



(51) International Patent Classification:

C08F 2/26 (2006.01) C09D 125/14 (2006.01)

C08F 212/08 (2006.01) C09D 143/02 (2006.01)

C09D 5/02 (2006.01)

(21) International Application Number:

PCT/EP2024/070134

(22) International Filing Date:

16 July 2024 (16.07.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

PCT/CN2023/111031

03 August 2023 (03.08.2023) CN

(71) Applicant: SPECIALTY OPERATIONS FRANCE

[FR/FR]; 9 rue des Cuirassiers, Immeuble Silex 2 Solvay, 69003 Lyon (FR).

(72) Inventors: MARTINEZ-CASTRO, Nemesio; 52 rue de

la Haie-Coq, 93300 Aubervilliers (FR). ANDERSON, Eugene J.; 350 George Patterson Boulevard, Bristol, Pennsylvania 19007-3624 (US). LEE, Dongcheel; 150, BUKAHYUN-RO, SEODAEMUN-GU, Seoul 120-140 (KR). KANG, Changheon; 150, BUKAHYUN-RO, SEODAEMUN-GU, Seoul 120-140 (KR). VEST, Brian; 350 George Patterson Boulevard, Bristol, Pennsylvania 19007-3624 (US). WANG, Yalan; 3966, JINDU ROAD, XINZHUANG INDUSTRIAL ZONE, SHANGHAI, Shanghai 201108 (CN). CHEN, Yanhui; 3966, JINDU ROAD, XINZHUANG INDUSTRIAL ZONE, SHANGHAI, Shanghai 201108 (CN). ZHOU, Lichang; 350 George Patterson Boulevard, Bristol, Pennsylvania 19007-3624 (US).

(74) Agent: MELMOUX, Florent; 85 rue des Frères Perret RI-

CL, 69192 Saint-Fons Cedex (FR).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY,

MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(54) Title: POLYMER COMPOSITION AND METHODS OF MAKING AND USING THEREOF

(57) Abstract: A phosphate ester composition including polymerizable phosphate mono-ester compound or a salt thereof, and polymerizable phosphate di-ester compound or a salt thereof. A polymer composition produced by polymerization utilizing polymerizable phosphate mono-ester compound or a salt thereof, and polymerizable phosphate di-ester compound or a salt thereof. Methods of making and using such polymer compositions, for example for use as waterborne coating compositions, and coating compositions having improved adhesion, corrosion resistance, water resistance, gloss, gloss retention, and hiding. Methods of improving adhesion, corrosion resistance, water resistance, gloss, gloss retention, and hiding of a coating composition by employing the polymer composition in the coating composition.



**POLYMER COMPOSITION AND METHODS OF MAKING AND USING THEREOF****Field of the Invention**

**[0001]** This invention relates to an emulsion polymer composition produced by emulsion polymerization utilizing polymerizable phosphate mono-ester compound or a salt, and polymerizable phosphate di-ester compound or a salt thereof. This invention also relates to methods of making and such emulsion polymer composition, e.g. as a waterborne coating composition, and coating compositions having improved adhesion, corrosion resistance, water resistance, gloss, gloss retention, and hiding. This invention relates to methods of improving adhesion, corrosion resistance, water resistance, gloss, gloss retention, and hiding of a coating composition employing the emulsion polymer composition. This is especially useful in Direct to Metal uses with improved adhesion, improved gloss, improved corrosion resistance and improved water resistance. This invention provides water based paint and industrial coating formulations to avoid solvent based formulations.

**Background to the Invention**

**[0002]** “Lattices” and “emulsions”, water based dispersions of polymers obtained by emulsion polymerization, are widely used in various applications such as paints, adhesives, paper coatings, and carpet backing. Although some applications do not require it, the major property of the latex is its ability to bind various substrates. Thus, adhesion is a key factor, and one of the most difficult aspects is the wet adhesion. However, adhesion of such paints or coatings to the substrates is generally adversely affected by the presence of large amounts of emulsifiers (surfactants) required in the emulsion polymerization process. For example, such emulsifiers affect adhesion and particularly wet adhesion in numerous ways.

**[0003]** One way such emulsifiers affect adhesion is by migrating to the interfaces during the drying process. The emulsifiers tend to migrate to the surface during the drying process and collect at the interface of the paint or coating and the substrate. At the interface between the coating and the substrate, it will reduce adhesion by forming double layers that are less adhesive and more sensitive to moisture or other external water. This effect can ruin the properties of the coating. At the interface of coating/air, it reduces the interfacial tension of the coating, allows water to spread easily on the surface, and increases the water diffusion through this interface.

**[0004]** Another way such emulsifiers affect adhesion is by forming interconnected clusters in the coating. Surfactants are very often incompatible with the coating and the pigments and have a tendency to segregate during and after the drying process. One of the negative aspects is that due to differences in refractive index, it will create haze in the coating, which is very detrimental in the clear coat type (adhesives for coatings). The major problem is the tremendous ability of these clusters to carry water throughout the film and to the interface film/substrate which impairs the mechanical properties, particularly adhesion, of the coating.

**[0005]** Additionally, many such emulsifiers are generally incompatible with the other coating or paint components and tend to segregate, carry water and cause haze formation.

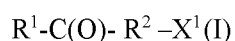
**[0006]** Beside this, surfactants can increase foaming and require the addition of a defoamer that may have other inconveniences such as the dewetting of the coating (such as the formation of fish eyes in the paint film). Finally, there are very often cross interactions in the coatings that may induce migration of the latex surfactants to the pigments leading to a destabilization of the paint. This phenomenon is detrimental to paint quality as well as to water resistance. Unfortunately, even though some trials have been done at the lab scale to run emulsion polymerization without surfactant, no known industrial process is known for doing so. Surfactant remains a necessary evil. Some decades ago, functional monomers with stabilizing groups (carboxylic, sulfate, sulfonate and the like) appeared and helped to reduce the amount of surfactant significantly thus improving properties. However, they are not surface active materials and thus are not able to stabilize the pre-emulsions of monomers or to be used solely during the nucleation period.

**[0007]** It is therefore desirable that there be available polymerizable monomers that enable one to eliminate or decrease the amount of such emulsifiers required in the emulsion polymerization process.

### Summary of the Invention

**[0008]** This invention provides a phosphate ester composition comprising:

(a) at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

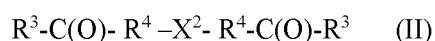
$R^1$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three, oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

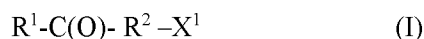
wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1.

**[0009]** This invention provides a polymer composition comprising monomeric units from:

(A) the at least one polymerizable phosphate mono-ester compound or salt thereof and the at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition as described in this specification comprising:

(a) the at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

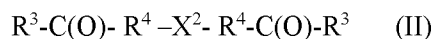
$R^1$  is a substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, preferably the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) the at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is a substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt,

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1; and

(B) at least one other polymerizable monomer.

**[0010]** In another aspect, this invention also provides a method for the production of the polymer composition of the present invention.

**[0011]** In particular, the present invention relates to a method for the production of the polymer composition comprising:

combining (A) the phosphate ester composition described herein, and (B) at least one other polymerizable monomer to form a mixture; and

polymerizing the at least one polymerizable phosphate mono-ester compound or salt thereof and the at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition and the at least one other polymerizable monomer.

**[0012]** Typically the polymer composition is a polymer composition further comprising a surfactant, preferably an anionic surfactant, most preferably a phosphate ester anionic surfactant, and the polymerization is by emulsion polymerization. However, the polymerization may be polymerization in the presence of polymerizable phosphate mono-ester compound, polymerizable phosphate di-ester compound and polymerizable monomer without added surfactant, for example polymerization of these ingredients in solvent.

**[0013]** Preferably the polymerizable phosphate mono-ester compound or a salt thereof and the polymerizable phosphate di-ester compound or a salt thereof have an absence of oxypropylene units.

**[0014]** The polymerizable phosphate mono-ester compounds and the polymerizable phosphate di-ester compounds act as polymerizable “monomers”. These monomers can be used in acid and basic form. For the basic form sodium hydroxide or potassium hydroxide or ammonium hydroxide are typically used for the neutralization.

**[0015]** The present invention has beneficial results especially to provide performance improvement for waterborne Industrial Coatings. The present invention preferably provides industrial coatings that meet ISO12944 CLASSIFICATION C3 and C4.

**[0016]** The high mono/di-ester polymerizable phosphated monomers of this invention makes it possible to eliminate or reduce traditional emulsifiers (surfactants) employed in emulsion polymerization and eliminate or reduce the problems or drawbacks associated with their presence in the resulting latices (emulsions) to be used for paints or coatings.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

**[0017]** FIG. 1 compares Paint C vs. Paint D.

**[0018]** FIG. 2 compares polished CRS panels to which was applied: Paint C; Paint A; and Paint B.

**[0019]** FIG. 3 shows a standard classification of adhesion test results according to the ASTM D3359 Cross Hatch Method.

**[0020]** FIG. 4 shows the results of testing paints for Metal Adhesion according to the ASTM D3359 method.

**[0021]** FIG. 5 shows the results of testing paints for Metal Adhesion according to the ASTM D3359 method using the procedure used to obtain Fig. 4.

- [0022] FIG. 6 shows a comparison of gloss retention for paints on 50  $\mu\text{m}$  DFT on treated aluminum panels tested by the Method of ASTM G154 (using UV-A lamps).
- [0023] FIG. 7 compares the Hiding Opacity percent of paints made with the styrene acrylic latex polymer made with 2 wt. % MAA and 3 wt. % the Inventive Monomer C, as compared to a control latex made with 5 % MAA without Inventive Monomer C.
- [0024] FIG. 8 summarizes benefits from making paints with the latex emulsified with the Inventive phosphate ester composition C.
- [0025] FIG. 9 compared Inventive Paint E1 and Inventive Paint E2.
- [0026] FIG. 10 shows photographs comparing a Control Paint and an Inventive Paint.
- [0027] FIG. 11 shows gloss retention for the tested specimen coated with the Paint F2 containing Benzophenone.
- [0028] FIG. 12A shows the tested sample coated with Paint AA made with Ex. 10 Latex AA.
- [0029] FIG. 12B shows the tested sample coated with Paint BB made with Ex. 10 Latex BB.
- [0030] FIG. 12C shows the tested sample coated with Paint CC made with Ex. 10 Latex CC.

## DETAILED DESCRIPTION OF THE INVENTION

- [0031] General Definitions
- [0032] The term and phrases “invention,” “present invention,” “instant invention,” and similar terms and phrases as used herein are non-limiting and are not intended to limit the present subject matter to any single embodiment, but rather encompasses all possible embodiments as described.
- [0033] Throughout the description, including the claims, the term “a” and the phrase “at least one” are synonymous, and likewise, the phrase “comprising one” or “comprising a” should be understood as being synonymous with the term “comprising at least one,” unless otherwise specified. Additionally, “between” should be understood as being inclusive of the limits. Further, throughout the description, including the claims, the terms “comprising” and “having” can be used interchangeably, and should be understood as being synonymous.
- [0034] It should be noted that in specifying any range of concentration, weight ratio or amount, any particular upper concentration, weight ratio or amount can be associated with any particular lower concentration, weight ratio or amount, respectively.
- [0035] As used herein, the term “alkyl” or “alkyl group” means a saturated hydrocarbon radical, which may be straight, branched or cyclic, such as, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, t-butyl, pentyl, n-hexyl, cyclohexyl.
- [0036] As used herein, the term “bicyclic” or “bicyclic group” means a radical containing at least two joined rings with at least two common atoms. In certain embodiments, the bicyclic group can contain at least two rings that can be fused, bridged, or both.
- [0037] As used herein, the term “cycloalkyl” or “cycloalkyl group” means a saturated hydrocarbon radical that includes one or more cyclic alkyl rings, such as, for example, cyclopentyl, cyclooctyl, and adamantanyl.

**[0038]** As used herein, the term "hydroxyalkyl" or "hydroxyalkyl group" means an alkyl radical, more typically an alkyl radical, that is substituted with a hydroxyl groups, such as for example, hydroxymethyl, hydroxyethyl, hydroxypropyl, and hydroxydecyl.

**[0039]** As used herein, the term "alkylene" or "alkylene group" means a bivalent acyclic saturated hydrocarbon radical, including but not limited to methylene, polymethylene, and alkyl substituted polymethylene radicals, such as, for example, dimethylene, tetramethylene, and 2-methyltrimethylene.

**[0040]** As used herein, the term "alkenyl" or "alkenyl group" means an unsaturated straight chain, branched chain, or cyclic hydrocarbon radical that contains one or more carbon-carbon double bonds, such as, for example, ethenyl, 1-propenyl, 2-propenyl.

**[0041]** As used herein, the term "aryl" or "aryl group" means a monovalent unsaturated hydrocarbon radical containing one or more six-membered carbon rings in which the unsaturation may be represented by three conjugated double bonds, which may be substituted one or more of carbons of the ring with hydroxy, alkyl, alkenyl, halo, haloalkyl, or amino, such as, for example, phenoxy, phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, chlorophenyl, trichloromethylphenyl, aminophenyl.

**[0042]** As used herein, the term "aralkyl" or "aralkyl group" means an alkyl group substituted with one or more aryl groups, such as, for example, phenylmethyl, phenylethyl, triphenylmethyl.

**[0043]** As used herein, "AGE" is allyl glycidyl ether.

**[0044]** As used herein, the terminology "(C<sub>n</sub>-C<sub>m</sub>)" in reference to an organic group, wherein n and m are each integers, indicates that the group may contain from n carbon atoms to m carbon atoms per group.

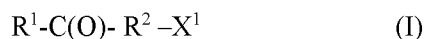
**[0045]** As used herein, the terminology "ethylenic unsaturation", "ethylenic unsaturated", or similar terms means a terminal (that is, e.g., α, β) carbon-carbon double bond.

**[0046]** As used herein, "DPUR" means dirt pick-up resistance.

**[0047]** Phosphate Ester Composition

**[0048]** In one aspect, this invention relates to a phosphate ester composition comprising:

(a) at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

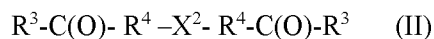
R<sup>1</sup> is an substituted or unsubstituted vinyl radical, preferably a C<sub>2</sub>-C<sub>5</sub>, more preferably a C<sub>2</sub>-C<sub>3</sub> vinyl radical, typically the vinyl radical is methyl substituted;

R<sup>2</sup> is a divalent polyoxyalkylene radical having one to five, preferably one to three, oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

X<sup>1</sup> is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1.

**[0049]** Typically the parts by weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 55:45 to 67:33, preferably from 60:40 to 67:33, furthermore preferably 64:36 to 67:33, wherein the total of the parts by weight of the polymerizable phosphate mono-ester compound and the polymerizable phosphate di-ester compound equals 100 parts by weight. For example, the parts by weight ratio range from 55:45 to 67:33 encompasses 55:45, 60:40, or 67:33. However, the parts by weight ratio range from 55:45 to 67:33 does not encompass 55:33 or 67:45.

**[0050]** The polyoxyalkylene unit can be derived from a variety of epoxyalkane compounds including ethylene oxide, propylene oxide, butylene oxide, styrene oxide, other alkyl, cycloalkyl or aryl substituted alkyl oxides or alkyl or aryl glycidyl ethers. It may additionally include hydrocarbon chain segments such as might be derived from ring opening of caprolactone by 2-hydroxyethyl methacrylate.

**[0051]** Typically  $R^1$  of the phosphate ester composition is selected from the group consisting of  $CH_2=CH-$ ,  $CH_2=C(CH_3)-$ , or  $cis-CH(COOH)=CH-$ .

**[0052]** Typically  $R^2$  of the phosphate ester composition has one to five, preferably one to three oxyethylene units.

**[0053]** Typically  $R^2$  of the phosphate ester composition has at least one oxyethylene unit.

**[0054]** Typically  $R^2$  of the phosphate ester composition has  $R^2$  has an absence of oxypropylene units.

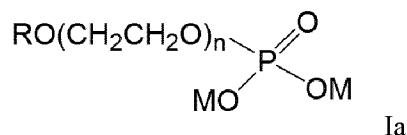
**[0055]** Typically  $R^3$  of the phosphate ester composition has is selected from the group consisting of  $CH_2=CH-$ ,  $CH_2=C(CH_3)-$ , or  $cis-CH(COOH)=CH-$ .

**[0056]** Typically  $R^4$  of the phosphate ester composition has is a divalent polyoxyalkylene radical having at least one oxyethylene unit.

**[0057]** Typically  $R^4$  of the phosphate ester composition has is a divalent polyoxyalkylene radical having one to three oxyethylene units.

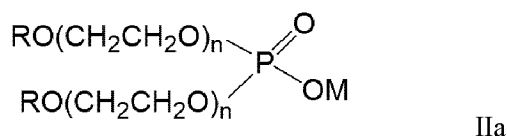
**[0058]** Preferably the polymerizable phosphate mono-ester compound or a salt thereof and the polymerizable phosphate di-ester compound or a salt thereof of the ester composition have an absence of oxypropylene units.

**[0059]** A typical polymerizable phosphate mono-ester compound of formula (I), also known as a mono alkyl phosphate (MAP), has the structural formula (Ia):



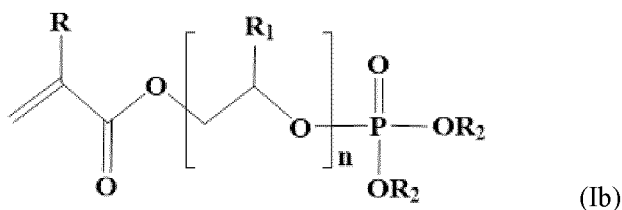
wherein R is an optionally substituted vinyl radical, preferably a C<sub>2</sub>-C<sub>5</sub>, more preferably a C<sub>2</sub>-C<sub>3</sub> vinyl radical; n is moles of ethylene oxide, M is H, NH<sub>4</sub>, Na, K.

**[0060]** A typical polymerizable phosphate di-ester compound of formula (II), also known as a dialkyl phosphate (DAP), has the structural formula (IIa):



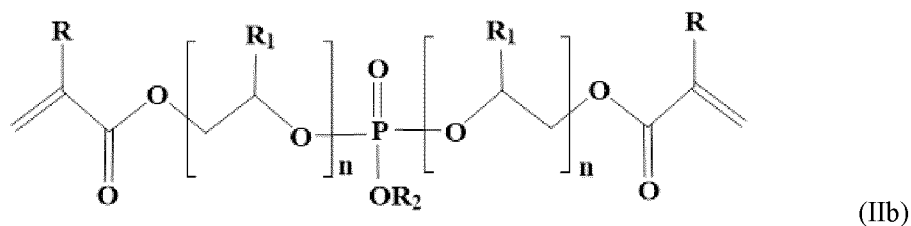
wherein R is an optionally substituted vinyl radical, preferably a C<sub>2</sub>-C<sub>5</sub>, more preferably a C<sub>2</sub>-C<sub>3</sub> vinyl radical; n is moles of ethylene oxide, M is H, NH<sub>4</sub>, K.

**[0061]** A typical polymerizable phosphate mono-ester compound of formula (I), also known as a mono alkyl phosphate (MAP), has the structural formula (Ib):



wherein R is H or Me, R<sub>1</sub> is H or Me, n is 1-5, each R<sub>2</sub> is independently H, NH<sub>4</sub>, Na, or K, typically H. Preferably, each R<sub>1</sub> is H, or at least 2 R<sub>1</sub> are H and at least one R<sub>1</sub> is Me.

**[0062]** A typical polymerizable phosphate di-ester compound of formula (II), also known as a dialkyl phosphate (DAP), has the structural formula (IIb):



wherein R is H or Me, R<sub>1</sub> is H or Me, n is 1-5, R<sub>2</sub> is H, NH<sub>4</sub>, Na, or K, typically H. Preferably, for the moiety on each side of the phosphate group each R<sub>1</sub> is H, or at least 2 R<sub>1</sub> are H and at least one R<sub>1</sub> is Me.

**[0063]** Typically ((2-methyl-1-oxopropane-1,3-diyl)bis(oxy))bis(ethane-2,1-diyl)bis(2-methacrylate) is 10 to 20 wt.%, more typically 15-20 wt% of the phosphate ester composition.

**[0064]** Typically ethylene glycol dimethacrylate is 1 to 10 wt.%, more typically 3-7 wt% of the phosphate ester composition.

**[0065]** Typically the phosphate ester composition further comprises phosphoric acid, preferably the weight ratio of the phosphoric acid to total polymerizable phosphate mono-ester compound of formula (I) and polymerizable phosphate di-ester compound of formula (II) is 10:90 to 25:75, more preferably 12:90 to 20:70.

**[0066]** The at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I) and polymerizable phosphate di-ester compound of formula (II) may be neutralized with one or more of sodium hydroxide, potassium hydroxide or ammonium hydroxide, preferably ammonium hydroxide.

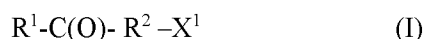
#### Method for the Production of the Above-Described Phosphate Ester Composition

**[0067]** In another aspect, this invention also provides a method for the production of the above-described phosphate ester composition having the high ratio of polyalkylene oxide (meth)acrylate polymerizable phosphate mono-ester to polyalkylene oxide (meth)acrylate polymerizable phosphate di-ester.

**[0068]** The polymerizable phosphate mono-ester compound and polymerizable phosphate di-ester compound can be made by different routes. For example, a preferred polymerizable phosphate mono- or di-ester compound wherein X is a phosphate  $-\text{OPO}_3\text{H}_2$  group can be made by phosphorylation of the product of esterification of a polyalkylene glycol with a vinyl-functional carboxylic acid, or anhydride or acid halide thereof. The phosphorylation may be conducted as disclosed in US Patents 5,463,101, 5,550,274 and 5,554,781, as well as in EP Patent publication number EP 0 675,076 A2. A polymerizable phosphate mono- or di-ester compound wherein X is a sulfate  $-\text{OSO}_3\text{H}_2$  group or sulfonate  $-\text{SO}_3\text{H}$  group can be made by sulfating one of the hydroxyl groups of a polyalkylene glycol, or replacing said hydroxyl group with a sulfonate group, and then esterifying the remaining hydroxyl group of said polyalkylene glycol with a vinyl-functional carboxylic acid, or anhydride or acid halide thereof.

**[0069]** In particular, the present invention relates to a method for the production of the phosphate ester composition comprising:

(a) at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

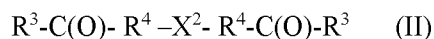
$\text{R}^1$  is an substituted or unsubstituted vinyl radical, preferably a  $\text{C}_2\text{-C}_5$ , more preferably a  $\text{C}_2\text{-C}_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$\text{R}^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three, oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$\text{X}^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the weight ratio of the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1; and

said method comprising the steps of:

A) preparing a phosphoric acid-alcohol reactant solution by

i) dissolving in a reactor:

a) from about 75 weight % to about 117 weight % phosphoric acid or polyphosphoric acid in

b) at least one alcohol medium of the formula  $R^1-C(O)-R^2-O-H$ , wherein  $R^1$  and  $R^2$  are as defined above, for example hydroxyethyl methacrylate, under essentially non-reactive temperature conditions;

B) then

ii) blending a stoichiometrically effective amount of phosphoric anhydride into said reactant solution and

iii) reacting the phosphoric acid in said reactant solution with the stoichiometrically effective amount of phosphoric anhydride; and

C) reacting the phosphorylation reagent so produced with the alcohol medium, typically at from about 75 °C. to about 100 °C. for a reaction hold time of from about 4 to about 20 hours. Following the hold, typically adding deionized water to the reactor to hydrolyze any residual pyrophosphates, followed by an additional 1-4 hour hold, and then cooling. To inhibit unwanted homopolymerization, methoxyhydroquinone (MEHQ) or other suitable inhibitor may be charged to the reactor and allowed to dissolve in the reactant solution.

**[0070]** For the purposes of the present description, the term stoichiometrically effective amount of phosphoric anhydride means an amount sufficient, in combination with the other ingredients, to make the phosphate ester composition.

**[0071]** Typically the parts by weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 55:45 to 67:33, preferably from 60:40 to 67:33, furthermore preferably 64:36 to 67:33, wherein the total of the parts by weight of the polymerizable phosphate mono-ester compound and the polymerizable phosphate di-ester compound equals 100 parts by weight. For example, the parts by weight ratio range from 55:45 to 67:33 encompasses 55:45, 60:40, or 67:33. However, the parts by weight ratio range from 55:45 to 67:33 does not encompass 55:33 or 67:45.

**[0072]** Preferably the polymerizable phosphate ester composition has a residual of the phosphoric acid wherein the weight ratio of the phosphoric acid to total polymerizable phosphate mono-ester compound of formula (I) and polymerizable phosphate di-ester compound of formula (II) is 10:90 to 25:75, typically 10:90 to 20:80, more typically 10:90 to 18:82, for example 11:89-16:84. For example, the polymerizable phosphate ester composition has a residual of the phosphoric acid is 10-16 wt.% of the polymerizable phosphate ester composition.

**[0073]** Preferably the polymerizable phosphate ester composition has a residual of the alcohol which is less than 6 weight percent of the polymerizable phosphate ester composition.

**[0074]** Preferably the polymerizable phosphate mono-ester compound or a salt thereof and the polymerizable phosphate di-ester compound or a salt thereof have an absence of oxypropylene units.

**[0075]** The polymerizable phosphate mono-ester compounds and the polymerizable phosphate di-ester compounds act as polymerizable “monomers”. These monomers can be used in acid and basic form. For the basic form sodium hydroxide or potassium hydroxide or ammonium hydroxide are typically used for the neutralization.

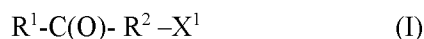
**[0076]** Polymer Composition Comprising Units From the Above-Described Polymerizable Phosphate Mono-Ester Compound and Polymerizable Phosphate Di-Ester Compound

**[0077]** The invention also relates to a polymer composition comprising units from the above-described polymerizable phosphate mono-ester compound and polymerizable phosphate di-ester compound.

**[0078]** In particular, the invention provides a polymer composition comprising monomeric units from:

(A) the at least one polymerizable phosphate mono-ester compound or salt thereof and the at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition as described in this specification comprising:

(a) the at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

$R^1$  is a substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, preferably the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) the at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is a substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt,

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1; and

(B) at least one other polymerizable monomer.

**[0079]** Typically the parts by weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 55:45 to 67:33, preferably from 60:40 to 67:33, furthermore preferably 64:36 to 67:33, wherein the total of the parts by weight of the polymerizable phosphate mono-ester compound and the polymerizable phosphate di-ester compound equals 100 parts by weight. For example, the parts by weight ratio range from 55:45 to 67:33 encompasses 55:45, 60:40, or 67:33. However, the parts by weight ratio range from 55:45 to 67:33 does not encompass 55:33 or 67:45.

**[0080]** The mixture typically further comprises a surfactant, wherein the composition comprises 0.5 to 3 wt.% said surfactant based on total monomer including the polymerizable phosphate mono-ester compound, polymerizable phosphate di-ester compound, and other polymerizable monomer. The surfactant is preferably anionic surfactant, more preferably a phosphate ester anionic surfactant. The polymer composition is typically an emulsion polymer composition.

**[0081]** The other polymerizable monomer is preferably one or more (co)polymerizable monomers comprising acrylate monomers, styrene monomers, vinyl ester monomers, butadiene, ethylene, or vinyl chloride.

**[0082]** The other polymerizable monomer is typically selected from methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate, 2-ethyl hexyl acrylate, other acrylates, methacrylates and their blends,

acrylic acid, methacrylic acid, cyclohexyl methacrylate, styrene, vinyl toluene, vinyl acetate, vinyl esters, e.g. vinyl versatate, acrylonitrile, acrylamide, butadiene, ethylene, vinyl chloride and the like, and mixtures thereof.

**[0083]** The invention may also provide a waterborne coating comprising the polymer composition.

**[0084]** The invention may also provide a method of improving the corrosion resistance of a metal substrate comprising contacting at least a portion of the surface of the metal substrate with the coating composition, wherein the coating composition comprises the polymer composition, compared to coating the metal substrate with a coating composition which is the same but does not include monomeric units from said polymerizable phosphate mono-ester compound or a salt thereof and said polymerizable phosphate di-ester compound or a salt thereof.

**[0085]** The invention may also provide a method of improving the water resistance of a coating composition to a substrate comprising contacting at least a portion of the surface of the substrate with the coating composition, wherein the coating composition comprises the polymer composition, compared to coating the substrate with a coating composition which is the same but does not include monomeric units from said polymerizable phosphate mono-ester compound or a salt thereof and said polymerizable phosphate di-ester compound or a salt thereof.

**[0086]** The invention may also provide a method of improving any one or more of gloss, gloss retention, and hiding of a coating composition on a substrate comprising contacting at least a portion of the surface of the substrate with the coating composition, wherein the coating composition comprises the emulsion polymer composition, compared to coating the substrate with a coating composition which is the same but does not include monomeric units from said polymerizable phosphate mono-ester compound or a salt thereof and said polymerizable phosphate di-ester compound or a salt thereof.

**[0087]** The invention may also provide a method of improving the adhesion of a coating composition to a metal substrate comprising contacting at least a portion of the surface of the substrate with the coating composition, wherein the coating composition comprises the polymer composition. The substrate is typically a metal, for example, aluminum, steel or galvanized steel.

**[0088]** The invention may also provide a method of improving the adhesion of a coating composition intended to be coated to a metal substrate comprising contacting at least a portion of the surface of the substrate with a coating composition, called conversion coating, wherein the conversion coating comprises the polymer composition of the invention. The substrate is typically a metal, for example, aluminum, steel or galvanized steel.

**[0089]** As mentioned above the invention relates to different methods of improving some properties of the substrate thanks to the coating composition of the invention.

**[0090]** In some of these situations, the coating composition of the invention may be used as an undercoat or under layer in a pre-treatment of the substrate, and is called “conversion coating”, because the polymer reacts with the metal and adheres to it, thereby improving the properties, such as the corrosion resistance of the substrate and/or the adhesion of a coating composition to be applied thereafter, over the conversion coating.

**[0091]** According to an embodiment, the conversion coating is applied on the metal surface to be treated, by reaction of said surface with the corresponding conversion composition (in other words, the conversion composition is applied on the metal surface for forming a conversion coating thereon).

**[0092]** Contacting the metal surface with the conversion coating may be made by any means known per se, such as dip coating in a conversion bath or spray coating for example.

**[0093]** The coating composition of the invention may thus be used both as a conversion coating (in a pre-treatment) and as a coating composition (such as a paint, a varnish or an adhesive) to treat the same substrate.

**[0094]** When the coating composition is used as a conversion coating, the latter is first applied on the metal surface of the substrate. A coating composition including the polymer composition (the same or different but still according to the invention) is then applied on the pretreated substrate. In other words, the polymer composition of the invention is used both in the conversion coating and in the coating composition applied on the conversion coating.

**[0095]** The material obtained comprises a metal surface which covered by:

- a first layer comprising a conversion coating, and
- a second layer comprising a coating composition, in particular a paint, a varnish or an adhesive.

**[0096]** An additional layer may be applied between the treated metal surface and the coating. This is for example the case for the treatment of metal foil on a first site, that have then to be coated, for example painted, on a second site: in that case, a lubricant may be applied on the treated foil, in order to allow to roll the foil and ease its transportation.

**[0097]** Any metal surface may be treated with the conversion composition of the invention, but the invention is especially suitable for treating metal surfaces of:

- aluminum or an aluminum-based alloy ; or
- steel, for example galvanized steel (hot dip galvanized HDG or electrogalvanized EG) ; or cold rolled steel (CRS) ; or
- magnesium or magnesium-based alloys ; or
- zinc or zinc-based alloys,
- titanium or titanium-based alloys.

**[0098]** The invention is especially interesting for metal surface of aluminum and aluminum alloys, such as Aluminum Alloy AA 5005 tested in the appended examples, or other alloys such as those of Series 1xxx, 2xxx, 3xxx, 4xxx, 5xxxx, 6xxx, such as AA1050, 2024, 3003, 5182, 5754, 6111, 6016, 6060, 6063, 6182, 7075.

**[0099]** The conversion composition used according to the invention may typically contain fluorides anions and cationic metals, e.g. compounds such as  $\text{H}_2\text{CrF}_6$ , or more preferably chromium free compounds such as  $\text{H}_2\text{TiF}_6$ ,  $\text{H}_2\text{ZrF}_6$ ,  $\text{H}_2\text{HfF}_6$ ,  $\text{H}_2\text{AlF}_6$ ,  $\text{H}_2\text{SiF}_6$ ,  $\text{H}_2\text{GeF}_6$ ,  $\text{H}_2\text{SnF}_4$ ,  $\text{HBF}_4$ , or  $\text{TiZr}$ .

**[00100]** The conversion composition may also include other compounds, such as silane precursors for example, and/or cerium salts, and/or terbium molybdate.

**[00101]** The invention also relates to a method of treating a first metal surface S1 of a first substrate intended to be bonded to a second surface S2 of a second substrate by adhesive bonding, and of imparting a resistance to the adhesive failure to the bonding, said method comprising contacting at least a portion of the first metal surface S1 with the coating composition.

**[00102]** An additional advantage of the adhesive bonding obtained according to the invention is that it is highly resistant to corrosive atmospheres and to wet atmospheres, which lead to long lasting adhesive bonding. In most cases, the coating composition is also used for obtaining this additional effect (namely for further imparting to the bonding a resistance to corrosive atmospheres and to wet atmospheres, in other words for obtaining both a very effective, but also long lasting adhesion). In other words, this method also provides a very good resistance to ageing of the adhesive bonding. Such a property can be measured according to tensile tests on so-called “Single Lap Shear” (SLS) assemblies, such as defined in ASTM D-1002 10, performed on freshly bonded SLS assemblies and performed on SLS assemblies after ageing in corrosive atmospheres, wet atmospheres, or repeated cycles of corrosive atmospheres followed by wet atmospheres, such as ASTM G85 A3. Other tests simultaneously combine a corrosion stress and a mechanical stress (eg compression load), such as the Bv 101-07, known as Ford Durability Stress Test For Adhesive Lap-shear Bonds or Arizona Proven Ground Exposure (APGE).

**[00103]** Preferably, the metal surface S1 is a surface comprising a metal selected from aluminum, steel, zinc, magnesium titanium, copper and their alloys, or cobalt-nickel alloys.

**[00104]** The metal surface S1 is preferably made of:

- aluminum or an aluminum-based alloy ; or
- steel, for example galvanized steel (hot dip galvanized HDG or electrogalvanized EG) ; or cold rolled steel (CRS) ; or
- magnesium or magnesium-based alloys ; or
- zinc or zinc-based alloys,
- titanium or titanium-based alloys.

**[00105]** The invention is especially interesting for metal surface of aluminum and aluminum alloys, such as Aluminum Alloy AA 5005 tested in the appended examples, or other alloys such as those of Series 1xxx, 2xxx, 3xxx, 4xxx, 5xxxx, 6xxx, such as AA1050, 2024, 3003, 5182, 5754, 6111, 6016, 6060, 6063, 6182, 7075.

**[00106]** Preferably, the second surface S2 is a metal surface. The second surface S2 may, however, be a non-metal surface, for example a plastic surface or a composite surface.

**[00107]** According to an embodiment, the second surface S2 is a surface comprising a metal, advantageously selected from aluminum, steel, zinc, magnesium titanium, copper and their alloys, or cobalt-nickel alloys.

**[00108]** According to one embodiment, the nature of the surfaces S1 and S2 is the same, but they can also be distinct according to other possible embodiments of the invention. According to a variant, both surfaces S1 and S2 are metal surface of aluminum or aluminum alloys.

**[00109]** According to another possible embodiment, the second surface S2 is a non-metallic surface, for example a plastic surface e.g. based on polyamide, polyether ether ketone (PEEK) or acrylonitrile butadiene styrene (ABS); or a composite surface based, e.g., on Carbon Fiber Reinforced Plastics (CFRP) or Glass Fiber Reinforced Plastics.

**[00110]** Typically, but not necessarily, the second surface S2 is also a metal surface, having or not the same nature as the first surface S1. According to an advantageous embodiment, the second surface S2 is a metal surface also treated with a coating composition, generally but not necessarily identical to the coating composition used in the treatment of the first surface S1.

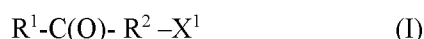
**[00111]** More generally, the polymer coating used in the method according to the invention is preferably used for treating both surfaces S1 and S2 before the adhesive bonding of the two surfaces, especially when S2 is a metal surface.

**[00112]** Method of Making the Above-described Polymer

**[00113]** In another aspect, this invention relates to a method of making the above-described polymer comprising the steps of:

combining:

(A) at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

$R^1$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three, oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1, and

(B) at least one other polymerizable monomer to form a mixture; and

polymerizing the at least one polymerizable phosphate mono-ester compound or salt thereof and the at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition and the at least one other polymerizable monomer.

**[00114]** Typically the parts by weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 55:45 to 67:33, preferably from 60:40 to 67:33, furthermore preferably 64:36 to 67:33, wherein the total of the parts by weight of the polymerizable phosphate mono-ester compound and the polymerizable phosphate di-ester compound equals 100 parts by weight. For example, the parts by weight ratio range from 55:45 to 67:33 encompasses 55:45, 60:40, or 67:33. However, the parts by weight ratio range from 55:45 to 67:33 does not encompass 55:33 or 67:45.

**[00115]** Typically combining (A) the phosphate ester composition of the invention, and (B) at least one other polymerizable monomer to form a mixture, wherein the weight ratio of phosphate ester monomers to the at least one other polymerizable monomer is typically 1-10:99-90, more typically 1-5:99-95, wherein the total of the parts by weight of the phosphate ester monomers and the at least one other polymerizable monomer equals 100 parts by weight. Thus, a parts by weight ratio of 1-10:99-90 means 1-10 parts by weight phosphate ester monomers per 100 parts by weight of total monomers of phosphate ester monomers and the at least one other polymerizable monomer.

**[00116]** Typically the mixture further comprises phosphoric acid, preferably wherein the weight ratio of the phosphoric acid to total polymerizable phosphate mono-ester compound of formula (I) and polymerizable phosphate di-ester compound of formula (II) 10:90 to 25:75, preferably 12:88 to 20:80.

**[00117]** Preferably the polymerizable phosphate mono-ester compound or a salt thereof and the polymerizable phosphate di-ester compound or a salt thereof produced by the method have an absence of oxypropylene units.

**[00118]** The phosphate ester may be neutralized with (NH<sub>4</sub>)OH, KOH, or NaOH to convert some phosphate ester to salt.

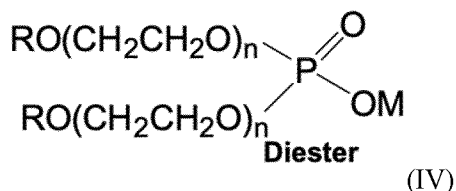
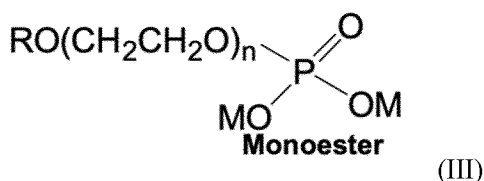
**[00119]** The polymerizable phosphate mono-ester compounds and phosphate di-ester compounds are ethylenically unsaturated monomers and, thus, are polymerizable through this unsaturation. The monomer may be useful in a variety of homopolymers and copolymers, e.g. those produced by solution, bulk or suspension polymerization, but should be most useful as a comonomer in the production of latices of low crosslinking density through emulsion polymerization. Emulsion polymerization is discussed in G. Pohlein, "Emulsion Polymerization", Encyclopedia of Polymer Science and Engineering, vol. 6, pp. 1-51 (John Wiley & Sons, Inc., NY, NY, 1986), the disclosure of which is incorporated herein by reference. Emulsion polymerization is a heterogeneous reaction process in which unsaturated monomers or monomer solutions are dispersed in a continuous phase with the aid of an emulsifier system and polymerized with

free-radical or redox initiators. The product, a colloidal dispersion of the polymer or polymer solution, is called a latex.

**[00120]** The mixture typically further comprises a surfactant, wherein the composition comprises 0.5 to 3 wt.% said surfactant based on total monomer including the polymerizable phosphate monoester compound, polymerizable phosphate di-ester compound, and other polymerizable monomer. The surfactant is preferably anionic surfactant, more preferably a phosphate ester anionic surfactant. The polymer composition is typically an emulsion polymer composition.

**[00121]** Suitable surfactants which may be used with the polymerizable phosphate mono-ester compound and polymerizable phosphate di-ester compound include ionic and nonionic surfactants such as alkyl polyglycol ethers such as ethoxylation products of lauryl, tridecyl, oleyl, and stearyl alcohols; alkyl phenol polyglycol ethers such as ethoxylation products of octyl or nonylphenol, diisopropyl phenol, triisopropyl phenol; alkali metal or ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates, and the like, including sodium lauryl sulfate, sodium octylphenol glycoether sulfate, sodium dodecylbenzene sulfonate, sodium lauryldiglycol sulfate, and ammonium tritertiarybutyl phenol and penta- and octa-glycol sulfonates, sulfosuccinate salts such as disodium ethoxylated nonylphenol half ester of sulfosuccinic acid, disodium n-octyldecyl sulfosuccinate, sodium dioctyl sulfosuccinate, and the like. Preferably the surfactant is anionic surfactant, most preferably phosphate ester anionic surfactant.

**[00122]** Typical phosphate ester surfactants have the structures (III) and (IV):



wherein R is an alkyl group, typically C10-20 alkyl, preferably C12-C16;

n is moles of ethylene oxide, typically n is 4-20; and

M is H, Na, K, or NH<sub>4</sub>.

**[00123]** The comonomers which are typically employed include such monomers as methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate, 2-ethyl hexyl acrylate, other acrylates, methacrylates and their blends, acrylic acid, methacrylic acid, cyclohexyl methacrylate, styrene, vinyl toluene, vinyl acetate, vinyl esters, e.g., vinyl versatate, acrylonitrile, acrylamide, butadiene, ethylene, vinyl chloride and the like, and mixtures thereof. Typical polymers (copolymers) are any such as styrene, methylmethacrylate, methacrylic acid, cyclohexyl methacrylate, ethylhexyl acrylate, and/or acetoacetoxyethyl methacrylate.

**[00124]** The polymerization method may be by emulsion polymerization. In the above method, suitable initiators, reducing agents, catalysts and surfactants are well known in the art of emulsion polymerization. Typical initiators include ammonium persulfate (APS), hydrogen peroxide, sodium, potassium or ammonium peroxydisulfate, dibenzoyl peroxide, lauryl peroxide, ditertiary butyl peroxide, 2,2'-azobisisobutyronitrile, t-butyl hydroperoxide, benzoyl peroxide, and the like.

**[00125]** Suitable reducing agents are those which increase the rate of polymerization and include for example, sodium bisulfite, sodium hydrosulfite, sodium formaldehyde sulfoxylate, ascorbic acid, isoascorbic acid, and mixtures thereof.

**[00126]** Suitable catalysts are those compounds which increase the rate of polymerization and which, in combination with the above-described reducing agents, promote decomposition of the polymerization initiator under the reaction conditions. Suitable catalysts include transition metal compounds such as, for example, ferrous sulfate heptahydrate, ferrous chloride, cupric sulfate, cupric chloride, cobalt acetate, cobaltous sulfate, and mixtures thereof.

**[00127]** A typical method of emulsion polymerization preferably involves charging water to a reactor and feeding as separate streams a pre-emulsion of the monomers and a solution of the initiator. A small amount of the pre-emulsion and a portion of the initiator may be charged initially at the reaction temperature to produce a "seed" latex. The "seed" latex procedure results in better particle-size reproducibility. Under "normal" initiation conditions, that is initiation conditions under which the initiator is activated by heat, the polymerization is normally carried out at about 60-90°C. A typical "normal" initiated process, for example, could employ ammonium persulfate as initiator at a reaction temperature of 80±2°C. Under "redox" initiation conditions, that is initiation conditions under which the initiator is activated by a reducing agent, the polymerization is normally carried out at 60-70°C. Normally, the reducing agent is added as a separate solution. A typical "redox" initiated process, for example, could employ potassium persulfate as the initiator and sodium metabisulfite as the reducing agent at a reaction temperature of 65 ± 2°C.

**[00128]** In the above emulsions, the polymer preferably exists as a generally spherical particle, dispersed in water, with a diameter of about 50 nanometers to about 500 nanometers. Gel content can be determined using the method taught in U.S. Pat. No. 5,371,148, incorporated herein by reference. Glass transition temperature ( $T_g$ ) is a calculated number based on the proportion of each monomer utilized and the corresponding  $T_g$  for a homopolymer of such a monomer. In addition to making emulsion polymers, it is contemplated that the polymerizable surfactants of the present invention can be used to form solution copolymers.

**[00129]** In particular, the phosphate mono-ester compounds and phosphate di-ester compounds of this invention may be incorporated in effective amounts in aqueous polymer systems, for example paints, to enhance the stability of emulsions of the polymers. The commonly used monomers in making acrylic

paints are butyl acrylate, methyl methacrylate, ethyl acrylate, cyclohexyl methacrylate and the like. In acrylic paint compositions the polymer is comprised of one or more esters of acrylic or methacrylic acid, typically a mixture, e.g. about 50/50 by weight, of a high  $T_g$  monomer (e.g. methyl methacrylate) and a low  $T_g$  monomer (e.g. butyl acrylate), with small proportions, e.g. about 0.5% to about 2% by weight, of acrylic or methacrylic acid. The vinyl-acrylic paints usually include vinyl acetate and butyl acrylate and/or 2-ethyl hexyl acrylate and/or vinyl versatate. In vinyl-acrylic paint compositions, at least 50% of the polymer formed is comprised of vinyl acetate, with the remainder being selected from the esters of acrylic or methacrylic acid. The styrene/acrylic polymers are typically similar to the acrylic polymers, with styrene substituted for all or a portion of the methacrylate monomer thereof. The phosphate mono-ester compounds and phosphate di-ester compounds of this invention may copolymerize with the typical monomers used to make latex for paint to produce paints having enhanced stability and adhesion to surfaces.

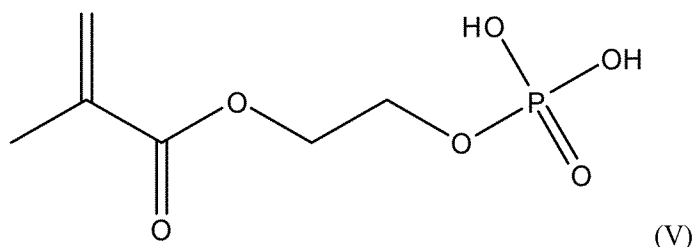
#### Example 1

##### **[00130] MAKING THE INVENTIVE PHOSPHATE MONOMER MIXTURE**

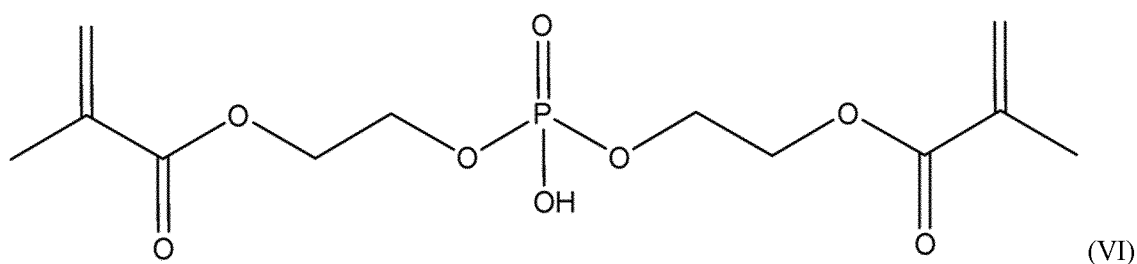
**[00131]** A 500 mL round bottom, 4-neck flask was fitted with a thermocouple, paddle stirrer, pressure equalizing addition funnel and two-head CLAISEN adapter with a dry air needle inlet and a water condenser venting to silicone oil filled bubbler. The flask was charged with 214.72g of hydroxyethyl methacrylate. Stirring and a slow flow (20ml/min) of subsurface dry air into the liquor were initiated. To inhibit unwanted homopolymerization, 1.75g of methoxyhydroquinone (MEHQ) was charged to the reactor and allowed to completely dissolve. The addition funnel was charged with 61.14g of 105 % polyphosphoric acid, followed by controlled addition over 35 minutes, during which the liquor temperature increased from 35°C to 42°C. The liquid addition funnel was replaced by an auger-type powder addition funnel containing 70.64g of phosphoric anhydride, which was slowly charged over 2.5 hours with a maximum reaction temperature of 55°C. The liquor temperature was increased to 80°C and maintained for 18 hours. Following the hold, 1.75g of deionized water was charged to the reactor to hydrolyze any residual pyrophosphates, followed by an additional 2 hour hold. The reaction mass was cooled and bottled as is.

**[00132]** The inventive specialty monomer composition contained a first monomer mono-ester phosphate (MAP), a second monomer di-ester phosphate (DAP), residual alcohol, and residual phosphoric acid.

**[00133]** The mono-ester phosphate was Ethylene glycol methacrylate phosphate having the structural formula (V):



**[00134]** The di-ester phosphate was Bis(ethylene glycol methacrylate) phosphate having the structural formula (VI):



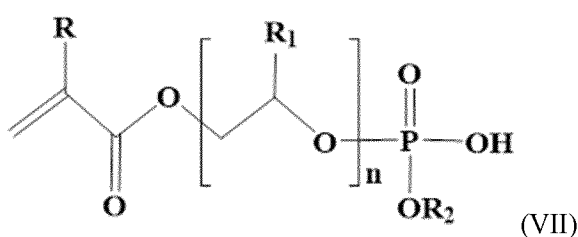
**[00135]** The average MAP:DAP molar ratio of the five samples of the Inventive Monomer C produced was 74.4:25.6. The average MAP (Ethylene glycol methacrylate phosphate):DAP (Bis(ethylene glycol methacrylate) phosphate) weight ratio of the five samples of the Inventive Monomer C produced was 65.4:34.6.

**[00136]** Example 2

**[00137]** This example compared an Inventive Coating C, including an Inventive Latex Polymer C made using an Inventive phosphate ester composition C, to comparative coatings.

**[00138]** The comparative coatings were a Comparative Coating A made with a Comparative Latex Polymer A made using Comparative Phosphate ester composition A or Comparative Coating B made using Comparative Latex Polymer B made using Comparative Phosphate ester composition B.

**[00139]** The Phosphate ester compositions had the formula (VII):



**[00140]** The Comparative Phosphate ester composition A had R = Methyl group; R<sub>1</sub> = H; n = 1; the ratio of Phosphate monoester and Phosphate diester was a 60:40 molar ratio; 1:1 mass ratio.

**[00141]** The Comparative Phosphate ester composition B had R = Methyl group; R<sub>1</sub> = Methyl group; n = 5; the ratio of Phosphate monoester and diester was a 13:1 molar ratio, 88:12 mass ratio (7.33:1 mass ratio).

**[00142]** The Inventive Phosphate ester composition C had R = Methyl group; R<sub>1</sub> = H; n = 1; the average ratio of the Phosphate mono and Phosphate diester of the five samples was 74.4:25.6 molar ratio,

65.4:34.6 mass ratio (1.89:1 mass ratio). The range of mass ratios for the five Inventive Monomer C samples was 1.82-1.98:1.

**[00143]** This example demonstrates that the Inventive Comparative Phosphate ester composition C of Example 1 stabilizes a pre-emulsion of monomers such as styrene, methyl methacrylate (MMA), 2-Ethylhexyl Acrylate (2HEA), and methacrylic acid (MAA).

**[00144]** The recipe for the pre-emulsion is shown in Table 1.

Table 1 – Pre-emulsification of Monomer Blend for Inventive Latex Polymer C

| Material Name*                             | Weight (g) | Solids, weight (g) |
|--------------------------------------------|------------|--------------------|
| styrene (STY)                              | 179.7      | 179.7              |
| methyl methacrylate (MMA)                  | 100        | 100                |
| 2-Ethylhexyl Acrylate (2HEA)               | 125        | 125                |
| methacrylic acid (MAA)                     | 13         | 13                 |
| Inventive phosphate ester composition C ** | 8.6        | 8.6                |
| Deionized Water**                          | 150        |                    |
| 1-dodecanethiol                            | 1.6        | 1.6                |
| Rhodafac RS 710 K25                        | 10         | 2.5                |

\* Monomer composition: STY/MMA/2EHA/MMA/Specialty monomer in a 42.2/23.5/29.3/3.0/2.0 weight ratio.

\*\* Monomer composition was dispersed in water at 50/50 weight ratio, and neutralized to pH = 7 by concentrated ammonia. The total PEMA amount is 2.0% based on total monomer (BOTM).

**[00145]** The Pre-emulsification of the Monomer Blend for Inventive Latex Polymer C was combined with emulsifier in an amount of 1.0 wt.% BOTM (based on total materials). The emulsifier was RHODAFAC RS 710 K25 phosphated anionic surfactant (potassium salt) which is APE (alkyl phenol ethoxylate)-free.

**[00146]** A small lab homogenizer (ULTRA-TURRAX T25 Homogenizer by IKA-Labortechnik), was used and a stable pre-emulsion was obtained which was useful for emulsion polymerization (>3 hours without separation). Some specialty monomer composition is still needed for the nucleation step. In the initial charge 0.2 % BOTM of the specialty monomer composition was used. The complete list of ingredients is given in Table 2. The pre-emulsion containing the Inventive phosphate ester composition C was then used to make the Inventive Latex Polymer C.

Table 2 - Emulsion Polymerization Ingredients to Make Inventive Latex Polymer C

| A. Kettle charge                                | Weight, g | Solids weight, g |
|-------------------------------------------------|-----------|------------------|
| Deionized (DI) Water                            | 360       |                  |
| Phosphate ester Emulsifier (Rhodafac RS710 K25) | 7.0       | 1.75             |
|                                                 |           |                  |
| B. Monomer emulsion*                            |           |                  |
| STY                                             | 179.7     | 179.7            |

|                                                  |      |        |
|--------------------------------------------------|------|--------|
| MAA                                              | 13   | 13     |
| 2EHA                                             | 125  | 125    |
| MMA                                              | 100  | 100    |
| Inventive phosphate ester composition C          | 8.6  | 8.6    |
| DI Water*                                        | 150  |        |
|                                                  |      |        |
| Phosphate ester Emulsifier (Rhodafac RS 710 K25) | 10   | 2.5    |
| 1-dodecanethiol                                  | 1.6  | 1.6    |
|                                                  |      |        |
| C. Initiator solution                            |      |        |
| Ammonium persulfate (APS)                        | 1.6  | 1.6    |
| DI Water                                         | 10   |        |
|                                                  |      |        |
| D. Initiator solution                            |      |        |
| Ammonium persulfate (APS)                        | 0.5  | 0.5    |
| DI Water                                         | 70   |        |
|                                                  |      |        |
| Total                                            | 1037 | 434.25 |
|                                                  |      |        |
| Theoretical % Solids: 40.65 wt%                  |      |        |

**[00147]** Procedure to make an Inventive Polymer made using Inventive phosphate ester composition C:

1. Heat the kettle charge to 78-80 °C; Add Initiator solution C and 29.4 g of Monomer emulsion B (5%); Hold the temperature at 80 °C for 15 minutes.
2. Add the remainder D and B over 3 hrs. Keep 80°C during the addition.
3. After the addition is completed, hold at 80 °C for 60 minutes.
4. Cool down to room temperature and adjust the pH to 8.0 using 28% ammonia solution.

**[00148]** The emulsification of the Monomer Blend for Inventive Latex Polymer C resulted in a styrene acrylic latex polymer having the following properties:

**[00149]** a glass transition temperature  $T_g$  of about 36°C . For purposes of this description  $T_g$  is calculated by the Fox equation (1):

$$1 / T_{g,mix} \approx \sum_i \omega_i / T_{g,i} \quad (1)$$

where  $T_{g,mix}$  and  $T_{g,i}$  are the glass transition temperature of the mixture / copolymer and of the components, respectively, and  $\omega_i$  is the mass fraction of component  $i$ . For two components A and B, the Fox equation reduces to the simplified Fox equation (2) used to calculate  $T_g$ :

$$1 / T_{g,mix} \approx \omega_A / T_{g,A} + \omega_B / T_{g,B} \quad (2).$$

**[00150]** Particle size of 100 to about 120 nm, Latex particle size measurements are generally conducted by dynamic light scattering (DLS) which arrive at substantially the same results (within 1 %). The particle size in the present disclosure is the “Z average”, unless otherwise indicated. The Z average is the intensity weighted mean hydrodynamic size of the ensemble collection of particles measured by dynamic light scattering (DLS). The Z average is derived from a Cumulants analysis of the measured

correlation curve, wherein a single particle size is assumed and a single exponential fit is applied to the autocorrelation function. Particle size can also be determined by electron microscopy.

**[00151]** 40.0 % solids (is this wt.%), and

**[00152]** has a pH of about 7.0 to about 8.0.

**[00153] Example 3 - Paint manufacture**

**[00154]** This example prepared the paints for comparing the properties for Direct to Metal (DTM) application of the following:

**[00155]** Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 2 wt% Inventive phosphate ester composition C and 3 wt% MAA;

**[00156]** Paint A formulated with Comparative Latex Polymer A made with 2 wt% phosphate ester composition A and 3% MAA;

**[00157]** Paint B formulated with Comparative Latex Polymer B made with 2 wt% phosphate ester composition B and a 3 wt% MAA; and

**[00158]** Paint D formulated with Comparative Latex Polymer D made with 5 % MAA and no Inventive phosphate ester composition C.

**[00159]** The latex of the paints being the above-described styrene acrylic latex having Tg of about 36°F in the paint formulation of 18PVC/ 36 % VS / about 150 g/l VOC.

**[00160]** By NMR, the average proportion of MAP : DAP in Inventive phosphate ester composition C was measured to have a MAP:DAP 74.4 : 25.6 ( $\pm 0.7$ ) mol. %; 65.4 : 34.6 ( $\pm 0.8$ ) wt. %. DAP was Ethylene glycol methacrylate phosphate. MAP was Bis(ethylene glycol methacrylate) phosphate. The Inventive phosphate ester composition C contained phosphoric acid in a range of 11.4 to 16.0 wt. %.

**[00161]** By NMR, the average proportion of MAP : DAP in Comparative phosphate ester composition A was measured to have a MAP:DAP molar ratio of: 60.4 : 39.6; and a MAP:DAP weight ratio of 49.8 : 50.2 wt. %. MAP was Ethylene glycol methacrylate phosphate. DAP was Bis(ethylene glycol methacrylate) phosphate. The Comparative phosphate ester composition A contained phosphoric acid in a range of 2.5 to 2.8 wt. %.

**[00162]** By NMR, the average proportion of MAP : DAP in Comparative phosphate ester composition B was measured to have a MAP:DAP molar ratio of about 93.2 : 6.8; and a MAP:DAP mass ratio of about 88.5 : 11.5.

**[00163]** The paints had the composition listed in Table 3.

| Table 3 – Paint Composition |                     |                    |
|-----------------------------|---------------------|--------------------|
| Materials                   |                     | Weight             |
| Grind                       |                     | 50.5% Latex solids |
| Water                       |                     | 62.3               |
| DOWANOL DPM                 | Coalescing agent    | 20                 |
| RHODOLINE 111               | Dispersing agent    | 9                  |
| TEGO AIREX 902W             | Defoamer            | 1                  |
| BYK348                      | Wetting agent       | 2                  |
| Ammonium Hydroxide (28%)    | Neutralizer         | 0.7                |
| Ti-Pure R-706               | Pigment             | 205                |
| Grind Sub-total             |                     | 300                |
| Let down                    |                     |                    |
| Latex (50.5%)               |                     | 491                |
| Water                       |                     | 140.5              |
| TEXANOL                     | Coalescing agent    | 37.5               |
| Sodium Nitrite (15%)        | Anti-rust additives | 9                  |
| TEGO AIREX 902W             | Defoamer            | 1                  |
| Ammonium Hydroxide (28%)    | Neutralizer         | 1 (as needed)      |
| Water                       |                     | 17.5               |
| ACRYSOL RM-8W               | Thickener           | 2.5                |
| Letdown Sub-total           |                     | 700                |
| Total                       |                     | 1000               |

**[00164]** The paints had the composition listed in Table 4.

| Table 4 - Paint Properties       |          |
|----------------------------------|----------|
| Weight Solids, %                 | 46%      |
| Volume Solids, %                 | 35%      |
| PVC, %*                          | 18%      |
| VOC, g/L**                       | 150      |
| Target KU                        | 90 - 100 |
| ~23% coalescent on binder solids |          |

\*PVC is pigment volume concentration which is a measure of how much volume of pigment there is in a paint compared to the volume of solid binder calculated as  $V_{\text{pigment}} / (V_{\text{pigment}} + V_{\text{binder}}) \times 100\%$ ,

wherein V pigment and V binder are the volumes of the pigment and binder. A gloss varnish has 0 PVC. Flat paints have PVCs in the range of 55-80 wt.%. Gloss paints can have PVCs from 0-20 wt% depending on the pigmentation.

\*\*VOC is volatile organic content.

**[00165]** Table 5 lists the Screening latex properties, except for the phosphate ester that varied among the different latexes.

Table 5 - Screening latex

| Property             | Ingredients              |
|----------------------|--------------------------|
| Surfactant type      | RS-710 K25               |
| Surfactant Dosage    | 1.0 p.h.m.               |
| Chain Transfer Agent | 0.38 wt.%                |
| Monomer composition  | Styrene, MMA, 2EHA, MAA* |
| Function monomer     | PAM – 2 wt%              |
| Particle Size        | 100~120 nm               |
| Solid                | 40.00 wt.%               |
| Tg                   | ~36°C                    |

\*methyl methacrylate (MMA); 2-ethylhexyl acrylate (2EHA); methacrylic acid (MAA)

**[00166] Example 4 - Salt spray resistance/Corrosion testing**

**[00167]** In a CCT-600 (Cyclic Corrosion Chamber) corrosion chamber the paints were tested for Salt spray resistance/Corrosion according to ASTM B117 with a Neutral salt spray (35°C / 5% NaCl).

The paints were drawn down on 4x6 Cold-rolled steel (CRS) panels

The paints were cured 7 days in Controlled Temperature and Controlled Humidity (CTCH)(50% RH/ 72°F (22°C)),

The panels were then wrapped in tape leaving the painted face exposed, then film thickness was measured, and then a two inch vertical scribe was made on the panel using a scribe tool with a 60° carbide tip.

Paint Dry Film Thickness (DFT) target was about 2 mils (about 50 µm)

The degree of surface rust (corrosion) of the paint was evaluated according to ASTM D610-95.

The degree of blistering of the paint was evaluated according to ASTM D714-87.

The degree of scribe corrosion of the paint was evaluated according to ASTM D 1654.

**[00168]** FIGs. 1 and 2 show the results of this Salt spray resistance/Corrosion testing according to ASTM B117 with a Neutral salt spray (35°C / 5% NaCl ) of a polished CRS (cold rolled steel) panel having a 50 µm dry film thickness that underwent a 7 day cure in CTCH (72°F/50% Relative Humidity (RH)).

**[00169]** FIG. 1 compares Paint C made with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C vs. Paint D made with Latex D made from the emulsified latex blend without any phosphate ester composition.

**[00170]** FIG. 2 compares polished CRS panels to which was applied: Paint C, made with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C; Paint A, made with Comparative Latex A made with Comparative phosphate ester composition A; and Paint B, made with Comparative Latex B made with Comparative phosphate ester composition B.

**[00171]** This data demonstrates that Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA had superior properties for Direct to Metal (DTM) application compared to (1) Paint A formulated with Comparative Latex Polymer A made with 3 wt% phosphate ester composition A and 2% MAA, (2) Paint B formulated with Comparative Latex Polymer B made with 3 wt% phosphate ester composition B and a 2 wt% MAA, and (3) Paint D formulated with Comparative Latex Polymer D made with 5 % MAA and no Inventive phosphate ester composition C.

**[00172] Example 5 - Metal Adhesion**

**[00173]** The paints were tested for Metal Adhesion according to ASTM D3359 – crosshatch adhesion (Adhesion Tape: ELCOMETER 99 ASTM D3359-09 CROSS HATCH ADHESION test tape). The samples were each a polished CRS panel of bare aluminum (hot roll A653) having a 50 um dry film thickness that underwent a 1 day and a 7 day cure in CTCH (72°F/50% Relative Humidity (RH)). It was tested for wet adhesion after a 30 minute soak and 30 minute recovery.

**[00174]** FIG. 3 shows a standard classification of adhesion test results according to the ASTM D3359 Cross Hatch Method.

**[00175]** In the test as shown in FIG. 3: ASTM Rating: 0B = complete fail (no adhesion); 5B = perfect adhesion (no paint is removed).

**[00176]** FIG. 4 shows the results of testing paints for Metal Adhesion according to the ASTM D3359 method. FIG. 4 compares the following:

**[00177]** Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA;

**[00178]** Paint A formulated with Comparative Latex Polymer A made with 3 wt% phosphate ester composition A and 2% MAA; and

**[00179]** Paint B formulated with Comparative Latex Polymer B made with 3 wt% phosphate ester composition B and 2 wt% MAA.

**[00180]** The latex of the paints being the above-described styrene acrylic latex having Tg of about 36°F in the paint formulation of 18PVC/ 36 % VS / about 150 g/l VOC. The tested panels were bare aluminum, polished cold rolled steel (CRD), and Hot Dipped Galvanized Exposed (HDGE) steel.

**[00181]** The panels were tested as indicated below.

- [00182] The paints were applied at a Dry Film Thickness of about 50  $\mu\text{m}$ .
- [00183] The panels were cured in the CTCH (72°F/50% RH).
- [00184] The panels were evaluated for adhesion at 1 day dry and 7 day dry (if necessary).
- [00185] For Dry Adhesion the panels were scribed in duplicates for testing. Then adhesion tape was applied directly on the scribed area, firmly pressed down onto film, and then pulled off at about 180 degree angle from the panel. The scribes were rated based on the ASTM D3359 method.
- [00186] For Wet Adhesion the panels were scribed in duplicates for testing. The scribes were then covered with a bi-fold towel and soaked with DI water for 30 minutes. After 30 minutes, the towels are removed, the panels were patted dry, and then allowed to fully air dry for 30 minutes. After 30 minutes, the adhesion is tested in same manner as dry adhesion.
- [00187] FIG. 4 shows the Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA, had excellent early wet and dry adhesion on the metal substrates. It performed better than Paint A formulated with Comparative Latex Polymer A made with 3 wt% phosphate ester composition A and 2% MAA; and Paint B formulated with Comparative Latex Polymer B made with 3 wt% phosphate ester composition B and a 2 wt% MAA.
- [00188] FIG. 5 shows the results of testing paints for Metal Adhesion according to the ASTM D3359 method using the procedure used to obtain Fig. 4. FIG. 5 compares Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA, and Paint D formulated with Comparative Latex Polymer D made with 5 % MAA and no phosphate ester composition. The latex being the above-described styrene acrylic latex having Tg of about 36°F in the paint formulation of 19PVC/ 36 % VS / about 150 g/l VOC. The tested panels were bare aluminum, polished cold rolled steel (CRD), and Hot Dipped Galvanized Exposed (HDGE) steel.
- [00189] FIGs. 4 and 5 show the Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C can improve adhesion to difficult metal surfaces.
- [00190] **Example 6 - Gloss development/improvement**
- [00191] According to ASTM D-523-89 the paints are drawn down on a Leneta Form 3B chart and allowed to dry for 7 days in Controlled temperature Room (CTR) at CTCH. Gloss is measured by placing a Byk micro tri- gloss meter on the paint and recording the gloss values at 20° and 60° angles. Three measurements are taken on each paint and the average is used for final results. This was a 3 mil wet drawdown on the form 3B chart. Cure was in CTCH (72°F/50%RH). Gloss measurements were recorded after 1 day and 7 days drying. As in the above examples the latex was styrene acrylic latex having Tg of 36°C and the paint formulation included 18 PVC / 36% VS / about 150 g/l VOC (Volatile Organic Content).
- [00192] Table 6 compares gloss improvement of the following:

**[00193]** Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA,

**[00194]** Paint A formulated with Comparative Latex Polymer A made with 3 wt% phosphate ester composition A and 2% MAA,

**[00195]** Paint B formulated with Comparative Latex Polymer B made with 3 wt% phosphate ester composition B and 2 wt% MAA, and

**[00196]** Paint D formulated with Comparative Latex Polymer D made with 5 % MAA and no phosphate ester composition.

Table 6

| Gloss Development<br>(7 day dry) | Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA | Paint A formulated with Comparative Latex Polymer A made with 3 wt% phosphate ester composition A and 2% MAA | Paint B formulated with Comparative Latex Polymer B made with 3 wt% phosphate ester composition B and 2 wt% MAA | Paint D formulated with Comparative Latex Polymer D made with 5 % MAA and no phosphate ester composition |
|----------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|
| 20                               | 74.1                                                                                                                                                        | 63.6                                                                                                         | 56.7                                                                                                            | 27                                                                                                       |
| 60                               | 91.2                                                                                                                                                        | 88.2                                                                                                         | 85.9                                                                                                            | 70.4                                                                                                     |

**[00197]** Table 6 shows improved gloss development with the Inventive phosphate ester composition C.

**[00198] Example 7 - Gloss Retention / yellowing**

**[00199]** Painted panels were also tested according to ASTM G154 – QUV for gloss retention by a cyclic method with UVA bulbs. This test was performed according to the following procedure.

**[00200]** Cycle 1: 8 hours, UV light 0.89 w/m<sup>2</sup>, 60°C

**[00201]** Cycle 2: 4 hours, dark, constant condensation

**[00202]** Repeat

**[00203]** The paint was applied to bare aluminum panels (A36 panels from a Q-lab Condensation Tester (QCT) humidity chamber used for testing and allowed to dry for 7 days in CTCH (72°F/50%RH). As in the above examples the latex was styrene acrylic latex having Tg of 36°C and the paint formulation included 18 PVC / 36% VS / about 150 g/l VOC.

**[00204]** Initial gloss measurements were taken at 20/60 degrees.

**[00205]** Initial L\*a\*b\* measurements were taken and recorded.

**[00206]** The panels were tested for up to 1000 hours with gloss and L\*a\*b\* measurements taken periodically.

**[00207]** FIG. 6 and Table 7 show a comparison of gloss retention for paints on 50 µm DFT on treated aluminum panels tested by the Method of ASTM G154 (using UV-A lamps). They compared

**[00208]** Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA;

**[00209]** Paint A formulated with Comparative Latex Polymer A made with 3 wt% phosphate ester composition A and 2% MAA;

**[00210]** Paint B formulated with Comparative Latex Polymer B made with 3 wt% phosphate ester composition B and 2 wt% MAA; and

**[00211]** Paint D formulated with Comparative Latex Polymer D made with 5 % MAA and no phosphate ester composition. As in the above examples the latex was styrene acrylic latex having Tg of 36°C and the paint formulation included 18 PVC / 36% VS / about 150 g/l VOC. The inventive paint had consistently good gloss retention.

Table 7 – Gloss Retention by the Method of ASTM G154

| Time hrs. | Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA | Paint A formulated with Comparative Latex Polymer A made with 3 wt% phosphate ester composition A and 2% MAA | Paint B formulated with Comparative Latex Polymer B made with 3 wt% phosphate ester composition B and 2 wt% MAA | Paint D formulated with Comparative Latex Polymer D made with 5 % MAA and no phosphate ester composition |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|
|           | 60 degree gloss – QUV: ASTM G154                                                                                                                            |                                                                                                              |                                                                                                                 |                                                                                                          |
| Initial   | 90.8                                                                                                                                                        | 84.6                                                                                                         | 84.7                                                                                                            | 64.9                                                                                                     |
| 300 hrs   | 77.6                                                                                                                                                        | 72.4                                                                                                         | 71.9                                                                                                            | 25.5                                                                                                     |
| 500 hrs   | 78.7                                                                                                                                                        | 75.6                                                                                                         | 76.9                                                                                                            | 23.7                                                                                                     |
| 715 hrs   | 76.7                                                                                                                                                        | 76.2                                                                                                         | 77.9                                                                                                            | 21.7                                                                                                     |
| 1000 hrs  | 78.9                                                                                                                                                        | 67.1                                                                                                         | 64                                                                                                              | 21.7                                                                                                     |

**[00212] Example 8 - Hiding / Opacity**

**[00213]** Painted panels were also tested for Hiding / Opacity. In this test the paints were drawn down with a 3 mil wet film applicator on a Leneta Form 3B opacity chart and allowed to dry for 7 days in the Control Temperature Room (CTCH)(22°C/50% RH) prior to measurement.

**[00214]** Opacity is then measured by comparing the contrast ratio measuring reflectance of the white paint over the black and white portion of the drawdown chart using an X-rite handheld spectrophotometer.

Contrast ratio (C/R) is defined as the apparent reflectance of the material backed by a perfectly absorbing surface (black) divided by its apparent reflectance when backed by a white surface according to formula (V).

$$C/R = (\text{Black "L" value} / \text{White "L" Value}) \quad (V)$$

**[00215]** The higher the value, the greater the hiding ability of the paint.

**[00216]** Contrast ratio may also be expressed as Hiding Opacity. Hiding Opacity is calculated according to formula (VI).

$$\text{Hiding Opacity (\%)} = (\text{reflectance over black} / \text{reflectance over white}) \times 100\% \quad (VI)$$

**[00217]** Fig. 7 compares the Hiding Opacity percent of paints made with the styrene acrylic latex polymer made with 2 wt. % MAA and 3 wt. % the Inventive Monomer C, as compared to a control latex made with 5 % MAA without Inventive Monomer C. As in the above examples the latex was styrene acrylic latex having Tg of 36°C and the paint formulation included 18 PVC / 36% VS / about 150 g/l VOC. The inventive paint had improved hiding opacity of 98.32 % as compared to 97.34 % for the paint made with the control latex that did not have the Inventive Monomer C.

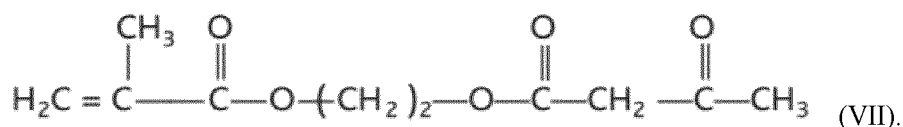
**[00218]** The percentages for monomer compositions, unless otherwise indicated, in the present description are weight percent based on weight of total monomer.

**[00219] Example 9 – Comparison of multiple properties**

**[00220]** FIG. 8 summarizes benefits from making paints with the latex emulsified with the Inventive phosphate ester composition C. In FIG. 8 a 0 is the lowest rating and a 10 is the highest rating. Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA had a better balance of properties of Corrosion resistance, Gloss, Aluminum adhesion, CRD adhesion, Galvanized metal adhesion, Gloss retention than (1) Paint A formulated with Comparative Latex Polymer A made with 3 wt% phosphate ester composition A and 2% MAA, (2) Paint B formulated with Comparative Latex Polymer B made with 3 wt% phosphate ester composition B and 2 wt% MAA, or (3) Paint D formulated with Comparative Latex Polymer D made with 5 % MAA and no phosphate ester composition.

**[00221] Example 10**

**[00222]** As opposed to the styrene acrylic latex made from the composition made from Sty 42.2 / MMA 23.5 / 2EHA 29.3 / MAA 3.0 / Inventive phosphate ester composition C 2.0 tested as explained above, another styrene acrylic latex was also made. This other styrene acrylic latex was made from Sty 41.66 / MMA 22.56 / 2EHA 27.07 / AAEM 3.8 / MAA 2.93 / Inventive phosphate ester composition C 2.0 (Specialty Monomer Composition). These values being wt. % based on total monomer (BOTM) in an emulsion polymerization mixture. AAEM is acetoacetoxyethyl methacrylate, also known as 2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl 3-oxobutanolate, and has formula (VII):



AAEM in combination with the polymerizable mono- and di-ester composition of the present invention further improves properties. AAEM is typically a cross-linker.

**[00223]** The styrene acrylic latex resulted from emulsion polymerization of Sty 41.66 / MMA 22.56 / 2EHA 27.07 / AAEM 3.8 / MAA 2.93 / Inventive phosphate ester composition C 2.0 in the presence of anionic surfactant as the emulsifier in an amount of 1.0 wt.% based on total monomer. The anionic surfactant was RHODAFAC RS 710 K25 phosphated anionic surfactant (potassium salt) which is APE (alkyl phenol ethoxylate)-free.

**[00224]** The styrene acrylic latex polymer had a Tg of about 37°C, particle size of about 90-100 nm; and was 40.0 wt.% solids and had a pH of about 7-8.

**[00225]** The data in FIG. 9 compared Inventive Paint E1 made with this styrene acrylic Latex Polymer E made with the Inventive phosphate ester composition C with AAEM and Inventive Paint E2 made with this styrene acrylic Latex Polymer E made with the Inventive phosphate ester composition C without AAEM. The paints were applied to form a coating of 50 µm thickness on a treated Al panel. Then the coating dried for 20 minutes at room temperature, and then 2 hours at 80 °C. The painted panel was then subjected to 100% relative humidity at 40°C for 120 hours in a QTC condensation tester in a Cleveland Condensation test.

**[00226]** The data in FIG. 9 shows AAEM addition boosted gloss retention in high humidity conditions.

**[00227]** FIG. 10 shows photographs comparing a Control Paint made with a control latex having (in parts by weight, pbw) Sty 41.66 / MMA 22.56 / 2EHA 27.07 / AAEM 3.8 / MAA 4.93 and an Inventive Paint made with the latex Sty 41.66 / MMA 22.56 / 2EHA 27.07 / AAEM 3.8 / MAA 2.93 / Inventive phosphate ester composition C 2.0. The inventive paint containing the latex having units of MAA and Inventive phosphate ester composition C had much better corrosion resistance than the Control paint.

**[00228]** Example 11 – Compare with and without benzophenone.

**[00229]** The performance of the paint and coating compositions of the present invention in the presence of typical paint additives can be important. Thus, this example tests the paint compositions of the present invention with and without Benzophenone which is a typical ultraviolet (UV) stabilizer ingredient in paints and coatings.

**[00230]** The styrene acrylic latex resulted from emulsion polymerization of (in parts by weight, pbw) Sty 42.2 / MMA 23.5 / 2EHA 29.3 / MAA 3.0 / Inventive phosphate ester composition C 2.0 as explained above in the presence of anionic surfactant as the emulsifier in an amount of 1.0 wt.% based on total monomer. The anionic surfactant was RHODAFAC RS 710 K25 phosphated anionic surfactant (potassium salt) which is APE (alkyl phenol ethoxylate)-free.

**[00231]** The styrene acrylic latex polymer had a Tg of about 36°C, particle size of about 100-120 nm; and was 40.0 wt.% solids and had a pH of about 7-8.

**[00232]** This example compares Paint F1 made with this latex containing 0.27 wt. % Benzophenone to Paint F2 made without made with this latex but without the Benzophenone.

**[00233]** The Grind (solid ingredients such as pigments and fillers) for the paint used to make the tested paint formulation had the composition shown in Table 8.

Table 8

| <b>Grind</b>     |                                                  |          |
|------------------|--------------------------------------------------|----------|
| Materials        |                                                  | Weight % |
| Water            |                                                  | 6.5      |
| DPNB             | Coalescing agent                                 | 1.4      |
| EDPLAN 490       | Dispersing agent                                 | 1.4      |
| RHODOLINE DF4226 | Defoamer                                         | 0.1      |
| AMP 95           | Neutralizer                                      | 0.05     |
| TiO <sub>2</sub> | Pigment                                          | 10       |
| Barium sulfate   | Filler                                           | 8.0      |
| NUBIROX 302      | Organophilized Calcium Strontium Phosphosilicate | 3.0      |
| Mica 1000        | Filler                                           | 5.0      |
| Water            |                                                  | 1.4      |
| Total            |                                                  | 36.85    |

**[00234]** The Let down used to make the tested paint formulation had the composition shown in Table 9. The Let down is when the rest of the paint (resin, water and additives) is combined and mixed. When the let-down and the Grind are completed, the Grind is added with stirring to the let-down. At this stage, if required by the formulation, any final additions are made and added in.

Table 9

| Let down         |                                |          |
|------------------|--------------------------------|----------|
| Materials        |                                | Weight % |
| Resin            | Latex                          | 49.0     |
| RHODOLINE DF4226 | Defoamer                       | 0.1      |
| DPNB             | Coalescing agent               | 1.2      |
| BYK 346          | Wetting agent (silicone based) | 0.1      |
| FA 179           | Anti-flash additive            | 0.5      |
| Grind            |                                | 36.85    |
| PUR 64 (10%)     | Thickener                      | 2.0      |
| Water            |                                | 10.25    |
| Total            |                                | 100      |

**[00235]** The Grind and Letdown are combined to make the paint formulation that had the parameters shown in Table 10.

Table 10

| Formulation parameters |       |
|------------------------|-------|
| Weight solid/%         | 47.1  |
| Volume solid/%         | 34.55 |
| PVC/%                  | 25.53 |
| Pigment /binder        | 1.23  |
| Target viscosity/KU    | 85-90 |

**[00236]** The paints were applied to respective treated Al panels – 6 mil metallic square , and then subjected to 7d dry CTCH (50% RH/ 72°F (22°C)), and then tested for gloss retention/yellowing according to ASTM G154 – QUV gloss retention; cyclic method; UVA bulbs including:

1. Cycle 1: 8 hours, UV light  $0.89\text{w/m}^2$ , 60°C
2. Cycle 2: 4 hours, dark, constant condensation
3. Repeat

**[00237]** The paint was applied to bare Aluminum panels (A36 panels from QCT) and allowed to dry for 7d in CTCH (50% RH/ 72°F (22°C)). Initial gloss measurements are taken at 20°C /60°C degrees. Initial L\*a\*b\* measurements are taken and recorded. The panels were tested for up to 1000 hrs. with gloss and L\*a\*b\* measurements taken periodically.

**[00238]** FIG. 11 shows excellent gloss retention for the tested specimen coated with the Paint F2 containing Benzophenone. This shows the monomeric units of polymerizable phosphate mono-ester compound and polymerizable phosphate mono-ester compound in the latex of the paint do not interfere with the UV protection function of the Benzophenone.

**[00239] Example 12**

**[00240]** This example compares the anti-corrosive performance of Inventive Latex Polymer C, and Comparative Phosphate ester composition A.

**[00241]** Control 258-04 vs 256-01 (2% Inventive Latex Polymer C) vs 255-03 (Comparative Phosphate ester composition A).

**[00242]** The latexes had the compositions listed in Table 11.

Table 11

| Latex | Ingredients in wt. % based on total monomers |                                                                        |
|-------|----------------------------------------------|------------------------------------------------------------------------|
| AA    | 1-dodecanthiol                               | SM/CHMA/2EHA/MAA<br>39.95/28.25/27.88/3.92                             |
| BB    |                                              | SM/CHMA/2EHA/MAA/ Inventive Monomer<br>39.95/28.25/27.88/1.96/1.96     |
| CC    |                                              | SM/CHMA/2EHA/MAA/ Comparative Polymer A<br>39.95/28.25/27.88/1.96/1.96 |

Note: SM (styrene monomer)/CHMA (cyclohexyl methacrylate)/2EHA (2-ethylhexyl acrylate)/MAA (methacrylic acid)

**[00243]** Fig. 12A shows the tested sample coated with Paint AA made with Ex. 10 Latex AA.

**[00244]** Fig. 12B shows the tested sample coated with Paint BB made with Ex. 10 Latex BB.

**[00245]** Fig. 12C shows the tested sample coated with Paint CC made with Ex. 10 Latex CC.

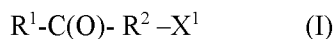
**[00246]** Comparison of Figures 12A-12C shows Paint BB made with Ex. 10 Latex BB was better than Paint AA made with Ex. 10 Latex AA or Paint CC made with Ex. 10 Latex CC.

**[00247] CLAUSES OF THE INVENTION**

**[00248]** The following clauses describe various aspect of the invention:

**[00249]** Clause 1. A phosphate ester composition comprising:

(a) at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

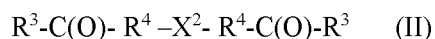
$R^1$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three, oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1.

**[00250]** Clause 2. The phosphate ester composition of clause 1, wherein the polymerizable phosphate mono-ester compound is 30-60, wt. %, typically 40-50 wt%, more typically 43-47 wt.% of the phosphate ester composition on a dry (water free) basis.

**[00251]** Clause 3. The phosphate ester composition of clause 1 or 2, wherein a yield of the polymerizable phosphate di-ester compound is 15-40 wt%, 20-30 wt%, more typically 21-26 wt% of the phosphate ester composition based on total weight of reactants.

**[00252]** Clause 4. The phosphate ester composition of any of the preceding clauses, wherein  $R^1$  is selected from the group consisting of  $CH_2=CH-$ ,  $CH_2=C(CH_3)-$ , or  $cis-CH(COOH)=CH-$ .

**[00253]** Clause 5. The phosphate ester composition of any of the preceding clauses, wherein  $R^2$  has one to five, preferably one to three oxyethylene units.

**[00254]** Clause 6. The phosphate ester composition of any of the preceding clauses, wherein  $R^2$  has at least one oxyethylene unit.

**[00255]** Clause 7. The phosphate ester composition of any of the preceding clauses, wherein  $R^2$  has an absence of oxypropylene units.

**[00256]** Clause 8. The phosphate ester composition of any of the preceding clauses, wherein  $R^3$  is selected from the group consisting of  $CH_2=CH-$ ,  $CH_2=C(CH_3)-$ , or  $cis-CH(COOH)=CH-$ .

**[00257]** Clause 9. The phosphate ester composition of any of the preceding clauses, wherein  $R^4$  is a divalent polyoxyalkylene radical having at least one oxyethylene unit.

**[00258]** Clause 10. The phosphate ester composition of any of the preceding clauses, wherein  $R^4$  is a divalent polyoxyalkylene radical having one to three oxyethylene units.

**[00259]** Clause 11. The phosphate ester composition of any of the preceding clauses, wherein ((2-methyl-1-oxopropane-1,3-diyl)bis(oxy))bis(ethane-2,1-diyl)bis(2-methacrylate) is 10 to 20 wt.%, more typically 15-20 wt%, for example 16-18 wt% of the phosphate ester composition.

**[00260]** Clause 12. The phosphate ester composition of any of the preceding clauses, wherein ethylene glycol dimethacrylate is 1 to 10 wt.%, typically 2-8 wt%, more typically 3-7 wt%, for example 4-6 wt% of the phosphate ester composition.

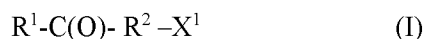
**[00261]** Clause 13. The phosphate ester composition of any of the preceding clauses, further comprising phosphoric acid, preferably the weight ratio of the phosphoric acid to total polymerizable phosphate mono-ester compound of formula (I) and polymerizable phosphate di-ester compound of formula (II) is 10:90 to 25:75, typically 10:90 to 20:80, more typically 10:90 to 18:82, further typically 11:89-16:84.

**[00262]** Clause 14. The phosphate ester composition of any of the preceding clauses, wherein the at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I) and the at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II) have been neutralized with one or more of sodium hydroxide, potassium hydroxide or ammonium hydroxide, preferably ammonium hydroxide.

**[00263]** Clause 15. A polymer composition comprising monomeric units from:

(A) the at least one polymerizable phosphate mono-ester compound or salt thereof and the at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition of any of the preceding clauses comprising:

(a) the at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

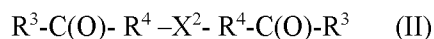
$R^1$  is a substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, preferably the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) the at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is a substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt,

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1; and

(B) at least one other polymerizable monomer.

**[00264]** Clause 16. The polymer composition of clause 15,

wherein the mixture further comprises a surfactant, wherein the composition comprises 0.5 to 3 wt.% said surfactant based on total monomer including the polymerizable phosphate mono-ester compound, polymerizable phosphate di-ester compound, and other polymerizable monomer;

wherein the surfactant is preferably anionic surfactant, more preferably a phosphate ester anionic surfactant;

wherein the polymer composition is an emulsion polymer composition.

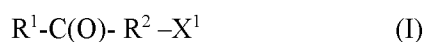
**[00265]** Clause 17. The polymer composition of clause 15 or 16, wherein the other polymerizable monomer is selected from methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate, 2-ethyl hexyl acrylate, other acrylates, methacrylates and their blends, acrylic acid, methacrylic acid, cyclohexyl methacrylate, styrene, vinyl toluene, vinyl acetate, vinyl esters, e.g. vinyl versatate, acrylonitrile, acrylamide, butadiene, ethylene, vinyl chloride and the like, and mixtures thereof.

**[00266]** Clause 18. A waterborne coating comprising the polymer composition of any of clauses 15 to 17.

**[00267]** Clause 19. A coating composition comprising a polymer formed from:

(A) a phosphate ester composition comprising at least one polymerizable phosphate mono-ester compound or salt thereof and at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition comprising:

(a) at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

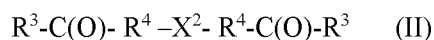
$R^1$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three, oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1;

(B) at least one other polymerizable monomer.

**[00268]** Clause 20. A method of improving the corrosion resistance of a metal substrate comprising contacting at least a portion of the surface of the metal substrate with the coating composition, wherein the coating composition comprises the polymer composition of any of clauses 15 to 17, compared to coating the metal substrate with a coating composition which is the same but does not include monomeric units from said polymerizable phosphate mono-ester compound or a salt thereof and said polymerizable phosphate di-ester compound or a salt thereof.

**[00269]** Clause 21. A method of improving the water resistance of a coating composition to a substrate comprising contacting at least a portion of the surface of the substrate with the coating composition, wherein the coating composition comprises the polymer composition of any of clauses 15 to 17, compared to coating the substrate with a coating composition which is the same but does not include monomeric units from said polymerizable phosphate mono-ester compound or a salt thereof and said polymerizable phosphate di-ester compound or a salt thereof.

**[00270]** Clause 22. A method of improving any one or more of gloss, gloss retention, and hiding of a coating composition on a substrate comprising contacting at least a portion of the surface of the substrate with the coating composition, wherein the coating composition comprises the emulsion polymer composition of any of clauses 15 to 17, compared to coating the substrate with a coating composition

which is the same but does not include monomeric units from said polymerizable phosphate mono-ester compound or a salt thereof and said polymerizable phosphate di-ester compound or a salt thereof.

**[00271]** Clause 23. A method of improving the adhesion of a coating composition to a metal substrate comprising contacting at least a portion of the surface of the substrate with the coating composition, wherein the coating composition comprises the polymer composition of any of clauses 15 to 17.

**[00272]** Clause 24. A method of improving the adhesion of a coating composition intended to be coated to a metal substrate, comprising contacting at least a portion of the surface of the substrate with a coating composition, called conversion coating, wherein the conversion coating comprises the polymer composition of any of clauses 15 to 17.

**[00273]** Clause 25. A method of treating a first metal surface S1 of a first substrate intended to be bonded to a second surface S2 of a second substrate by adhesive bonding, and of imparting a resistance to the adhesive failure to the bonding, said method comprising contacting at least a portion of the first metal surface S1 with a coating composition, wherein the coating composition comprises the polymer composition of any of clauses 15 to 17.

**[00274]** Clause 26. The method of clause 20-25, wherein the substrate is aluminum, steel or galvanized steel.

**[00275]** Clause 27. A method of making a polymer composition comprising:

combining (A) the phosphate ester composition of any of clauses 1-14, and (B) at least one other polymerizable monomer to form a mixture; and

polymerizing the at least one polymerizable phosphate mono-ester compound or salt thereof and the at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition and the at least one other polymerizable monomer.

**[00276]** Clause 28. The method of clause 27,

wherein the mixture further comprises a surfactant, wherein the mixture comprises 0.5 to 3 wt.% said surfactant based on total monomer including the polymerizable phosphate mono-ester compound, polymerizable phosphate di-ester compound, and other polymerizable monomer;

wherein the surfactant is preferably anionic surfactant, more preferably a phosphate ester anionic surfactant; and

the composition is an emulsion polymer composition, and

the polymerization is by emulsion polymerization of the mixture.

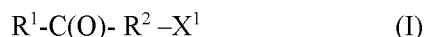
**[00277]** Clause 29. The method of clause 27 or 28, wherein the mixture further comprises phosphoric acid, preferably wherein the weight ratio of the phosphoric acid to total polymerizable phosphate mono-ester compound of formula (I) and polymerizable phosphate di-ester compound of formula (II) 10:90 to 25:75, preferably 12:88 to 20:80.

**[00278]** Having described the invention in detail by reference to the preferred embodiments and specific examples thereof, it will be apparent that modifications and variations are possible without departing from the spirit and scope of the disclosure and claims.

## CLAIMS

1. A phosphate ester composition comprising:

(a) at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

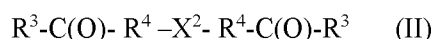
$R^1$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three, oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1.

2. The phosphate ester composition of claim 1, wherein the polymerizable phosphate mono-ester compound is 30-60, wt. %, typically 40-50 wt%, more typically 43-47 wt.% of the phosphate ester composition on a dry (water free) basis.

3. The phosphate ester composition of claim 1 or 2, wherein a yield of the polymerizable phosphate di-ester compound is 15:40 wt%, 20-30 wt%, more typically 21-26 wt% of the phosphate ester composition based on total weight of reactants.

4. The phosphate ester composition of any of the preceding claims, wherein  $R^1$  is selected from the group consisting of  $CH_2=CH-$ ,  $CH_2=C(CH_3)-$ , or  $cis-CH(COOH)=CH-$ .
5. The phosphate ester composition of any of the preceding claims, wherein  $R^2$  has one to five, preferably one to three oxyethylene units.
6. The phosphate ester composition of any of the preceding claims, wherein  $R^2$  has at least one oxyethylene unit.
7. The phosphate ester composition of any of the preceding claims, wherein  $R^2$  has an absence of oxypropylene units.
8. The phosphate ester composition of any of the preceding claims, wherein  $R^3$  is selected from the group consisting of  $CH_2=CH-$ ,  $CH_2=C(CH_3)-$ , or  $cis-CH(COOH)=CH-$ .
9. The phosphate ester composition of any of the preceding claims, wherein  $R^4$  is a divalent polyoxyalkylene radical having at least one oxyethylene unit.
10. The phosphate ester composition of any of the preceding claims, wherein  $R^4$  is a divalent polyoxyalkylene radical having one to three oxyethylene units.
11. The phosphate ester composition of any of the preceding claims, wherein ((2-methyl-1-oxopropane-1,3-diyl)bis(oxy))bis(ethane-2,1-diyl)bis(2-methacrylate) is 10 to 20 wt.%, more typically 15-20 wt%, typically 16-18 wt% of the phosphate ester composition.
12. The phosphate ester composition of any of the preceding claims, wherein ethylene glycol dimethacrylate is 1 to 10 wt.%, typically 2-8 wt%, more typically 3-7 wt%, most typically 4-6 wt% of the phosphate ester composition.
13. The phosphate ester composition of any of the preceding claims, further comprising phosphoric acid, preferably the weight ratio of the phosphoric acid to total polymerizable phosphate mono-ester compound of formula (I) and polymerizable phosphate di-ester compound of formula (II) is 10:90 to 25:75, typically 10:90 to 20:80, more typically 10:90 to 18:82, further typically 11:89-16:84.
14. The phosphate ester composition of any of the preceding claims, wherein the at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I) and the at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II) have been neutralized with one or

more of sodium hydroxide, potassium hydroxide or ammonium hydroxide, preferably ammonium hydroxide.

15. A polymer composition comprising monomeric units from:

(A) the at least one polymerizable phosphate mono-ester compound or salt thereof and the at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition of any of the preceding claims comprising:

(a) the at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

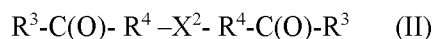
$R^1$  is a substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, preferably the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) the at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is a substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^2$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt,

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1; and

(B) at least one other polymerizable monomer, preferably one or more (co)polymerizable monomers comprising acrylate monomers, styrene monomers, vinyl ester monomers, butadiene, ethylene, or vinyl chloride.

16. The polymer composition of claim 15,

wherein the mixture further comprises a surfactant, wherein the composition comprises 0.5 to 3 wt.% said surfactant based on total monomer including the polymerizable phosphate mono-ester compound, polymerizable phosphate di-ester compound, and other polymerizable monomer;

wherein the surfactant is preferably anionic surfactant, more preferably a phosphate ester anionic surfactant;

wherein the polymer composition is an emulsion polymer composition.

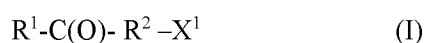
17. The polymer composition of claim 15 or 16, wherein the other polymerizable monomer is selected from methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate, 2-ethyl hexyl acrylate, other acrylates, methacrylates and their blends, acrylic acid, methacrylic acid, cyclohexyl methacrylate, styrene, vinyl toluene, vinyl acetate, vinyl esters, acrylonitrile, acrylamide, butadiene, ethylene, vinyl chloride and the like, and mixtures thereof.

18. A waterborne coating comprising the polymer composition of any of claims 15 to 17.

19. A coating composition comprising a polymer formed from:

(A) a phosphate ester composition comprising at least one polymerizable phosphate mono-ester compound or salt thereof and at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition comprising:

(a) at least one polymerizable phosphate mono-ester compound or a salt thereof having the formula (I):



wherein:

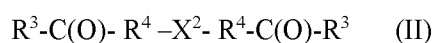
$R^1$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^2$  is a divalent polyoxyalkylene radical having one to five, preferably one to three, oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

$X^1$  is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

(b) at least one polymerizable phosphate di-ester compound or a salt thereof having the formula (II):



wherein:

$R^3$  is an substituted or unsubstituted vinyl radical, preferably a  $C_2-C_5$ , more preferably a  $C_2-C_3$  vinyl radical, typically the vinyl radical is methyl substituted;

$R^4$  is a divalent polyoxyalkylene radical having one to five, preferably one to three oxyethylene units, oxypropylene units, or a mixtures thereof, further preferably one to five, or one to three, oxyethylene units;

X<sup>2</sup> is a phosphate group,

wherein the salt, if present, is preferably sodium, potassium or ammonium salt; and

wherein the weight ratio of the polymerizable phosphate mono-ester compound of formula (I) to the polymerizable phosphate di-ester compound of formula (II) ranges from 1.2-2.1:1, or typically 1.4-2.1:1, 1.5-2.1:1, 1.5-2.0:1, 1.6-1.9:1, 1.7-1.9:1, or 1.8-1.9:1;

(B) at least one other polymerizable monomer.

20. A method of improving the corrosion resistance of a metal substrate comprising contacting at least a portion of the surface of the metal substrate with the coating composition, wherein the coating composition comprises the polymer composition of any of claims 15 to 17, compared to coating the metal substrate with a coating composition which is the same but does not include monomeric units from said polymerizable phosphate mono-ester compound or a salt thereof and said polymerizable phosphate di-ester compound or a salt thereof.

21. A method of improving the water resistance of a coating composition to a substrate comprising contacting at least a portion of the surface of the substrate with the coating composition, wherein the coating composition comprises the polymer composition of any of claims 15 to 17, compared to coating the substrate with a coating composition which is the same but does not include monomeric units from said polymerizable phosphate mono-ester compound or a salt thereof and said polymerizable phosphate di-ester compound or a salt thereof.

22. A method of improving any one or more of gloss, gloss retention, and hiding of a coating composition on a substrate comprising contacting at least a portion of the surface of the substrate with the coating composition, wherein the coating composition comprises the emulsion polymer composition of any of claims 15 to 17, compared to coating the substrate with a coating composition which is the same but does not include monomeric units from said polymerizable phosphate mono-ester compound or a salt thereof and said polymerizable phosphate di-ester compound or a salt thereof.

23. A method of improving the adhesion of a coating composition to a metal substrate comprising contacting at least a portion of the surface of the substrate with the coating composition, wherein the coating composition comprises the polymer composition of any of claims 15 to 17.

24. A method of improving the adhesion of a coating composition intended to be coated to a metal substrate, comprising contacting at least a portion of the surface of the substrate with a coating composition, called conversion coating, wherein the conversion coating comprises the polymer composition of any of claims 15 to 17.

25. A method of treating a first metal surface S1 of a first substrate intended to be bonded to a second surface S2 of a second substrate by adhesive bonding, and of imparting a resistance to the adhesive failure to the bonding, said method comprising contacting at least a portion of the first metal surface S1 with a coating composition, wherein the coating composition comprises the polymer composition of any of claims 15 to 17.

26. The method of any of claims 20 to 25, wherein the substrate(s) is aluminum, steel or galvanized steel.

27. A method of making a polymer composition comprising:

combining (A) the phosphate ester composition of any of claims 1-14, and (B) at least one other polymerizable monomer to form a mixture; and

polymerizing the at least one polymerizable phosphate mono-ester compound or salt thereof and the at least one polymerizable phosphate di-ester compound or salt thereof of the phosphate ester composition and the at least one other polymerizable monomer.

28. The method of claim 27,

wherein the mixture further comprises a surfactant, wherein the mixture comprises 0.5 to 3 wt.% said surfactant based on total monomer including the polymerizable phosphate mono-ester compound, polymerizable phosphate di-ester compound, and other polymerizable monomer;

wherein the surfactant is preferably anionic surfactant, more preferably a phosphate ester anionic surfactant; and

the composition is an emulsion polymer composition, and

the polymerization is by emulsion polymerization of the mixture.

29. The method of claim 27 or 28, wherein the mixture further comprises phosphoric acid, preferably wherein the weight ratio of the phosphoric acid to total polymerizable phosphate mono-ester compound of formula (I) and polymerizable phosphate di-ester compound of formula (II) 10:90 to 25:75, preferably 12:88 to 20:80.

FIG. 1

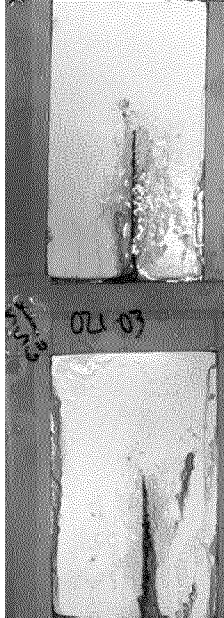
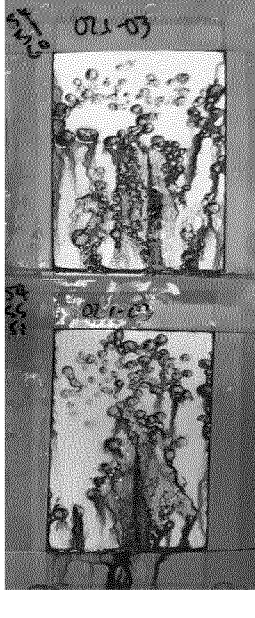
| 240 hours                                                                          |                                                                                    | 528 hours                                                                           |                                                                                      |
|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| Paint D made with Comparative Latex Polymer D                                      | Paint C made with Inventive Monomer C                                              | Paint D made with Comparative Latex Polymer D                                       | Paint C made with Inventive Monomer C                                                |
|  |  |  |  |

FIG. 2

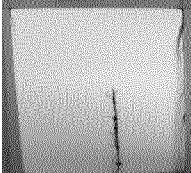
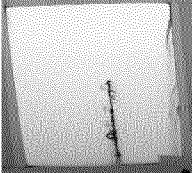
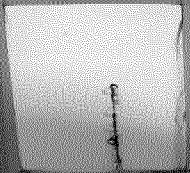
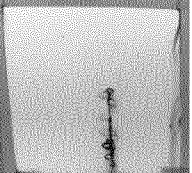
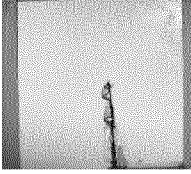
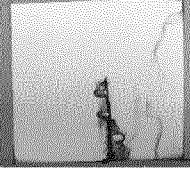
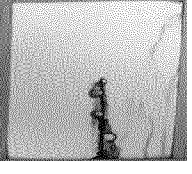
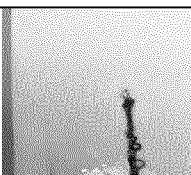
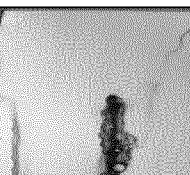
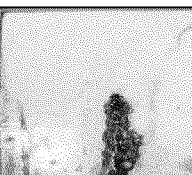
|                                                     | 240 hr                                                                              | 336 hr                                                                              | 406 hr                                                                               | 528 hr                                                                                |
|-----------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Paint C made with Inventive Monomer C               |  |  |  |  |
| Paint A formulated with Comparative Latex Polymer A |  |  |  |  |
| Paint B formulated with Comparative Latex Polymer B |  |  |  |  |

FIG. 3

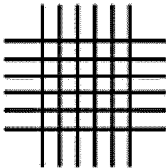
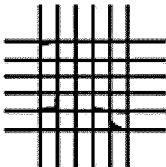
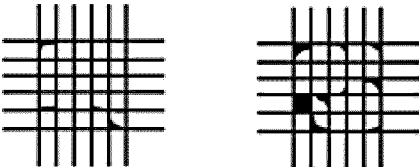
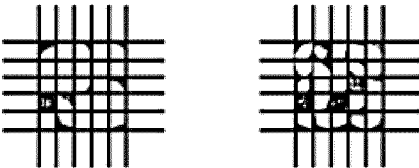
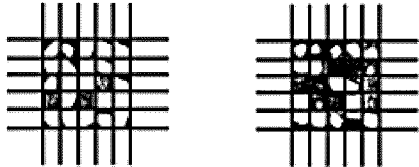
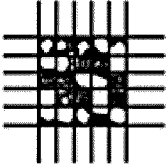
| CLASSIFICATION OF ADHESION TEST RESULTS |                      |                                                                                                               |
|-----------------------------------------|----------------------|---------------------------------------------------------------------------------------------------------------|
| CLASSIFICATION                          | PERCENT AREA REMOVED | SURFACE OF CROSS-CUT AREA FROM WHICH FLAKING HAS OCCURRED FOR SIX PARALLEL CUTS AND ADHESION RANGE BY PERCENT |
| 5B                                      | 0%<br>None           |                             |
| 4B                                      | Less than 5%         |                             |
| 3B                                      | 5 – 15%              |                            |
| 2B                                      | 15 – 35%             |                           |
| 1B                                      | 35 – 65%             |                           |
| 0B                                      | Greater than 65%     |                           |

FIG. 4 – 1Day Adhesion ASTM D3359 Cross Hatch Method

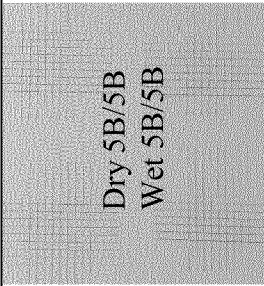
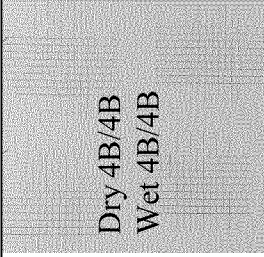
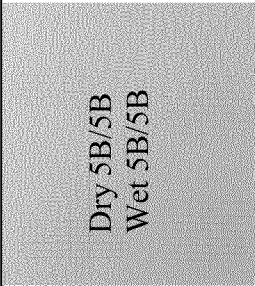
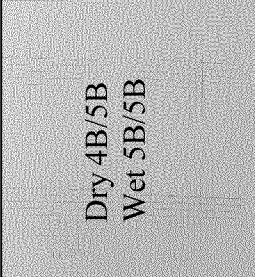
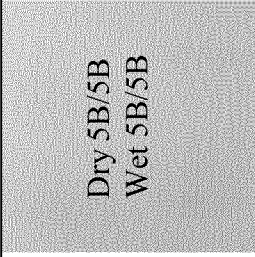
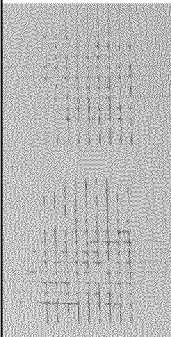
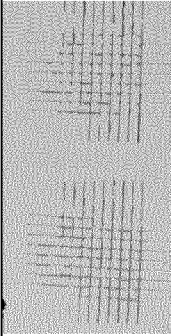
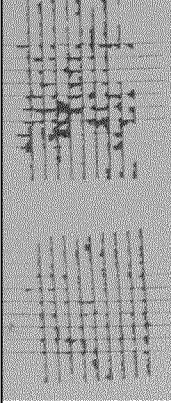
|                    |     | Paint C formulated with Inventive Latex<br>Polymer C made from the emulsified latex<br>blend with the 3 wt% Inventive phosphate<br>ester composition C and 2 wt% MAA | Paint A formulated with Comparative<br>Latex Polymer A made with 3 wt%<br>comparative phosphate ester composition<br>A and 2% MAA | Paint B formulated with Comparative Latex<br>Polymer B made with 3 wt% comparative<br>phosphate ester composition B and 2 wt% MAA |
|--------------------|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|
| Aluminum<br>Panels | Dry | <br>Dry 5B/5B<br>Wet 5B/5B                                                        | <br>Dry 4B/4B<br>Wet 4B/5B                      | <br>Dry 4B/4B<br>Wet 4B/4B                       |
|                    | Wet |                                                                                                                                                                      |                                                                                                                                   |                                                                                                                                   |
| CRS Panels         | Dry | <br>Dry 5B/5B<br>Wet 5B/5B                                                        | <br>Dry 4B/5B<br>Wet 5B/5B                      | <br>Dry 5B/5B<br>Wet 5B/5B                       |
|                    | Wet |                                                                                                                                                                      |                                                                                                                                   |                                                                                                                                   |
| HDGE<br>Panels     | Dry | <br>Dry 3B/3B                                                                    | <br>Dry 2B/2B                                  | <br>Dry 2B/1B                                   |

FIG. 5 – 1 Day Adhesion ASTM D3359 Cross Hatch Method

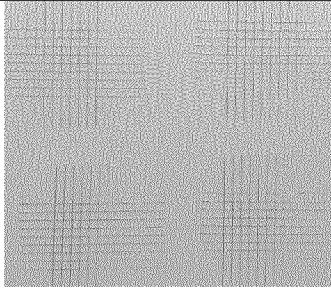
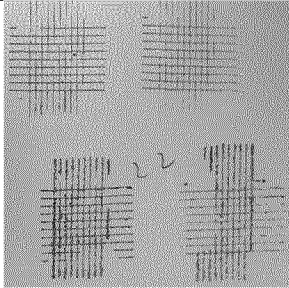
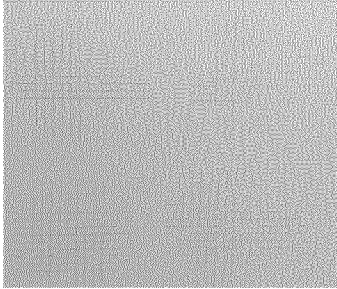
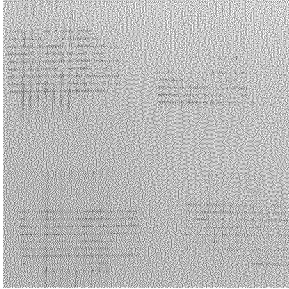
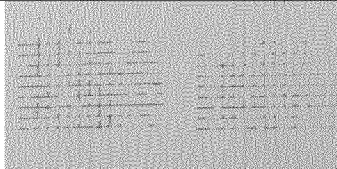
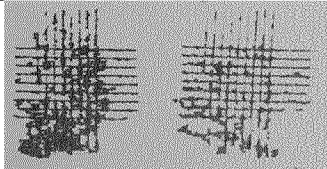
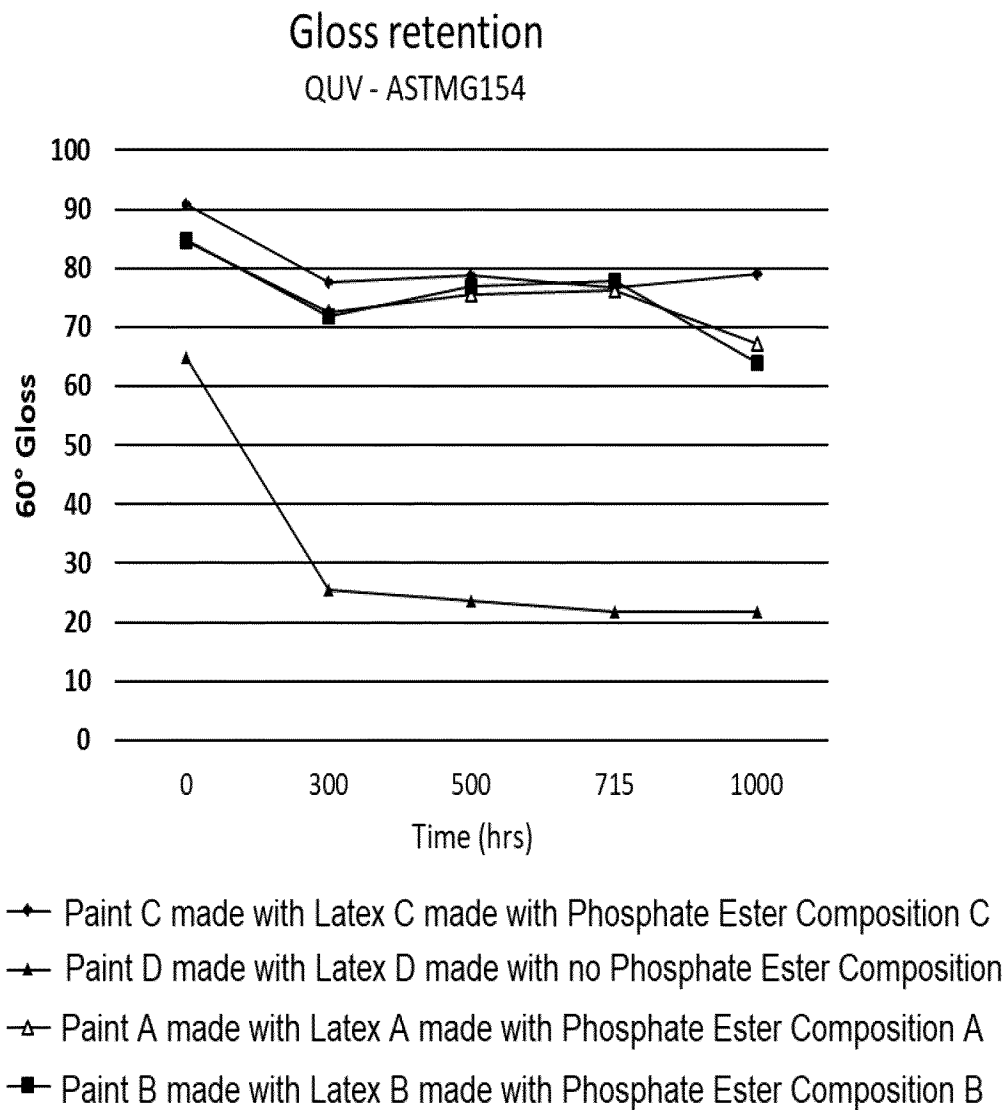
|                 | Paint C formulated with Inventive Latex Polymer C made from the emulsified latex blend with the 3 wt% Inventive phosphate ester composition C and 2 wt% MAA | Paint D formulated with Comparative Latex Polymer D made with 5 % MAA and no phosphate ester composition         |
|-----------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|
| Aluminum Panels |  <p>Dry 5B/5B; Wet 5B/5B</p>                                               |  <p>Dry 3B/3B; Wet 2B/2B</p>  |
| CRS Panels      |  <p>Dry 5B/5B; Wet 5B/5B</p>                                              |  <p>Dry 2B/2B; Wet 2B/2B</p> |
| HDGE Panels     |  <p>Dry 3B/3B</p>                                                        |  <p>Dry 0B/1B</p>            |

FIG. 6



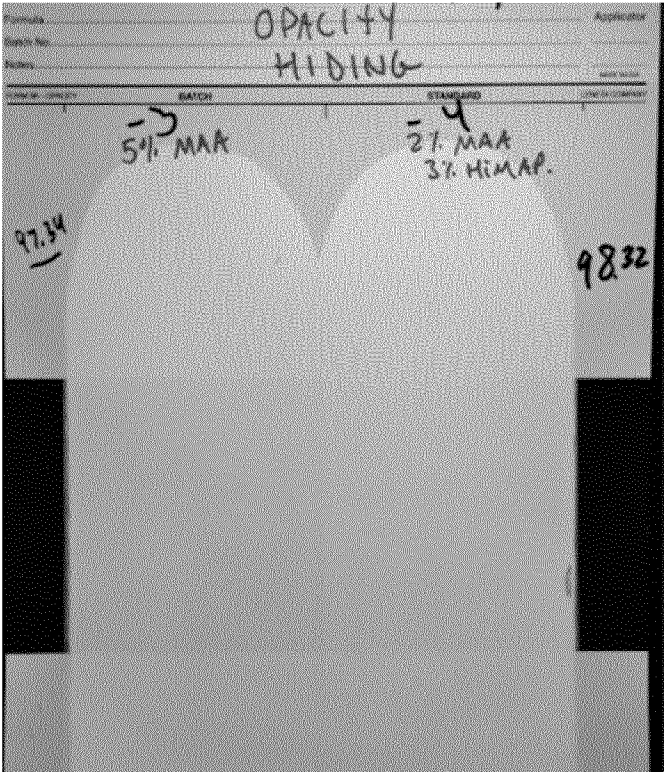


FIG. 7

FIG. 8

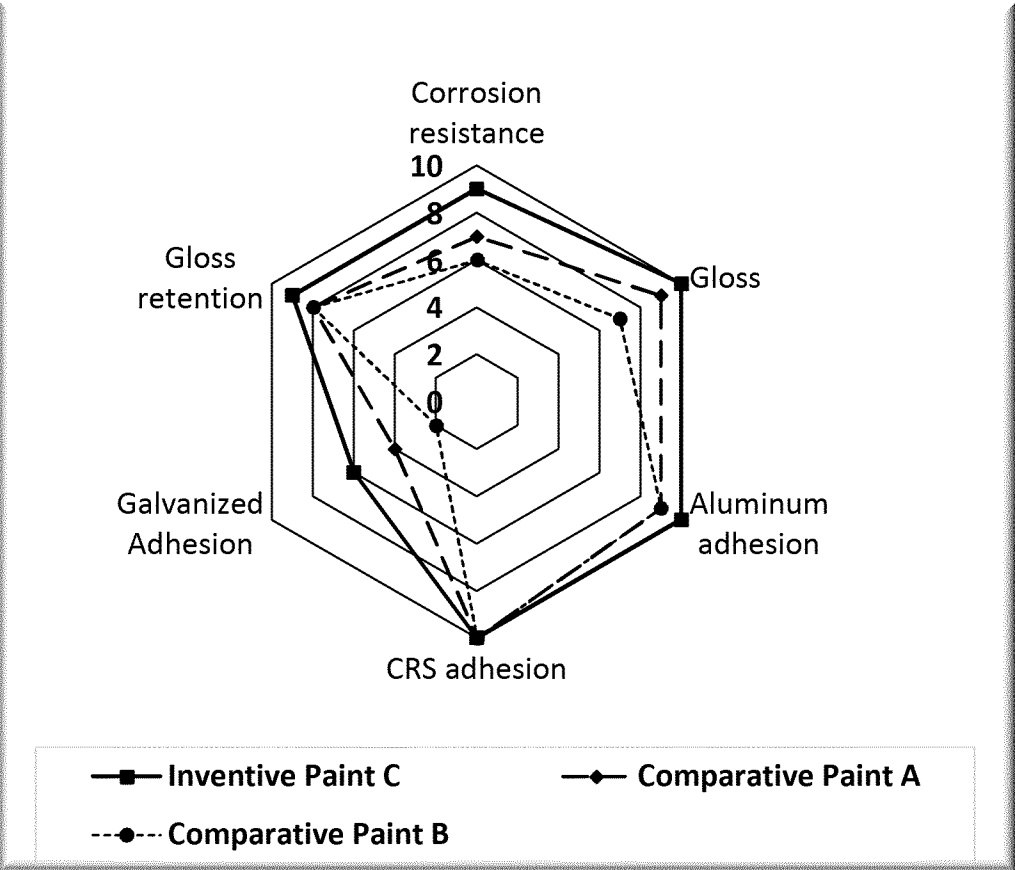


FIG. 9

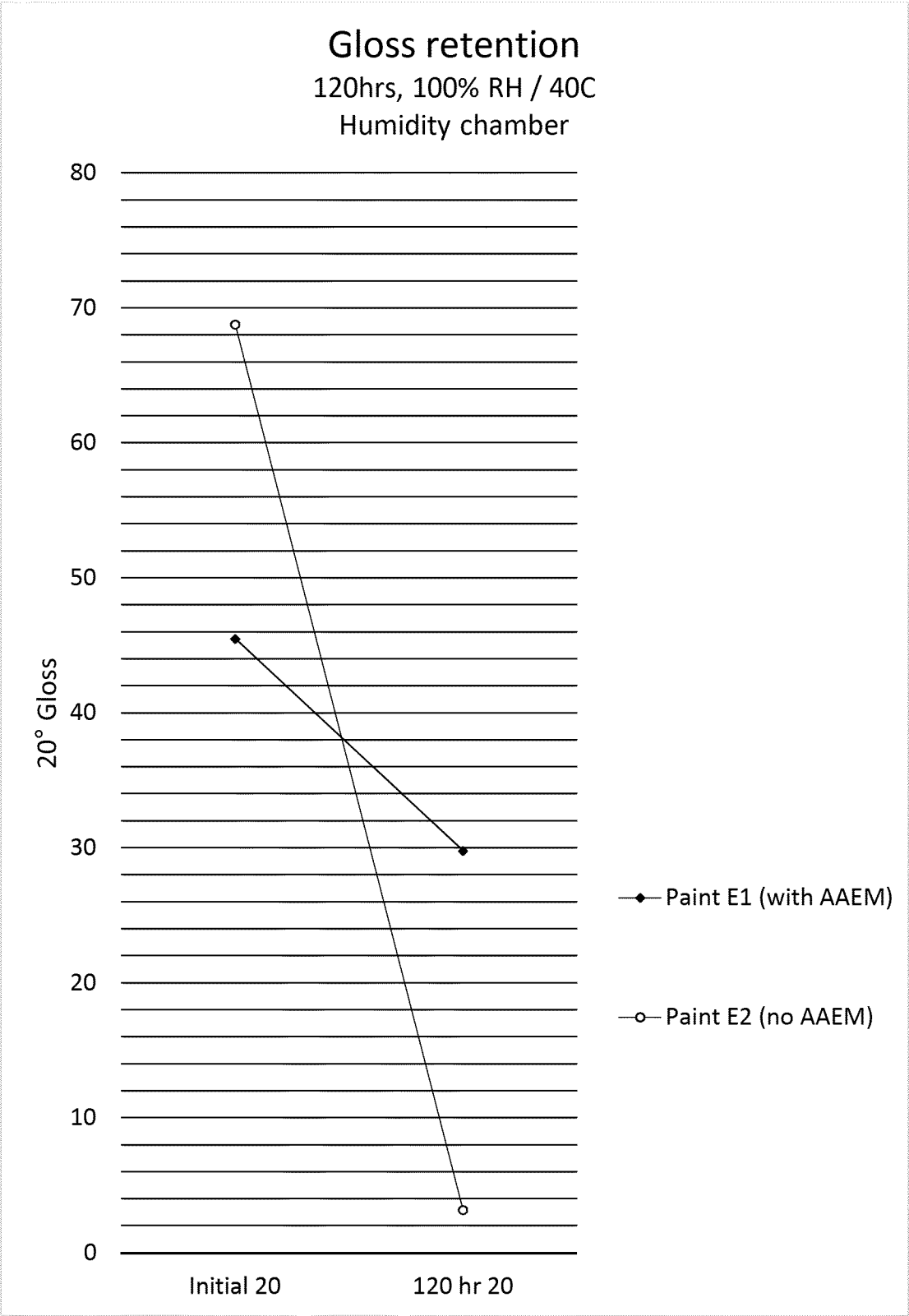


FIG. 10

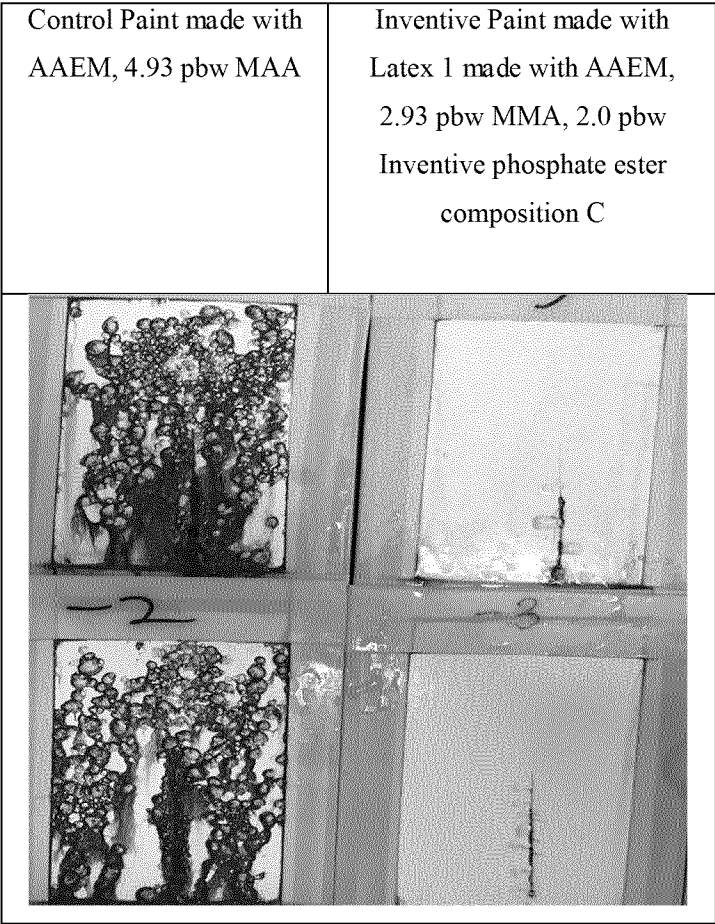
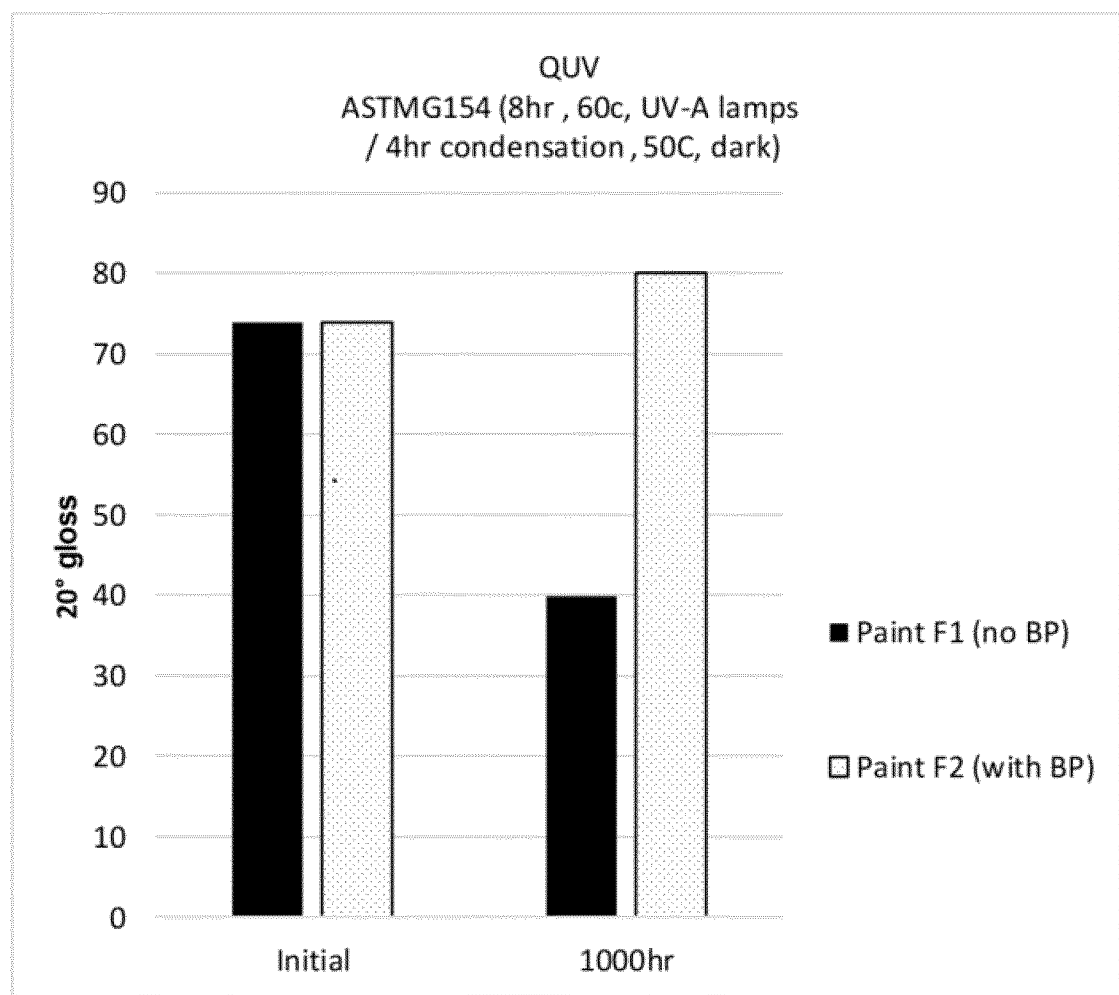


FIG. 11



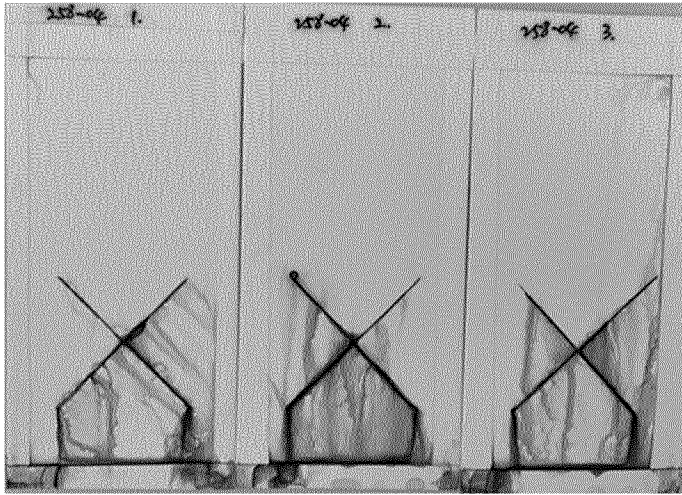


FIG. 12A - Paint AA made with Ex. 10 Latex AA

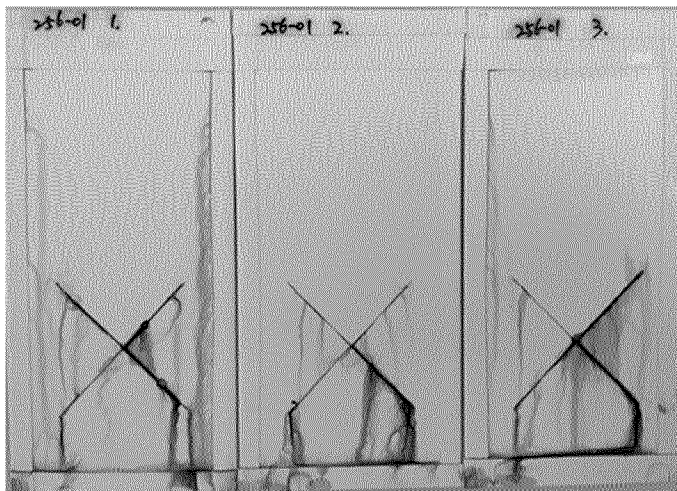


FIG. 12B - Paint BB made with Ex. 10 Latex BB

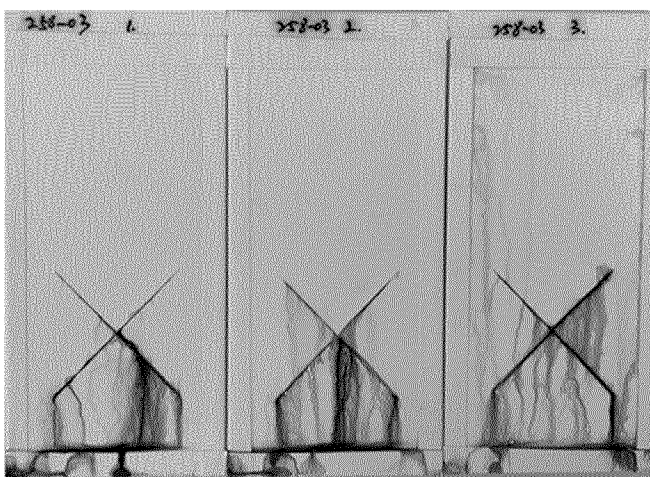


FIG. 12C - Paint CC made with Ex. 10 Latex CC

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2024/070134

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                      |                                                                      |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>INV. C08F2/26 C08F212/08 C09D5/02 C09D125/14 C09D143/02<br>ADD.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                      |                                                                      |
| According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                      |                                                                      |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>C08F C09D<br><br>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br><br>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br><br>EPO-Internal, CHEM ABS Data                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                      |                                                                      |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                      |                                                                      |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                   | Relevant to claim No.                                                |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | US 5 889 116 A (SUZUKI TAKAO [JP] ET AL)<br>30 March 1999 (1999-03-30)<br><br>column 1, lines 8-19<br>column 2, line 50 - column 6, line 56<br>column 9, line 63 - column 11, line 8;<br>example 1; table 1<br>----- | 1,4-10,<br>15,17,<br>19,27                                           |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | EP 1 739 109 A1 (ZAKIKHANI MOHSEN [GB])<br>3 January 2007 (2007-01-03)<br><br>paragraphs [0001], [0005] - [0015],<br>[0021] - [0029]; claims 1-34; example 9<br>-----                                                | 1-10,15,<br>17-19,<br>21,22,27                                       |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | JP H10 338709 A (NIPPON ZEON CO)<br>22 December 1998 (1998-12-22)<br><br>paragraphs [0001] - [0055]; examples 1-3<br>-----<br>-/-                                                                                    | 1,4-10,<br>14,15,<br>17,19,27                                        |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                      |                                                                      |
| <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p> |                                                                                                                                                                                                                      |                                                                      |
| Date of the actual completion of the international search<br><br>16 October 2024                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                      | Date of mailing of the international search report<br><br>31/10/2024 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                      | Authorized officer<br><br>Dessemond, C                               |

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/070134

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                              |                       |
|------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                           | Relevant to claim No. |
| X                                                    | JP 2008 115339 A (KAO CORP)<br>22 May 2008 (2008-05-22)<br>paragraphs [0001], [0005] - [0060],<br>[0062], [0063]<br>method B<br>-----                                                        | 1-10, 15,<br>17, 27   |
| A                                                    | WO 00/55223 A1 (CHEMETALL GMBH [DE]; ADLER<br>HANS JUERGEN [DE] ET AL.)<br>21 September 2000 (2000-09-21)<br>page 1, lines 4-6<br>page 6, line 1 - page 16, line 22; claims<br>1-16<br>----- | 1-29                  |

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/070134

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|----|---------------------|----------------------------|---------------------|
| US 5889116                                | A  | 30-03-1999          | DE 69603244 T2             | 11-11-1999          |
|                                           |    |                     | EP 0778297 A1              | 11-06-1997          |
|                                           |    |                     | US 5889116 A               | 30-03-1999          |
| -----                                     |    |                     |                            |                     |
| EP 1739109                                | A1 | 03-01-2007          | EP 1739109 A1              | 03-01-2007          |
|                                           |    |                     | GB 2427867 A               | 10-01-2007          |
|                                           |    |                     | US 2007145338 A1           | 28-06-2007          |
| -----                                     |    |                     |                            |                     |
| JP H10338709                              | A  | 22-12-1998          | JP 3846516 B2              | 15-11-2006          |
|                                           |    |                     | JP H10338709 A             | 22-12-1998          |
| -----                                     |    |                     |                            |                     |
| JP 2008115339                             | A  | 22-05-2008          | JP 4754461 B2              | 24-08-2011          |
|                                           |    |                     | JP 2008115339 A            | 22-05-2008          |
| -----                                     |    |                     |                            |                     |
| WO 0055223                                | A1 | 21-09-2000          | AU 3556500 A               | 04-10-2000          |
|                                           |    |                     | DE 19911843 A1             | 28-09-2000          |
|                                           |    |                     | WO 0055223 A1              | 21-09-2000          |
| -----                                     |    |                     |                            |                     |