is present in an amount of about 3% to 5% by weight of the basecoat paint composition;

20 the isobornyl acrylate monomer is present in an amount of about 55% to 65% by weight of the basecoat paint composition; and

the photoinitiator is present in an amount of about 3% to 7% by weight of the basecoat paint composition.

11. The photocurable basecoat paint composition of claim 10, wherein:

25 the at least one aliphatic acrylated oligomers is present in an amount of about 6% by weight of the basecoat paint composition;

the acrylated epoxy oligomer is present in an amount of about 4% by weight of the basecoat paint composition;

30 the isobornyl acrylate monomer is present in an amount of about 60% by weight of the basecoat paint composition;

the pigment is present in an amount of about 12% by weight of the basecoat composition; and

the photoinitiator is present in an amount of about 5% by weight of the basecoat paint composition.

5 12. The photocurable basecoat paint composition of claim 8 further comprising:

an adhesion promoter; and
a flow promoting agent.

10 13. The basecoat paint composition as set forth in claim 8 wherein the at least one aliphatic acrylate oligomer is selected from the group consisting of:
aliphatic urethane diacrylate diluted 10% with 1,6-hexanediol diacrylate;

aliphatic urethane triacrylate diluted 15% with 1,6-hexanediol diacrylate;

15 aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate;

aliphatic urethane diacrylate blended with 25% ethoxylated trimethylol propane triacrylate;

20 aliphatic urethane diacrylate blended with 19% 2(2-ethoxyethoxy)ethyl acrylate;

aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate; and

aliphatic urethane diacrylate blended with 20% tripropylene glycol diacrylate.

25 14. The basecoat paint composition as set forth in claim 8 wherein the photoinitiator is selected from the group consisting of:

1-hydroxycyclohexyl phenyl ketone;

2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-;

30 the combination of 50% 1-hydroxy cyclohexyl phenyl ketone and 50% benzophenone;

2,2-dimethoxy-1,2-diphenylethan-1-one;
the combination of 25 % bis(2,6-dimethoxybenzoyl-2,4-, 4-trimethyl
pentyl phosphine oxide and 75 % 2-hydroxy-2-methyl-1-phenyl-propan-1-one;
2-hydroxy-2-methyl-1-phenyl-1-propane;
5 the combination of 50% 2,4,6-trimethylbenzoyldiphenyl-phosphine
oxide and 50% 2-hydroxy 2-methyl-1-phenyl-propan-1-one;
mixed triaryl sulfonium hexafluoroantimonate salts;
mixed triaryl sulfonium hexafluorophosphate salts; and
mixtures thereof.

10

15. A photocurable primer paint composition comprising:
an aliphatic acrylated oligomers;
an acrylated epoxy oligomer;
an isobornyl acrylate monomer;
15 a blend consisting of a polyacrylic monomer and an acrylate
monomer;
a UV absorber;
a light stabilizer; and
a photoinitiator.

20

16. The photocurable primer paint composition of claim 15,
wherein:
the at least one aliphatic acrylated oligomers is present in an amount
of about 6% to 12% by weight of the topcoat paint composition;
the acrylated epoxy oligomer is present in an amount of about 2% to
25 10% by weight of the topcoat paint composition;
the isobornyl acrylate monomer is present in an amount of about 40%
to 70% by weight of the topcoat paint composition;
the UV absorber is present in an amount of about 1% to 3% by
weight of the topcoat paint composition;
30 the blend consisting of a polyacrylic monomer and an acrylate
monomer is present in an amount of about 6% to 12% by weight of the primer paint
composition;

the light stabilizer is present in an amount of about 0.5% to 3% by weight of the topcoat paint composition; and

the photoinitiator is present in an amount of about 4% to 12% by weight of the topcoat paint composition.

5 17. The photocurable primer paint composition of claim 15 further comprising:

an adhesion promoter; and
a flow promoting agent.

10 18. The primer paint composition of claim 17 wherein the adhesion promoter is selected from the group consisting of:

methacrylated acidic adhesion promoter;
acrylated polyester adhesion promoter;
trifunctional acid ester; and
mixtures thereof.

15 19. A method of forming a multilayer paint coating on a substrate, the method comprising:

applying a photocurable primer paint composition to said substrate to form an uncured primer coating;

20 curing said uncured primer coating with sufficient UV light to form a cured primer coating;

applying a photocurable basecoat paint composition to the cured primer coating to form an uncured basecoat coating;

25 curing said uncured basecoat coating with sufficient light to form a cured basecoat coating;

applying a photocurable topcoat paint composition to the cured basecoat coating to form an uncured topcoat coating; and

curing said uncured topcoat coating with sufficient light to form a cured topcoat coating.

20. The method as set forth in claim 19, wherein the topcoat paint composition comprises:

- at least one aliphatic acrylated oligomers;
- an acrylated epoxy oligomer;
- 5 an isobornyl acrylate monomer;
- a UV absorber;
- a light stabilizer; and
- a photoinitiator.

21. The method as set forth in claim 19, wherein the basecoat paint composition comprises:

- an aliphatic acrylated oligomers;
- an acrylated epoxy oligomer;
- an isobornyl acrylate monomer;
- 15 a blend consisting of a polyacrylic monomer and an acrylate monomer;
- at least one pigment; and
- a photoinitiator.

22. The method as set forth in claim 19, wherein the primer paint composition comprises:

- 20 an aliphatic acrylated oligomers;
- an acrylated epoxy oligomer;
- an isobornyl acrylate monomer;
- a blend consisting of a polyacrylic monomer and an acrylate monomer;
- 25 a UV absorber;
- a light stabilizer; and
- a photoinitiator.