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(54) Title: AN AQUEOUS COATING COMPOSITION AND A PACKAGE COATED THEREWITH

(57) Abstract: A package coated on at least a portion thereof with a coating, the coating being derived from an aqueous coating composition, the aqueous coating composition comprising: a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality; b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material; and c) a carrier comprising water, wherein the coating composition does not comprise an emulsion polymerised acrylic material; and wherein, when two or more different solution polymerised acrylic materials are present, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material. The invention also extends to aqueous coating compositions and methods of forming the same.



AN AQUEOUS COATING COMPOSITION AND A PACKAGE COATED THEREWITH

FIELD OF THE INVENTION

[01] The present invention relates to an aqueous coating composition and to a package coated on at least a portion thereof with a coating, the coating being derived from an aqueous coating composition. For example, the present invention relates to an aqueous coating composition comprising a solution polymerised acid functional acrylic material, a neutraliser operable to at least partially neutralise the solution polymerised acid functional acrylic material, and a carrier comprising water and to a package coated on at least a portion thereof with a coating, the coating being derived from the aqueous coating composition. The present invention also extends to a method of coating a package and to methods of making coating compositions.

BACKGROUND OF THE INVENTION

[02] The application of various treatment and pre-treatment solutions to metals to retard or inhibit corrosion is well established. This can be true in the area of metal food and/or beverage packaging, such as food and/or beverage cans. Coatings are applied to the interior of such containers to prevent the contents from contacting the metal of the container. Contact between the metal and the food and/or beverage can lead to corrosion of the metal container, which can then contaminate the food and/or beverage. This may be of concern when the contents of the can are acidic in nature, such as tomato-based products and soft drinks for example. The coatings applied to the interior of food and/or beverage cans also help prevent corrosion in the head space of the cans, which is the area between the fill line of the food product and the can lid, for example when used with food products having a high salt content.

[03] Various epoxy-based coatings and polyvinyl chloride-based coatings have been used in the past to coat the interior of metal cans to prevent corrosion. The recycling of materials containing polyvinyl chloride or related halide-containing vinyl polymers can generate toxic by-products. Moreover, these polymers may be formulated with epoxy-functional plasticizers. In addition, epoxy-based coatings are prepared from monomers such as bisphenol A and bisphenol A diglycidylether ("BADGE"). BPA is perceived as being harmful to human health and it is therefore desirable to eliminate it from coatings. Derivatives of BPA such as diglycidyl ethers of bisphenol A (BADGE), epoxy novolak resins and polyols prepared from BPA and bisphenol F (BPF) are also perceived to be problematic. Government authorities, particularly in Europe, are becoming even more restrictive on the amount of free BADGE or its by-products that are acceptable.

SUMMARY OF THE INVENTION

[04] According to the present invention there is provided a package coated on at least a portion thereof with a coating, the coating being derived from an aqueous coating composition, the aqueous coating composition comprising:

- a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
- b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material; and

- c) a carrier comprising water,

wherein the coating composition does not comprise an emulsion polymerised acrylic material;
and wherein, when two or more different solution polymerised acrylic materials are present, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material.

[05] There is also provided a package coated on at least a portion thereof with a coating, the coating being derived from an aqueous coating composition, the aqueous coating composition being obtainable by a process comprising the steps of:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;
- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
- iii) at least partially neutralising the acid functionality of the solution polymerised acrylic material with a neutraliser; and
- iv) dispersing the solution polymerised acrylic material in water.

[06] There is also provided an aqueous coating composition, comprising:

- a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
- b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material;
- c) a carrier comprising water; and
- d) a further solution polymerised acrylic material, different from the solution polymerised acid functional acrylic material "a)";

wherein the coating composition does not comprise an emulsion polymerised acrylic material;
and wherein, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material.

[07] There is also provided a package coated on at least a portion thereof with a coating, the coating being derived from an aqueous coating composition, the aqueous coating composition comprising:

- a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
- b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material;
- c) a carrier comprising water; and
- d) a further solution polymerised acrylic material, different from the at least one solution polymerised acid functional acrylic material "a)";

wherein the coating composition does not comprise an emulsion polymerised acrylic material;
and wherein, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material.

[08] There is also provided an aqueous coating composition, obtainable by a process comprising the steps of:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;
- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the solution polymerised acrylic material;
wherein at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of solution polymerised acrylic material and/or the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the solution polymerised acrylic material and the further solution polymerised acrylic material in water.

[09] There is also provided a method of making a coating composition, the method comprising the steps of:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;
- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the solution polymerised acrylic material;
wherein at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of the solution polymerised acrylic material and/or the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the solution polymerised acrylic material and the further solution polymerised acrylic material in water.

[10] The invention disclosed herein also extends to a package, such as a food or beverage can, coated on at least a portion thereof with a coating, the coating being derived from any of the aqueous coating compositions disclosed herein.

DETAILED DESCRIPTION OF THE INVENTION

[11] The aqueous coating compositions of the present invention comprises a solution polymerised acrylic material. As used herein, "solution polymerised" means a polymer that is formed by a polymerisation method whereby a monomer is substantially dissolved in a solvent and polymerised. Once said monomer has been polymerised, the resultant solution polymerised acrylic material is suitably substantially soluble in said solvent.

[12] In the present invention, where there are two or more solution polymerised acrylic materials, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material. This can be measured and confirmed by many different techniques well known to a person skilled in the art. For example, this can be confirmed by infra-red spectroscopy, GPC, gas chromatography etc. A person skilled in the art will be aware of the appropriate technique to use, depending on the functionality of the solution acrylics in question.

[13] However, as a general technique to determine that there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material, a person skilled in the art can use triple detector GPC to generate a Mark-Houwink-Sakurada plot of the materials before and after mixing. If the slope of this plot is linear and shows a gradient of greater than 0.5, then there is no branched material within the polymers, therefor no linkage between the solution polymerised acrylic materials.

[14] As reported herein Gel Permeation Chromatography (GPC) Triple detection was used to characterize the polymer samples and to thereby determine that there is no covalent linkage between one solution polymerized acrylic material and another solution polymerized acrylic material. Samples with solvent were vacuum dried (without heating) prior to analysis. Analysis was performed using a HPLC separation module with a Wyatt Technology Light Scattering detector (DAWN); a differential refractive index detector (Optilab rEX)) and a Differential Viscometer detector (Viscostar). The performance of instrument was validated by a polystyrene standard of 30,000 Da. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 ml min⁻¹, and three PL Gel Mixed C columns were used for separation. A Mark-Houwink-Sakurada plot of the materials before and after mixing was generated from the results and the slope and gradient of the plot reviewed the determine if covalent linkage had occurred.

[15] The aqueous coating composition may comprise a solution polymerised acrylic material and a further solution polymerised acrylic material. Unless specifically referenced otherwise herein, references to a "solution polymerised acrylic material" refer equally to a solution polymerised acrylic material and to a further solution polymerised acrylic material.

[16] The aqueous coating composition may comprise any suitable solution polymerised acrylic material. The solution polymerised acrylic material is suitably formed from an acrylic monomer. Suitable

acrylic monomers will be well known to a person skilled in the art. The solution polymerised acrylic material may be formed from more than one acrylic monomer. Suitable acrylic monomers include, but are not limited to, alkyl (alk)acrylate, such as C₁ to C₆ alkyl (C₁ to C₆ alk)acrylate, for example, C₁ to C₆ alkyl (meth)acrylate, and (alk)acrylic acid, such as (C₁ to C₆ alk)acrylic acid. The acrylic monomers may comprise a functional group, such as an acid group. For example, the acrylic monomer may comprise acrylic acid or methacrylic acid.

[17] The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) comprises acidic functionality. By this, it is meant that the solution polymerised acrylic material comprises pendant acid groups, such as pendant carboxylic acid groups, for example. This may be achieved, by way of example, by including an acid functional acrylic monomer, such as acrylic acid or methacrylic acid, for example, in the preparation of the solution polymerised acrylic material.

[18] As used herein, "(alk)acrylate", "(meth)acrylate" and like terms are used conventionally and herein to refer to both alkacrylate and acrylate, such as methacrylate and acrylate.

[19] Examples of suitable acrylic monomers include, but are not limited to, acrylic acid, methacrylic acid, methyl acrylate; methyl methacrylate; ethyl acrylate; ethyl methacrylate; propyl acrylate; propyl methacrylate; butyl acrylate; butyl methacrylate, isobornyl acrylate, isobornyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, glycidyl methacrylate; ethylene glycol diacrylate; ethylene glycol dimethacrylate; 1,6-hexanediol diacrylate; 1,6-hexanediol dimethacrylate; 4-hydroxybutyl acrylate; 4-hydroxybutyl methacrylate; allyl methacrylate; benzyl methacrylate; phosphate esters of 2-hydroxyethyl methacrylate; those sold under the trade name SIPOMER such as SIPOMER PAM-100, SIPOMER PAM-200 and SIPOMER PAM-300 (phosphate esters of polypropylene glycol monoacrylate commercially available from Solvay); and combinations thereof. Any other acrylic monomers known to those skilled in the art could also be used.

[20] The solution polymerised acrylic material may comprise acrylic acid, methacrylic acid, ethyl acrylate, ethyl methacrylate, butyl methacrylate, butyl acrylate, hydroxyethyl methacrylate, hydroxyethyl acrylate or combinations thereof.

[21] The solution polymerised acrylic material may comprise acrylic acid, methacrylic acid, ethyl methacrylate, ethyl acrylate or combinations thereof.

[22] The solution polymerised acrylic material may comprise acrylic acid, methacrylic acid, ethyl acrylate, hydroxyethyl methacrylate or combinations thereof.

[23] The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may comprise methacrylic acid and/or acrylic acid. The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may comprise any suitable amount of methacrylic acid and/or acrylic acid. The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may comprise from 2 to 75 wt%, such as from 2 to 60 wt%, such as from 2 to 55 wt%, such as from 2 to 50 wt% methacrylic acid and/or acrylic acid based on the total weight of the monomers in the solution

polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material).

[24] The solution polymerised acrylic material and/or the further solution polymerised acrylic material may be formed from a monomer component comprising an optionally substituted styrene or a styrene-mimicking ethylenically unsaturated monomer. The solution polymerised acrylic material may be formed from a substituted styrene monomer component. The substituted styrene monomer component may comprise a 2, 3 or 4- alkyl or aryl substituted styrene.

[25] Examples of suitable substituted styrene monomers include but are not limited to, alpha-methyl styrene; 3,4-alpha-methyl styrene; methyl styrenes such as 2-methyl styrene, 4-methyl styrene (vinyl toluene) and the like; dimethyl styrenes such as 2,3-dimethyl styrene; 2-ethyl styrene; 4-tertbutylstyrene; 4-methoxystyrene; 4-phenylstyrene; 4-phenoxy styrene; 4-propyl styrene; 4-benzylstyrene; 4-cyclohexyl styrene; 4-dodecyl styrene; 4-(phenyl butyl)styrene; 2-methyl-4-isopropyl styrene; 2-ethyl-4-benzyl styrene; halostyrenes such as 4-chlorostyrene, 2,5-dichlorostyrene, 3,4-dichlorostyrene, 2,6-dichlorostyrene, 4-fluorostyrene; divinylbenzene; isopropyl styrene, t-butyl styrene; trans-beta-styrene.

[26] The styrene-mimicking ethylenically unsaturated monomer may comprise an optionally saturated monocyclic group, for example, benzyl acrylate, benzyl methacrylate, cyclohexyl acrylate or cyclohexyl methacrylate. The solution polymerised acrylic material and/or the further solution polymerised acrylic material may be formed from a monomer component comprising terpene monomers or derivatives thereof, rosin monomers or derivatives thereof, and/or cardanol monomers or derivatives thereof. Examples of terpene monomers or derivatives thereof include but are not limited to, monoterpenes such as α -pinene, β -pinene, camphene, sabinene, limonene and myrcene; sesquiterpenes such as bisabolene and nerolidol; and diterpenes. Examples of rosin monomers or derivatives thereof include but are not limited to, rosin, rosin acids, abietic acid, neabietic acid, palustric acid, pimaric acid, levopimaric acid, maleopimaric acid, fumaropimaric acid, isopimaric acid, rosin-formaldehyde resin, rosin (meth)acrylate, rosin alcohol and rosin phenol. Examples of cardanol monomers or derivatives thereof include but are not limited to cardanol, cardanyl (meth)acrylate, cardanol (meth)acrylate, anacardic acid, cardanol glycidyl ether, cardanol-formaldehyde resin, cardanol epoxies, cardanol phenols and cardanol alcohols.

[27] The solution polymerised acrylic material may be formed from an additional ethylenically unsaturated monomer. Suitable additional ethylenically unsaturated monomers include, but are not limited to, aryl substituted ethylenically unsaturated monomers such as, for example, styrene; unsaturated carboxylic acids or diacids (or anhydrides), such as maleic acid (or anhydride) or itaconic acid (or anhydride); and combinations thereof. The solution polymerised acrylic material may comprise styrene. Other ethylenically unsaturated monomers include C₂ to C₆ alkenes, such as ethylene, propylene, and/or butylene, for example.

[28] The solution polymerised acrylic material may be substantially free, may be essentially free or may be completely free of styrene. By substantially free in relation to styrene, is meant that the solution polymerised acrylic material is formed from monomers which comprise less than 5 wt% of styrene based on the total weight of the monomers from which the solution polymerised acrylic material is formed. By

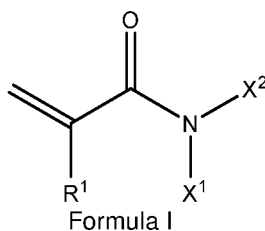
essentially free in relation to styrene, is meant that the solution polymerised acrylic material is formed from monomers which comprise less than 1 wt% of styrene based on the total weight of the monomers from which the solution polymerised acrylic material is formed. By completely free in relation to styrene, is meant that the solution polymerised acrylic material is formed from monomers which comprise less than 0.01 wt% of styrene based on the total weight of the monomers from which the solution polymerised acrylic material is formed. Suitably, solution polymerised acrylic material is formed from monomers which comprise no, i.e. 0 wt%, styrene based on the total weight of the monomers from which the solution polymerised acrylic material is formed.

[29] Advantageously, the solution polymerised acrylic material may be completely free of styrene.

[30] The solution polymerised acrylic material may be substantially free, may be essentially free or may be completely free of C₂ to C₆ alkenes. By substantially free in relation to C₂ to C₆ alkenes, is meant that the solution polymerised acrylic material is formed from monomers which comprise less than 10 wt% of C₂ to C₆ alkenes based on the total weight of the monomers from which the solution polymerised acrylic material is formed. By essentially free in relation to C₂ to C₆ alkenes, is meant that the solution polymerised acrylic material is formed from monomers which comprise less than 5 wt% of C₂ to C₆ alkenes based on the total weight of the monomers from which the solution polymerised acrylic material is formed. By completely free in relation to C₂ to C₆ alkenes, is meant that the solution polymerised acrylic material is formed from monomers which comprise less than 1 wt% of C₂ to C₆ alkenes based on the total weight of the monomers from which the solution polymerised acrylic material is formed. Suitably, solution polymerised acrylic material is formed from monomers which comprise less than 0.1wt% of C₂ to C₆ alkenes or even no, i.e. 0 wt%, C₂ to C₆ alkenes based on the total weight of the monomers from which the solution polymerised acrylic material is formed.

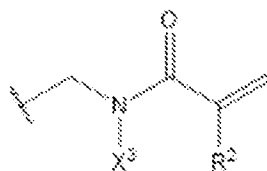
[31] The solution polymerised acrylic material may be substantially free, may be essentially free or may be completely free of ethylene. By substantially free in relation to ethylene, is meant that the solution polymerised acrylic material is formed from monomers which comprise less than 10 wt% of ethylene based on the total weight of the monomers from which the solution polymerised acrylic material is formed. By essentially free in relation to ethylene, is meant that the solution polymerised acrylic material is formed from monomers which comprise less than 5 wt% of ethylene based on the total weight of the monomers from which the solution polymerised acrylic material is formed. By completely free in relation to ethylene, is meant that the solution polymerised acrylic material is formed from monomers which comprise less than 1 wt% of ethylene based on the total weight of the monomers from which the solution polymerised acrylic material is formed. Suitably, solution polymerised acrylic material is formed from monomers which comprise less than 0.1 wt% of ethylene, or even, no, i.e. 0 wt%, ethylene based on the total weight of the monomers from which the solution polymerised acrylic material is formed.

[32] The solution polymerised acrylic material and/or further solution polymerised acrylic material may be formed from a monomer component comprising an acrylamide monomer of formula I:



wherein R¹ represents a H or alkyl group; and

X¹ represents a linear or branched alkyl, a -Y-O-Z group; or is according to formula II;



wherein

Y represents a bivalent linear or branched alkylene bridging group, and

Z represents linear or branched alkyl group, or is according to formula II, or H;

X³ represents a H or alkyl group;

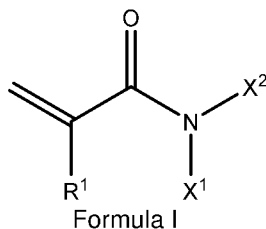
R² represents a H or alkyl group;

X² represents a linear or branched alkyl, H or a -Y-O-Z group;

wherein

Y represents a bivalent linear or branched alkylene bridging group, and Z represents a linear or branched alkyl group, or H.

[33] The solution polymerised acrylic material and/or further solution polymerised acrylic material may be formed from a monomer component comprising an acrylamide monomer of formula I:



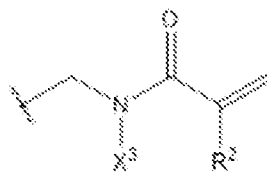
wherein R¹ represents a H or alkyl group; and

X¹ represents a linear or branched alkyl, or a -Y-O-Z group;

wherein

Y represents a bivalent linear or branched alkylene bridging group, and

Z represents linear or branched alkyl group, or is according to formula II, or H;



Formula II

wherein

X^3 represents a H or alkyl group;

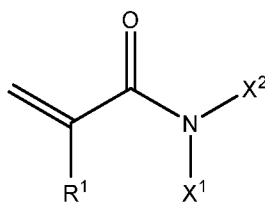
R^2 represents a H or alkyl group;

X^2 represents a linear or branched alkyl, H or a -Y-O-Z group;

wherein

Y represents a bivalent linear or branched alkylene bridging group, and Z represents a linear or branched alkyl group, or H.

[34] The solution polymerised acrylic material and/or further solution polymerised acrylic material may be formed from a monomer component comprising an acrylamide monomer of formula I:



Formula I

wherein R^1 represents a H or alkyl group; and

X^1 represents a linear or branched alkyl, or a -Y-O-Z group;

wherein

Y represents a bivalent linear or branched alkylene bridging group, and

Z represents linear or branched alkyl group, or H;

X^2 represents a linear or branched alkyl, H or a -Y-O-Z group;

wherein

Y represents a bivalent linear or branched alkylene bridging group, and

Z represents a linear or branched alkyl group, or H.

[35] R^1 may represent H or C_1 - C_{20} alkyl group, such as C_1 - C_{10} alkyl group, such as C_1 - C_8 alkyl group, such as C_1 - C_6 alkyl group, such as C_1 - C_4 alkyl group. R^1 may represent H, methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclohexyl or cycloheptyl group. R^1 may represent H or C_1 - C_4 alkyl group, such as methyl, ethyl, propyl or butyl group. R^1 may represent H.

[36] R² may represent H or C₁-C₂₀ alkyl group, such as C₁-C₁₀ alkyl group, such as C₁-C₈ alkyl group, such as C₁-C₆ alkyl group, such as C₁-C₄ alkyl group. R² may represent H, methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclohexyl or cycloheptyl group. R² may represent H or C₁-C₄ alkyl group, such as methyl, ethyl, propyl or butyl group. R² may represent H.

[37] X¹ may represent a linear or branched C₁-C₂₀ alkyl group, such as C₁-C₁₀ alkyl group, such as C₁ to C₈ alkyl group, such as C₁-C₆ alkyl group, such as C₁-C₄ alkyl group. X¹ may represent methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclohexyl or cycloheptyl group. X¹ may represent a C₁-C₄ alkyl group, such as methyl, ethyl, propyl or butyl group. X¹ may represent -Y-O-Z group.

[38] X² may represent a linear or branched C₁-C₂₀ alkyl group, such as C₁-C₁₀ alkyl group, such as C₁ to C₈ alkyl group, such as C₁-C₆ alkyl group, such as C₁-C₄ alkyl group, or H. X² may represent H, methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclohexyl or cycloheptyl group. X² may represent H or C₁-C₄ alkyl group, such as methyl, ethyl, propyl or butyl group. X² may represent a -Y-O-Z group. X² may represent H.

[39] X³ may represent a linear or branched C₁-C₂₀ alkyl group, such as C₁-C₁₀ alkyl group, such as C₁ to C₈ alkyl group, such as C₁-C₆ alkyl group, such as C₁-C₄ alkyl group, or H. X³ may represent H, methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclohexyl or cycloheptyl group. X³ may represent a H or C₁-C₄ alkyl group, such as methyl, ethyl, propyl or butyl group. X³ may represent H.

[40] Y may represent a bivalent linear or branched alkylene bridging group, such as C₁-C₁₀ alkylene bridging group, such as C₁-C₈ alkylene bridging group, such as C₁-C₆ alkylene bridging group, such as C₁-C₄ alkylene bridging group. Y may represent methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene or decylene. Y may represent a methylene, ethylene or propylene group.

[41] Z may represent a linear or branched C₁-C₂₀ alkyl group, such as C₁-C₁₀ alkyl group, such as C₁ to C₈ alkyl group, such as C₂-C₇ alkyl group, such as C₂-C₆ alkyl group, or H. Z may represent H, methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclohexyl or cycloheptyl group. Z may represent H or C₂-C₆ alkyl group, such as, ethyl, propyl, butyl group, pentyl or hexyl.

[42] R¹, X¹ and X² may each be selected independently from the above lists to for any combination of an acrylamide of formula I according to the invention. For example, both X¹ and X² may each independently be selected as the same, or different -Y-O-Z groups. At least two of R¹, X¹ or X² may be the same. At least X¹ and X² may be different groups.

[43] X¹ and X² may be covalently linked such as to form a cyclic structure.

[44] The solution polymerised acrylic material and/or further solution polymerised acrylic material may be formed from a monomer component comprising an acrylamide monomer of formula I wherein R¹ represents H or C₁-C₄ alkyl group; X¹ represents a C₁-C₁₀ alkyl group or a -Y-O-Z group wherein Y represents a C₁-C₈ alkylene bridging group and Z represents a C₁-C₁₀ alkyl group; and X² represents H or C₁-C₄ alkyl group.

[45] The solution polymerised acrylic material and/or further solution polymerised acrylic material may be formed from a monomer component comprising an acrylamide monomer of formula I wherein R¹ represents H or C₁-C₄ alkyl group; X¹ represents a -Y-O-Z group wherein Y represents a C₁-C₄ alkylene bridging group and Z represents a C₂-C₇ alkyl group; and X² represents H.

[46] The solution polymerised acrylic material and/or further solution polymerised acrylic material may be formed from a monomer component comprising an acrylamide monomer of formula I wherein R¹ represents H or methyl; X¹ represents a -Y-O-Z group wherein Y represents a methylene or ethylene bridging group and Z represents a C₂-C₆ alkyl group; and X² represents H.

[47] The solution polymerised acrylic material and/or further solution polymerised acrylic material may be formed from a monomer component comprising n-butoxymethyl acrylamide (NBMA).

[48] The solution polymerised acrylic material may comprise at least 0.5 wt% acrylamide monomer of formula I based on the total weight of the monomers in the solution polymerised acrylic material, such as at least 1 wt%, such as at least 1.5 wt%, such as at least 2 wt%, such as at least 5 wt%. The solution polymerised acrylic material may comprise at least 20 wt% acrylamide monomer of formula I based on the total weight of the monomers in the solution polymerised acrylic material, such as at least 30 wt%, such as at least 40 wt%. The solution polymerised acrylic material may comprise at least 2 wt% acrylamide monomer of formula I based on the total weight of the monomers in the solution polymerised acrylic material and/or further solution polymerised acrylic material, such as more than 2 wt%.

[49] The further solution polymerised acrylic material may comprise at least 1 wt% acrylamide monomer of formula I based on the total weight of the monomers in the further acrylic material, such as at least 2 wt%, such as at least 3 wt%, such as at least 4 wt%, such as at least 5 wt%. The further solution polymerised acrylic material may comprise at least 20 wt% acrylamide monomer of formula I based on the total weight of the monomers in the further acrylic material, such as at least 30 wt%, such as at least 40 wt%. The further solution polymerised acrylic material may comprise at least 1 wt% acrylamide monomer of formula I based on the total weight of the monomers in the further solution polymerised acrylic material, such as at least 2 wt%, such as at least 5 wt%, such as at least 10 wt%, such as at least 15 wt%, such as at least 25 wt%, or even at least 40 wt%. The further solution polymerised acrylic material may comprise at least 5 wt% acrylamide monomer of formula I based on the total weight of the monomers in the solution polymerised acrylic material and/or further solution polymerised acrylic material, such as more than 5 wt%.

[50] The solution polymerised acrylic material and further solution polymerised acrylic material may comprise at least 1 wt% acrylamide monomer of formula I based on the total weight of the monomers in the solution polymerised acrylic material and further solution polymerised acrylic material, such as at least 2 wt%, such as at least 5 wt%, such as at least 10 wt%, such as at least 15 wt%, such as at least 25 wt%, or even at least 40 wt%. The solution polymerised acrylic material and further solution polymerised acrylic material may comprise at least 5 wt% acrylamide monomer of formula I based on the total weight of the monomers in the acrylic material and/or further acrylic material, such as more than 5 wt%.

[51] The aqueous coating compositions described herein may comprise at least 1 wt% acrylamide monomer of formula I based on the total solid weight of the aqueous coating composition, such as at least 2 wt%, such as at least 5 wt%, such as at least 10 wt%, such as at least 15 wt%.

[52] The aqueous coating compositions described herein comprising an solution polymerised acrylic material and further solution polymerised acrylic material wherein only one of the solution polymerised acrylic material or further acrylic material is formed from a monomer component comprising an acrylamide monomer of formula I, the wt% ratio of the acrylamide containing solution polymerised acrylic material to the non-acrylamide containing solution polymerised acrylic material may be less than 1.2:1, such as less than 1:1, such as less than 0.8:1, such as less than 0.5:1.

[53] By non-acrylamide containing solution polymerised acrylic material it is meant either the solution polymerised acrylic material or further solution polymerised acrylic material that is not formed from a monomer component comprising an acrylamide monomer of formula I.

[54] The solution polymerised acrylic material is formed by a solution polymerisation method. Suitable solution polymerisation methods will be well known to a person skilled in the art. The solution polymerisation method suitably comprises a plurality of components, which may be referred to as a solution polymerisation reaction mixture.

[55] The solution polymerisation reaction mixture may comprise a solution polymerisation monomer component. The solution polymerisation monomer component may comprise the first, second or further monomer component. The solution polymerisation monomer component may comprise an acrylic monomer as described above. The solution polymerisation monomer component may optionally comprise additional ethylenically unsaturated monomers as described above.

[56] The solution polymerisation reaction mixture may further comprise an initiator. The initiator may be a free radical initiator. Suitable initiators include, but are not limited to, tertiary butyl perbenzoate; tert butyl peroxy 3,5,5 trimethylhexanoate; tertiary butyl peroxy 2-ethyl hexanoate; di tertiary butyl peroxide; tertiary butyl peracetate; tertiary butyl peroctoate; azo type initiators such as, for example, 2,2'- azobis(isobutyronitrile), 2,2'-Azobis(2-methylbutyronitrile), 2,2'-Azobis(2,4-dimethyl valeronitrile) and 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile); persulphate initiators such as, for example, ammonium persulphate, sodium persulphate or potassium persulphate; and combinations thereof. The initiator may be soluble in the solution polymerisation reaction mixture. The initiator may be soluble in the monomer mixture.

[57] The initiator may comprise tert butyl peroxy 3,5,5 trimethylhexanoate, tertiary butyl peroctoate, di-tertiary amyl peroxide, or combinations thereof.

[58] The solution polymerisation reaction mixture may comprise a solvent or mixture of solvents. Suitable solvents will be well known to a person skilled in the art. Examples of suitable solvents include, but are not limited to, alcohols such as, for example, n-butanol, pentanol or hexanol; glycols such as, for example, butyl glycol; glycol ethers such as, for example, 2-butoxy ethanol, 1-methoxy propan-2-ol or dipropylene glycol mono methyl ether; and combinations thereof. The solvent may comprise a mixture of solvents, such as n-butanol and butyl glycol. It will be appreciated by a person skilled in the

art that the solvent or mixture of solvents may be chosen such that the monomer mixture is substantially soluble in said solvent or mixture of solvents.

[59] The solution polymerisation monomer component is caused to undergo polymerisation in the solvent or mixture of solvents to form the solution polymerised acrylic material. The solution polymerisation of the solution polymerisation monomer component may be carried out as a free radical initiated solution polymerisation in a solvent or mixture of solvents.

[60] Solution polymerisation may be carried out in a suitable reaction vessel. The solution polymerisation monomer component, initiator and/or solvent or mixture of solvents may be added to the reaction vessel in any suitable order. For example, the solvent or mixture of solvents may be added to the reaction vessel before the solution polymerisation monomer component and/or initiator are added to the reaction vessel. The solution polymerisation monomer component and initiator are added to the reaction vessel at the same time. The solution polymerisation monomer component and/or initiator may be added to the reaction vessel over any suitable period of time. The solution polymerisation monomer component and/or initiator may be added to the reaction vessel over a time period of 0 to 12 hours, suitably 30 minutes to 8 hours, such as 1 hour to 6 hours, or even 2 hours to 4 hours. The solution polymerisation monomer component and/or initiator may be added to the reaction vessel over a time period of 3 hours. For the avoidance of doubt, when the solution polymerisation monomer component and/or initiator are added over a time period of 0 hours, all of the solution polymerisation monomer component and/or initiator are added at the same time (i.e., in one single addition).

[61] Solution polymerisation may be carried out at any suitable temperature. Solution polymerisation may be carried out at an elevated temperature. Solution polymerisation may be carried out at a temperature from 80°C to 200°C, suitably from 100 to 180°C, such as from 120 to 160°C, or even from 130 to 150°C. Solution polymerisation may be carried out at a temperature from 135 to 140°C. Solution polymerisation may be carried out at reflux. Solution polymerisation may be carried out at a temperature of 80°C or above, such as 100°C or above, such as 120°C or above, such as 130°C or above, or even 135°C or above. Solution polymerisation may be carried out at a temperature of 250°C or below, such as 200°C or below, such as 180°C or below, such as 160°C or lower, such as 150°C or lower, or even 145°C or lower.

[62] The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have any suitable number-average molecular weight (M_n). The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have an M_n from 500 to 250,000 Daltons ($\text{Da} = \text{g/mole}$), such as from 500 to 100,000 Da, such as from 1,000 to 50,000 Da, such as from 2,500 to 20,000 Da, or even from 4,000 to 10,000 Da.

[63] As reported herein, the M_n was determined by gel permeation chromatography using a polystyrene standard according to ASTM D6579-11 ("Standard Practice for Molecular Weight Averages and Molecular Weight Distribution of Hydrocarbon, Rosin and Terpene Resins by Size Exclusion Chromatography". RI detector, solvent: unstabilised THF, retention time marker: toluene, sample concentration: 10mg/ml).

[64] The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have any suitable weight-average molecular weight (Mw). The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have an Mw from 500 to 250,000 Daltons (Da = g/mole), such as from 1,000 to 200,000 Da, such as from 2,500 to 100,000 Da, such as from 5,000 to 75,000 Da, such as from 10,000 to 50,000 Da, such as from 10,000 to 30,000 Da, or even from 15,000 to 25,000 Da.

[65] As reported herein, the Mw was determined by gel permeation chromatography using a polystyrene standard according to ASTM D6579-11 ("Standard Practice for Molecular Weight Averages and Molecular Weight Distribution of Hydrocarbon, Rosin and Terpene Resins by Size Exclusion Chromatography". UV detector; 254nm, solvent: unstabilised THF, retention time marker: toluene, sample concentration: 2mg/ml).

[66] The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have any suitable acid value (AV) expressed on solids. The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have an AV expressed on solids of from 0 to 400 mg KOH/g, such as from 5 to 350 mg KOH/g, such as from 10 to 250 mg KOH/g, such as from 20 to 200 mg KOH/g, such as from 30 to 150 mg KOH/g, such as from 40 to 100 mg KOH/g, or even from 50 to 80 mg KOH/g.

[67] The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have any suitable acid value (AV) expressed on solution. The solution may be a 50 wt% solution in a solvent. The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have an AV expressed on solution of from 0 to 200 mg KOH/g, such as from 2.5 to 175 mg KOH/g, such as from 5 to 125 mg KOH/g, such as from 10 to 100 mg KOH/g, such as from 15 to 75 mg KOH/g, such as from 20 to 50 mg KOH/g, or even from 25 to 40 mg KOH/g.

[68] As reported herein, the acid value (AV) expressed on solids was determined by titration with 0.1M methanolic potassium hydroxide (KOH) solution. A sample of solid polymer (0.1 to 3g depending on acid number) was weighed accurately into a conical flask and is dissolved, using light heating and stirring as appropriate, in 25ml of dimethyl formamide containing phenolphthalein indicator. The solution was then cooled to room temperature and titrated with the 0.1M methanolic potassium hydroxide solution. The resulting acid number is expressed in units of mg KOH/g and is calculated using the following equation:

$$\text{Acid value} = \frac{\text{titre of KOH solution (ml)} \times \text{molarity KOH solution (M)} \times 56.1}{\text{weight of solid sample (g)}}$$

[69] It will be appreciated by a person skilled in the art that the method for measuring the acid value (AV) expressed on solution was the same as described above for the acid value (AV) expressed on

solids with the exception that the polymer was added to the 25ml of dimethyl formamide containing phenolphthalein indicator as a 50wt% solution in a solvent.

[70] The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have any suitable glass transition temperature (T_g). The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may have a T_g from -20 to 100°C, such as from -20 to 75°C, such as from -20 to 50°C, or even from -20 to 25°C.

[71] As reported herein, the T_g was measured according to ASTM D6604-00(2013) ("Standard Practice for Glass Transition Temperatures of Hydrocarbon Resins by Differential Scanning Calorimetry". Heat-flux differential scanning calorimetry (DSC), sample pans: aluminium, reference: blank, calibration: indium and mercury, sample weight: 10mg, heating rate: 20°C/min).

[72] The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may be formed from an epoxy containing monomer, such as an epoxy containing acrylic monomer, such as, for example, glycidyl methacrylate. Therefore, for example, one or both of the first monomer component and the second monomer component may comprise an epoxy containing monomer, such as an epoxy containing acrylic monomer, such as, for example, glycidyl methacrylate. Therefore, the solution polymerised acrylic material may comprise epoxy groups. In such a scenario, the epoxy group on the solution polymerised acrylic material may be reacted. For example, the epoxy group on the solution polymerised acrylic material may be chemically reacted, such as by reacting the epoxy group on the solution polymerised acrylic material with an epoxy reactive material, which may thereby remove the epoxy functionality of the solution polymerised acrylic. In this manner, an epoxy reacted solution polymerised material may be formed.

[73] The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may comprise any suitable amount of an epoxy containing monomer. The solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material) may comprise from 10 to 90 wt%, such as from 30 to 80 wt%, such as from 50 to 75 wt%, such as from 55 to 70 wt% epoxy containing monomer based on the total weight of the monomers of the solution polymerised acrylic material (or at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material).

[74] The epoxy reactive material comprises any material that reacts with the epoxy group to thereby remove the epoxy functionality. Suitable examples of epoxy reactive materials will be well known to a person skilled in the art. The epoxy reactive material may comprise, for example, an acid material, such as an organic acid material. For example, the epoxy reactive material may comprise phosphoric acid, phenyl phosphinic acid, benzoic acid, acetic acid, and/or itaconic acid.

[75] For the avoidance of doubt, as used herein reference to the epoxy group being chemically "reacted" means that the epoxy group has been removed.

[76] The solution polymerised acrylic material may be formed from an epoxy containing monomer. The epoxy group on the solution polymerised acrylic material may be reacted. The epoxy groups on

the solution polymerised acrylic material may be reacted by reacting the epoxy group with an organic acid, such as benzoic acid. In this manner, an epoxy reacted solution polymerised acrylic material may be formed. The epoxy group of the solution polymerised acrylic material may be reacted prior to contacting the solution polymerised acrylic material with the second monomer component. The epoxy group of the solution polymerised acrylic material may be reacted prior to contacting the solution polymerised acrylic material with the second monomer component such that all epoxy functionality of the solution polymerised acrylic material is removed prior to contacting the solution polymerised acrylic material with the second monomer component.

[77] There is also provided an aqueous coating composition obtainable by a process comprising:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier, which first monomer component comprises an epoxy functional monomer;
- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material; wherein the solution polymerised acrylic material comprises an epoxy group;
- iib) reacting the epoxy group on the solution polymerised acrylic material with an epoxy reactive material to form an epoxy reacted solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the epoxy reacted solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the epoxy reacted solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the epoxy reacted solution polymerised acrylic material; wherein at least one of the epoxy reacted solution polymerised acrylic material and the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of the epoxy reacted solution polymerised acrylic material and/or the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the epoxy reacted solution polymerised acrylic material and the further solution polymerised acrylic material in water.

[78] There is also provided an aqueous coating composition obtainable by a process comprising:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier, which first monomer component comprises an epoxy functional monomer;
- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material; wherein the solution polymerised acrylic material comprises an epoxy group;

- iib) reacting the epoxy group on the solution polymerised acrylic material with an epoxy reactive material to form an epoxy reacted solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the epoxy reacted solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the epoxy reacted solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the epoxy reacted solution polymerised acrylic material;
wherein the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the epoxy reacted solution polymerised acrylic material and the further solution polymerised acrylic material in water.

[79] There is also provided an aqueous coating composition obtainable by a process comprising:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier, which first monomer component comprises an epoxy functional monomer;
- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material; wherein the solution polymerised acrylic material comprising an epoxy group;
- iib) reacting the epoxy group on the solution polymerised acrylic material with an epoxy reactive material to form an epoxy reacted solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the epoxy reacted solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the epoxy reacted solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material;
wherein at least one of the epoxy reacted solution polymerised acrylic material and the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of the epoxy reacted solution polymerised acrylic material and/or the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the epoxy reacted solution polymerised acrylic material and the further solution polymerised acrylic material in water.

[80] There is also provided an aqueous coating composition obtainable by a process comprising:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier, which first monomer component comprises an epoxy functional monomer;

- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material; wherein the solution polymerised acrylic material comprises an epoxy group;
- iib) reacting the epoxy group on the solution polymerised acrylic material with an epoxy reactive material to form an epoxy reacted solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the epoxy reacted solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the epoxy reacted solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material; wherein the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the epoxy reacted solution polymerised acrylic material and the further solution polymerised acrylic material in water.

[81] The first monomer component may comprise any suitable amount of an epoxy containing monomer. The first monomer component may comprise from 10 to 90 wt%, such as from 30 to 80 wt%, such as from 50 to 75 wt%, such as from 55 to 70 wt% epoxy containing monomer based on the total weight of the first monomer component.

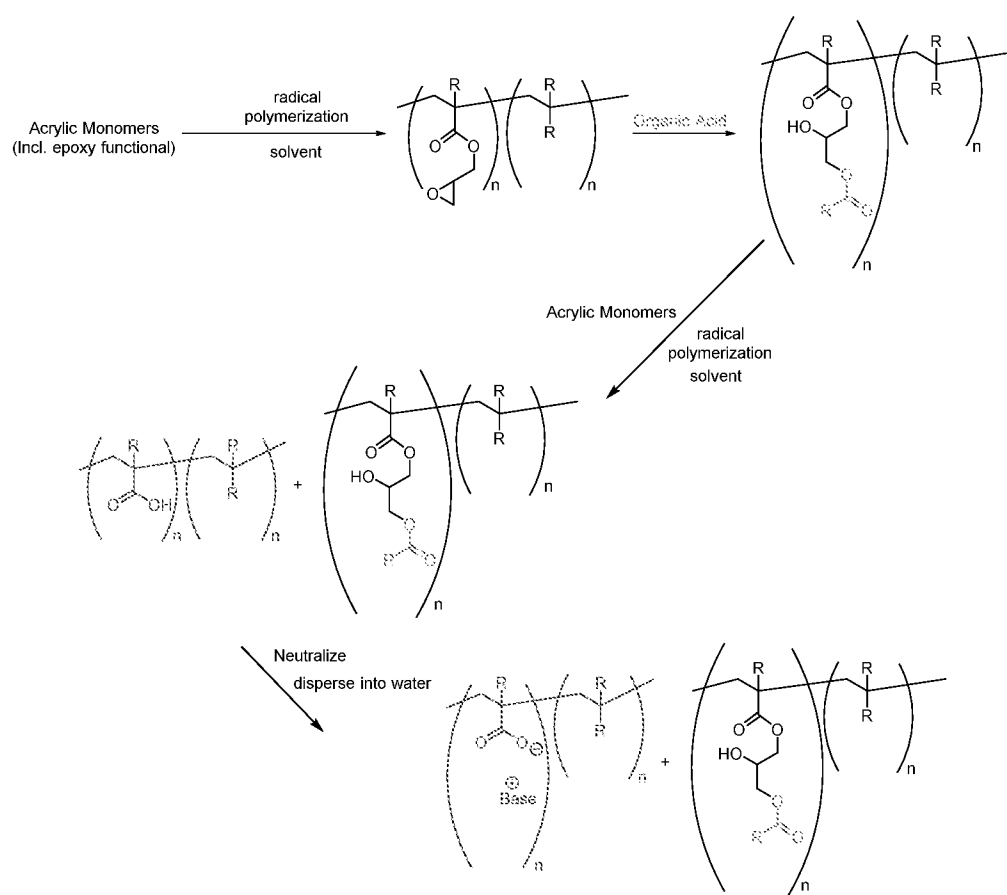
[82] Where the solution polymerised acrylic material comprises epoxy groups, the epoxy reactive material may be added to the solution polymerised acrylic material in any suitable amount. The epoxy reactive material may be added in an amount suitable to react with all of the epoxy groups on the solution polymerised acrylic material. The epoxy reactive material may be added in an amount in excess of the epoxy material, in terms of the equivalents of epoxy to reactive group on the epoxy reactive group. For example, the epoxy reactive material may be added in an amount suitable to react with all of the epoxy groups on the solution polymerised acrylic material to form an epoxy reacted solution polymerised acrylic material that is not epoxy functional. In other words, all of the epoxy functionality has been reacted.

[83] A person skilled in the art will readily be able to use one of many suitable techniques to determine that all of the epoxy functionality has been reacted. For example, this may be confirmed by the epoxy equivalent weight, Infra-Red spectroscopy (using ASTM E168 and ASTM E1252) and triple detector GPC as per ASTM D1652. Using ASTM D1652 the epoxy equivalent weight after being reacted is infinite, demonstrating that the epoxy group is fully reacted with the epoxy reactive group. Infra-red spectroscopy also demonstrates disappearance of epoxy group after reaction with the epoxy reactive group (by disappearance of the epoxy peak in the IR spec).

[84] The second monomer component may comprise methacrylic acid and/or acrylic acid. The second monomer component may comprise any suitable amount of methacrylic acid and/or acrylic acid. The second monomer component may comprise from 10 to 99 wt% of methacrylic acid and/or acrylic acid based on the total weight of the monomers in the second solution polymerised acrylic material.

[85] By way of example, the aqueous coating composition may be obtainable by the following pictorially represented approach (labelled Approach 1).

[86] It will be understood that the schematic experimental scheme labelled Approach 1 is representative only of the process and should not be restricted to the individual monomers, epoxy reactive material, or any other materials shown thereon. However, its inclusion is useful in generally highlighting how an epoxy functional solution polymerised acrylic material may be formed, then reacted with an epoxy reactive material (in this case, an organic acid) to form an epoxy reacted solution polymerised acrylic material. The further solution polymerised acrylic material (which is acid functional in Approach 1) is then polymerised in the presence of the epoxy reacted solution polymerised acrylic material to lead to a mixture of the two solution polymerised polymers that are not covalently linked. The materials are then neutralized and dispersed in water to create an aqueous dispersion of the two-solution polymerised acrylic materials.



Approach 1

[87] The first and/or second monomer component, suitably one of the first or second monomer component, may comprise methacrylic acid and/or acrylic acid. The first and/or second monomer component, such as the first or second monomer component may comprise any suitable amount of

methacrylic acid and/or acrylic acid. The first and/or second monomer component, such as the first or second monomer component may comprise from 10 to 99 wt%, such as from 15 to 99 wt%, such as from 30 to 95 wt%, such as from 50 to 95 wt% methacrylic acid and/or acrylic acid based on the total weight of the monomers in that monomer component. The first and/or second monomer component, such as the first or second monomer component may comprise from 75 to 95 wt%, such as from 80 to 95 wt%, such as from 85 to 95 wt% methacrylic acid and/or acrylic acid based on the total weight of the monomers in that monomer component.

[88] The solution polymerised acrylic material and the further solution polymerised acrylic material may be present in the aqueous coating composition in a weight ratio of from 1:100 to 100:1, such as from 1:50 to 50:1, such as from 20:1 to 1:20, such as from 1:10 to 10:1. The solution polymerised acrylic material may be present in excess of the further solution polymerised acrylic material in the aqueous coating composition, such as in a ratio of from greater than 1:1 to 20:1, such as from greater than 1:1 to 15:1, such as from greater than 1:1 to 10:1. The solution polymerised acrylic material and the further solution polymerised acrylic material may be present in the aqueous coating composition in a weight ratio of from 1.1:1 to 20:1, such as from 1.1:1 to 10:1, such as from 2:1 to 8:1, such as from 3:1 to 7:1, such as from 3:1 to 5:1.

[89] The further solution polymerised acrylic material may be present in excess of the solution polymerised acrylic material in the aqueous coating composition, such as in a ratio of from greater than 1:1 to 20:1, such as from greater than 1:1 to 15:1, such as from greater than 1:1 to 10:1. The further solution polymerised acrylic material and the solution polymerised acrylic material may be present in the aqueous coating composition in a weight ratio of from 1.1:1 to 20:1, such as from 1.1:1 to 10:1, such as from 2:1 to 8:1, such as from 3:1 to 7:1, such as from 3:1 to 5:1.

[90] There is also provided an aqueous coating composition, comprising:

- a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
- b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material;
- c) a carrier comprising water; and
- d) a further solution polymerised acrylic material, different from the solution polymerised acid functional acrylic material "a)";

wherein the coating composition does not comprise an emulsion polymerised acrylic material;

and wherein, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material;

wherein the solution polymerised acrylic material and the further solution polymerised acrylic material are present in the aqueous coating composition in a weight ratio of from 1:2 to 1:10, such as a weight ratio of from 1:3 to 1:6.

[91] There is also provided an aqueous coating composition, obtainable by a process comprising:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;

- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material;
 - iii) mixing a second monomer component comprising an acrylic monomer with the solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the solution polymerised acrylic material;
- wherein at least one of the first monomer component or the second monomer component comprises from 70 to 99 wt%, such as from 80 to 95 wt%, such as from 85 to 95 wt% methacrylic acid and/or acrylic acid based on the total weight of the monomers in that monomer component, and thereby at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of solution polymerised acrylic material and/or the further solution polymerised acrylic material with a neutraliser; and
 - v) dispersing the solution polymerised acrylic material and the further solution polymerised acrylic material in water.

[92] There is provided an aqueous coating composition, obtainable by a process comprising the steps of:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;
 - ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material;
 - iii) mixing a second monomer component comprising an acrylic monomer with the solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the solution polymerised acrylic material;
- wherein at least one of the first monomer component or the second monomer component comprises from 70 to 99 wt%, such as from 80 to 95 wt%, such as from 85 to 95 wt% methacrylic acid and/or acrylic acid based on the total weight of the monomers in that monomer component, and thereby at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material comprises acid functionality;

- iv) at least partially neutralising the acid functionality of solution polymerised acrylic material and/or the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the solution polymerised acrylic material and the further solution polymerised acrylic material in water.

[93] There is also provided an aqueous coating composition, obtainable by a process comprising:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;
- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the solution polymerised acrylic material;

wherein the second monomer component comprises from 70 to 99 wt%, such as from 80 to 95 wt%, such as from 85 to 95 wt% methacrylic acid and/or acrylic acid based on the total weight of the monomers in the second monomer component, and thereby the further solution polymerised acrylic material comprises acid functionality;

- iv) at least partially neutralising the acid functionality of the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the solution polymerised acrylic material and the further solution polymerised acrylic material in water;

wherein the solution polymerised acrylic material and the further solution polymerised acrylic material are present in the aqueous coating composition in a weight ratio of from 2:1 to 10:1, such as a weight ratio of from 3:1 to 6:1.

[94] There is provided an aqueous coating composition, obtainable by a process comprising:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;
- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material;

wherein the second monomer component comprises from 70 to 99 wt%, such as from 80 to 95 wt%, such as from 85 to 95 wt% methacrylic acid and/or acrylic acid

- based on the total weight of the monomers in the second monomer component, and thereby the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of the further solution polymerised acrylic material with a neutraliser; and
 - v) dispersing the solution polymerised acrylic material and the further solution polymerised acrylic material in water;
- wherein the solution polymerised acrylic material and the further solution polymerised acrylic material are present in the aqueous coating composition in a weight ratio of 2:1 to 10:1, such as in a weight ratio of 3:1 to 6:1.

[95] The aqueous coating composition of the present invention may comprise any suitable amount of solution polymerised acrylic material. The aqueous coating composition may comprise from 10 to 99 wt%, such as from 30 to 99 wt%, such as from 50 to 99 wt%, such as from 70 to 95wt%, such as from 75 to 95 wt%, such as from 80 to 95 wt% of solution polymerised acrylic material based on the total solid weight of the aqueous coating composition.

[96] The aqueous coating composition may comprise at least 10wt%, suitably at least 25 wt%, such as at least 40 wt%, or even at least 50 wt% of solution polymerised acrylic material based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise up to 99.9 wt%, suitably up to 99 wt%, such as up to 97 wt%, such as up to 95 wt%, such as up to 92 wt%, or even up to 90 wt% of solution polymerised acrylic material based on the total solid weight of the aqueous coating composition.

[97] The coating composition comprises a neutraliser. Suitable neutralisers will be well known to a person skilled in the art. Examples of suitable neutralisers include, but are not limited to tertiary amines such as, for example, dimethylethanolamine (DMEA), trimethyl amine, methyl diethanol amine, ethyl methyl ethanol amine, dimethyl ethyl amine, dimethyl propyl amine, dimethyl 3-hydroxy-1-propyl amine, dimeyethylbenzyl amine, dimethyl 2-hydroxy-1-propyl amine, diethyl methyl amine, dimethyl 1-hydroxy-2-propyl amine, triethyl amine, tributyl amine, N-methyl morpholine; ammonia; hydrazine; metallic aluminium; metallic zinc; water-soluble oxides of the elements Li, Na, K, Mg, Ca, Fe(II) and Sn(II); water-soluble hydroxides of the elements Li, Na, K, Mg, Ca, Fe(II) and Sn(II); water-soluble carbonates of the elements Li, Na, K, Mg, Ca, Fe(II) and Sn(II); and combinations thereof. The neutraliser may comprise a tertiary amine. The neutraliser may comprise dimethylethanolamine (DMEA).

[98] The aqueous coating composition may comprise any suitable amount of neutraliser. The amount of neutraliser may be a suitable amount to neutralise the acid functionality such that the solution polymerised acrylic material disperses in water. The amount of neutraliser may be a suitable amount to neutralise at least 10%, suitably at least 20%, such as at least 30%, such as at least 40%, or even at least 50% of the acid functionality of the solution polymerised acrylic material. By, for example, 'neutralise at least 20%' is meant that at least 20% of the available acid groups of the solution polymerised acrylic material are neutralised. A person skilled in the art will therefore appreciate that at least 30%, at least 40%, at least 50% neutralised etc. means that at least 30%, at least 40%, at least 50% of the available acid groups of the solution polymerised acrylic material are neutralised. The acid

functionality of the solution polymerised acrylic material may be 50% neutralised with the neutraliser. For example, at least 0.1, at least 0.2, at least 0.3, such as at least 0.4, or even at least 0.5 equivalents of neutraliser may be added to the solution polymerised acrylic material per equivalent of acid groups.

[99] The aqueous coating composition may further comprise a crosslinker material. The crosslinker material may be operable to crosslink the acid functionality of the solution polymerised acrylic material. Suitable crosslinker materials will be well known to the person skilled in the art. It will be understood by a person skilled in the art that the aqueous coating composition may be provided as a single component coating composition or a multiple component coating composition. In the case of a multiple component coating composition, the crosslinker material may be provided in a different component to the solution polymerised acrylic material, for example.

[100] Suitable crosslinker materials include, but are not limited to, the following: phenolic resins (or phenol-formaldehyde resins); aminoplast resins (or triazine-formaldehyde resins); amino resins; epoxy resins; epoxy-mimic resins, such as those based on bisphenols and other bisphenol A (BPA) replacements; isocyanate resins, isocyanurate resins, such as triglycidylisocyanurate; hydroxy (alkyl) amide resins, such as β -hydroxy (alkyl) amide resins; hydroxy(alkyl) urea resins; carbodiimide resins; oxazolines; and combinations thereof.

[101] Non-limiting examples of phenolic resins are those formed from the reaction of a phenol with an aldehyde or a ketone, suitably from the reaction of a phenol with an aldehyde, such as from the reaction of a phenol with formaldehyde or acetaldehyde, or even from the reaction of a phenol with formaldehyde. Non-limiting examples of phenols which may be used to form phenolic resins are phenol, butyl phenol, xlenol and cresol. General preparation of phenolic resins is described in "The Chemistry and Application of Phenolic Resins or Phenoplasts", Vol V, Part I, edited by Dr Oldring; John Wiley and Sons/Cita Technology Limited, London, 1997. Suitably, the phenolic resins are of the resol type. By "resol type" we mean resins formed in the presence of a basic (alkaline) catalyst and optionally an excess of formaldehyde. Suitable examples of commercially available phenolic resins include, but are not limited to those sold under the trade name PHENODUR (RTM) commercially available from Cytec Industries, such as PHENODUR EK-827, PHENODUR VPR1785, PHENODUR PR 515, PHENODUR PR516, PHENODUR PR 517, PHENODUR PR 285, PHENODUR PR612 or PHENODUR PH2024; resins sold under the trade name BAKELITE (RTM) commercially available from Momentive, such as BAKELITE 6582 LB, BAKELITE 6535, BAKELITE PF9989 or BAKELITE PF6581; SFC 112 commercially available from Schenectady; DUREZ (RTM) 33356 commercially available from SHHPP; ARALINK (RTM) 40-852 commercially available from Bitrez; or combinations thereof.

[102] The crosslinker material may be selected from phenolic resins; hydroxy (alkyl) amide resins, such as β -hydroxy (alkyl) amide resins; hydroxy(alkyl) urea resins; carbodiimide resins, such as polycarbodiimide resins; oxazolines; isocyanurate resins, such as triglycidylisocyanurate; oxazolines; epoxy-mimic resins, such as those based on bisphenols and other bisphenol A (BPA) replacements; or combinations thereof.

[103] The crosslinker material may be selected from hydroxy (alkyl) amide resins, such as β -hydroxy (alkyl) amide resins; phenolic resins, hydroxy(alkyl) urea resins; carbodiimide resins, such as

polycarbodiimide resins; oxazolines; isocyanurate resins, such as triglycidylisocyanurate; oxazolines; epoxy-mimic resins, such as those based on bisphenols and other bisphenol A (BPA) replacements; or combinations thereof.

[104] The crosslinker material may comprise a phenolic resin, such as a resole phenolic resin.

[105] The crosslinker material may be selected from phenolic resins, hydroxy (alkyl) amide resins, such as β -hydroxy (alkyl) amide resins, hydroxy(alkyl) urea resins, carbodiimide resins, oxazolines or combinations thereof. The crosslinker material may be selected from hydroxy (alkyl) amide resins, such as β -hydroxy (alkyl) amide resins, hydroxy(alkyl) urea resins, carbodiimide resins, oxazolines or combinations thereof. The crosslinker material may be selected from hydroxy (alkyl) amide resins, such as β -hydroxy (alkyl) amide resins and/or hydroxy(alkyl) urea resins.

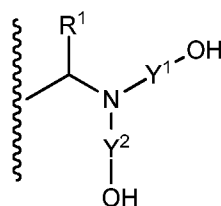
[106] The crosslinker material may comprise a hydroxyalkylamide material and/or a hydroxyalkylurea material and/or a carbodiimide resin. The crosslinker material may comprise a hydroxyalkylamide material and/or a hydroxyalkylurea material.

[107] The crosslinker material may comprise a hydroxyalkylamide material and a phenolic resin, such as a hydroxyalkylamide material and a resole phenolic resin, such as a β -hydroxyalkylamide material and a resole phenolic resin.

[108] The crosslinker material may contain nitrogen, which may be in the form of an amine or amide material. The crosslinker material may comprise a hydroxyl substituted amine or amide material.

[109] The crosslinker material may comprise a hydroxyalkylamide material, such as a β -hydroxyalkylamide material.

[110] The crosslinker material may contain a terminal chemical group as shown in Formula I.



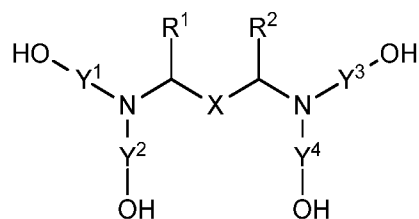
Formula I

[111] wherein R^1 represents an electron withdrawing group, such as (=O); and Y^1 and Y^2 each, independently, represents a C_1 to C_3 alkylene group.

[112] The terminal chemical group of Formula I may be connected to a further chemical structure, not shown. Additionally, or alternatively, the chemical group of Formula I may be suspended from a carrier substrate, such as a silica carrier substrate, for example.

[113] The hydroxyalkylamide crosslinker may contain a plurality of terminal chemical groups as shown in Formula I. For example, the hydroxyalkylamide crosslinker may contain 2, 3 or 4 terminal chemical groups as shown in Formula I.

[114] The hydroxyalkylamide crosslinker may comprise a moiety according to Formula II:



Formula II

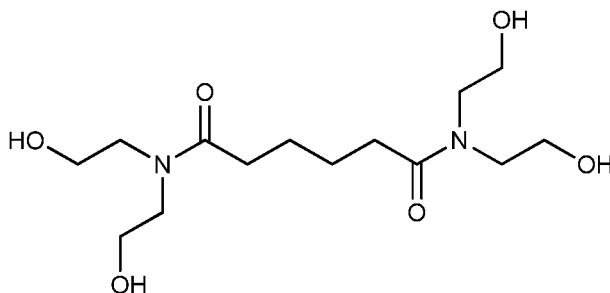
[115] wherein R¹ and R² with reference to Formula II each, independently, represent an electron withdrawing group, such as (=O); Y¹, Y², Y³ and Y⁴ with reference to Formula II each, independently, represent a C₁ to C₃ alkylene group; and X is a C₂ to C⁶ alkylene group.

[116] Each of R¹ and R² with reference to Formula II may represent a (=O) group.

[117] Each of Y¹, Y², Y³ and Y⁴ with reference to Formula II may represent an ethylene group.

[118] X may represent a butylene group.

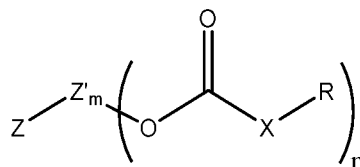
[119] Accordingly, the hydroxyalkylamide crosslinker may comprise a material of formula III:



Formula III

[120] The aqueous coating composition of the present invention may comprise a commercially available hydroxyalkylamide crosslinker such as, for example, PRIMID XL-552 (available from EMS Chemie); PRIMID QM-1260 (available from EMS Chemie); PRIMID SF-4510 (available from EMS Chemie) and N,N,N',N'-tetrakis(2-hydroxypropyl)adipamide.

[121] The hydroxyalkylamide crosslinker may comprise a polyhydroxyalkylamide material having the formula (IV):



formula (IV)

wherein, with reference to formula (IV), Z represents a polymer or an alkylene, alkenylene, alkynylene or arylene group;

Z' represents a bivalent organic linking group;

m is 0 or 1;

X represents a bivalent organic bridging group;

R represents a hydroxyalkylamide group; and

n is at least 2

[122] Z with reference to formula (IV) may represent a polymer or an alkylene, alkenylene, alkynylene or arylene group.

[123] Z with reference to formula (IV) may represent a polymer. Z with reference to formula (IV) may represent any suitable polymer. Suitable polymers include, but are not limited to, acrylic polymers, polyester polymers, polyester amide polymers, polyurethane polymers, epoxy polymers, and combinations thereof. Z with reference to formula (IV) may represent an acrylic polymer, a polyester polymer or a combination thereof. Z with reference to formula (IV) may represent an acrylic polymer grafted to a polyester or a polyester grafted to an acrylic polymer.

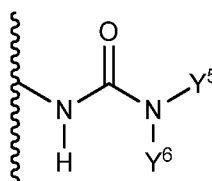
[124] Z with reference to formula (IV) may represent an acrylic polymer. Z with reference to formula (IV) may represent an acrylic polymer derived from monomers having ethylenic unsaturation.

[125] Further examples of suitable polyhydroxyalkylamide materials are disclosed in WO2020/123893, the entire contents of which are incorporated herein by reference

[126] The crosslinker material may be in the form of a urea material. The crosslinker material may comprise a hydroxyl substituted urea material.

[127] The crosslinker material may comprise a hydroxy functional alkyl polyurea material.

[128] The crosslinker material may contain a terminal chemical group as shown in Formula XVII.



Formula XVII

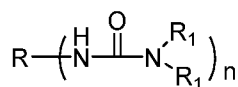
wherein Y⁵ and Y⁶ each, independently, represent hydrogen, an alkyl or a hydroxy functional alkyl having two or more carbon atoms and at least one of Y⁵ and Y⁶ is a hydroxyl functional alkyl having two or more carbon atoms.

[129] The Y⁵ and Y⁶ groups may exclude ether linkages.

[130] The terminal chemical group of Formula XVII may be connected to a further chemical structure, not shown. Additionally, or alternatively, the chemical group of Formula XVII may be suspended from a carrier substrate, such as a silica carrier substrate, for example.

[131] The crosslinker material may contain a plurality of terminal chemical groups as shown in Formula IV. For example, the crosslinker may contain 2 to 6 terminal chemical groups as shown in Formula XVII, such as 2, 3 or 4 terminal chemical groups as shown in Formula XVII.

[132] The crosslinker material may comprise a moiety according to Formula XVIII:

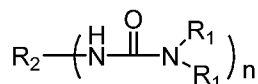


Formula XVIII

wherein R with reference to Formula XVIII comprises the residue of an isocyanurate, biuret, allophonate, glycoluril, benzoguanamine, polyetheramine, and/or polymeric moiety having an Mn of 500 or greater; each R₁ with reference to Formula XVIII is independently a hydrogen, an alkyl or a hydroxy functional alkyl having 2 or more carbons; and n is 2-6.

[133] The R₁ group with reference to Formula XVIII may exclude ether linkages.

[134] The crosslinker may comprise a moiety according to Formula XIX:



Formula XIX

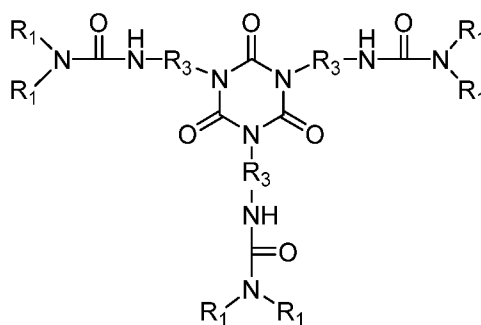
wherein R₂ with reference to Formula XIX comprises a substituted or unsubstituted C₁ to C₃₆ alkyl group, an aromatic group, or the residue of an isocyanurate, biuret, allophonate, glycoluril, benzoguanamine, polyetheramine, and/or a polymeric moiety having an Mn of 500 or greater; each R₁ with reference to Formula VI is independently a hydrogen, an alkyl group having 1 or more carbons, or a hydroxy functional alkyl having 2 or more carbons and at least one R₁ with reference to Formula VI is a hydroxy functional alkyl having 2 or more carbons; and n is 2-6.

[135] When R₂ with reference to Formula XIX is a substituted or unsubstituted C₁ to C₃₆ alkyl group the acid functional polyester material may comprise COOH functionality that reacts with the polyurea to form an ester linkage.

[136] The R₁ group with reference to Formula XIX may exclude ether linkages.

[137] R and R₂ with reference to Formula XIX may comprise the residue of an isocyanurate, biuret, allophonate, glycoluril, benzoguanamine, polyetheramine and/or polymeric moiety having an Mn of 500 or greater. An isocyanurate will be understood as referring to a compound having three isocyanate groups, such as in ring form, and is sometimes referred to as a trimer. This can include compounds having an isocyanurate moiety.

[138] An example of a hydroxy functional alkyl polyurea crosslinker material formed from an isocyanurate is shown in Formula XX:

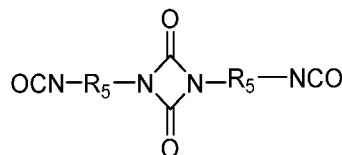


Formula XX

wherein R_1 with reference to Formula XX is as described above with regard to Formula XVIII; and each R_3 independently comprises an alkyl, aryl, alkylaryl, arylalkyl, alicyclic, and/or polyetheralkyl group.

[139] A biuret will be understood as referring to a compound that results upon the condensation of two molecules of urea and is sometimes referred to as a carbamylurea. Biurets are commercially available from Vencore X Chemical and Covestro as, for example, DESMODUR N-75, DESMODUR N-100, and DESMODUR N-3200, HDB 75B, HDB 75M, HDB 75MX, HDB-LV.

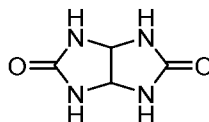
[140] Uretidione is a dimer of diisocyanate, examples of which include DESMODUR N-3400 polyisocyanate, a blend of the trimer and uretidione of HDI:



wherein each R_5 independently comprises an alkyl, aryl, alkylaryl, arylalkyl, alicyclic, and/or polyetheralkyl group.

[141] As used herein, an “allophonate” means a compound made from urethane and isocyanate.

[142] As used herein a “glycoluril” means a compound composed of two cyclic urea groups joined across the same two-carbon chain, an example of which includes the below:



[143] As used herein a “polyether amine” means a compound having an amine group attached to a polyether backbone such as one characterized by propylene oxide, ethylene oxide, or mixed propylene oxide and ethylene oxide repeating units in their respective structures, such as, for example, one of the Jeffamine series products.

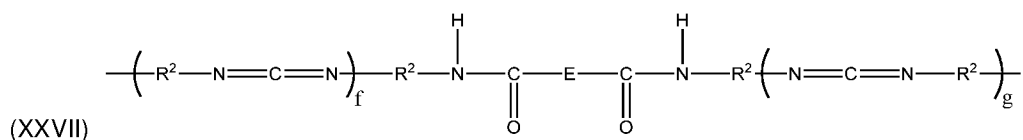
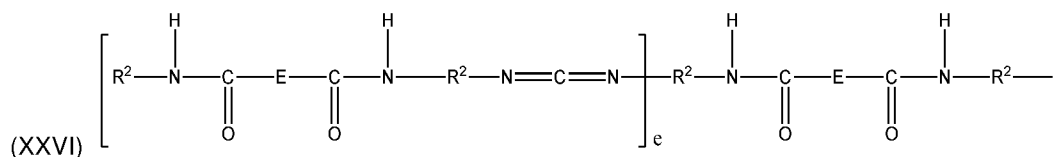
[144] Certain hydroxy functional alkyl polyureas of, and/or used according to, the invention may be made by reacting an isocyanate-containing compound with amino alcohol. Any isocyanate-containing compound having at least two isocyanate groups can be used, such as any of those described above.

[145] The hydroxyl functional alkyl polyureas can be made by reacting amino alcohol with an isocyanate-containing compound in an organic polar solvent, such as alcohol or water. The equivalent ratio of amine to isocyanate may be from 2-1:1-2, such as 1:1.

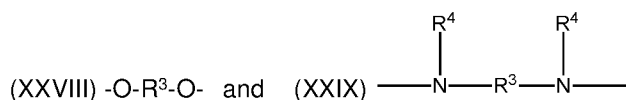
[146] The hydroxy functional alkyl polyureas may be made by alternative methods as well. For example, amino alcohols can react with carbonate to form hydroxylalkyl carbamate, and hydroxylalkyl carbamate can further react with amines to form hydroxy functional alkyl polyureas.

[147] Further examples of suitable hydroxy functional alkyl polyureas are provided in WO2017/123955, the contents of which are incorporated herein by reference.

[148] The crosslinker material may be in the form of a carbodiimide resin. The crosslinker may comprise a polycarbodiimide. Suitably, the crosslinker may comprise a polycarbodiimide having the following structural units (XXVI) or (XXVII) including mixtures thereof:



where e is an integer of from 2 to 20; f and g are each at least 1, and f+g is an integer up to 20; E is a radical selected from



where R² with reference to structural units (XXVIII) or (XXIX) comprises a cyclic radical and R³ with reference to (XXVIII) or (XXIX) is a linear hydrocarbon radical containing at least 4 carbon atoms and R⁴ with reference to (XXIX) is hydrogen or an alkyl radical.

[149] The polycarbodiimides may be prepared by reacting an organic group containing a polyisocyanate in the presence of a suitable catalyst to form a polycarbodiimide having terminal NCO-functionality, wherein an active hydrogen-containing compound is added before, during or after polycarbodiimide formation.

[150] The polyisocyanate may be an aliphatic, including cycloaliphatic, or an aromatic polyisocyanate or mixture of the two. The aliphatic may comprise cycloaliphatic polyisocyanate and/or alkaryl polyisocyanate. The polyisocyanate may comprise from 2 to 4, such as 2 isocyanate groups per molecule. Examples of suitable higher polyisocyanates are 1,2,4-benzene triisocyanate and polymethylene polyphenyl isocyanate, or combinations thereof. Examples of suitable aromatic diisocyanates are 4,4'-diphenylmethane diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate and tolylene diisocyanate or combinations thereof. Examples of suitable aliphatic diisocyanates are straight chain aliphatic diisocyanates, such as 1,4-tetramethylene diisocyanate and 1,6-hexamethylene diisocyanate; and alkaryl polyisocyanates, such as m-tetramethylxylene diisocyanate or combinations thereof. Cycloaliphatic diisocyanates may be employed. Examples include 1,4-cyclohexyl diisocyanate, isophorone diisocyanate, alpha, alpha-xylene diisocyanate and 4,4-methylene-bis(cyclohexyl isocyanate) or combinations thereof. Substituted organic group-containing polyisocyanates may be used in which the substituents comprise nitro, chloro, alkoxy and/or other groups that are not reactive with hydroxyl groups or active hydrogens and provided the substituents are not positioned to render the isocyanate group unreactive.

[151] The active hydrogen-containing compound used in the preparation of the polycarbodiimide may be a chain extender or spacer linking polyisocyanates together to form NCO-adducts or to link NCO-functional polycarbodiimides together. Any suitable organic compound containing active hydrogens may be used. As used herein, "active hydrogen atoms" means hydrogens which, because of their position in the molecule, display activity according to the Zerewitinoff test. Accordingly, active hydrogens include hydrogen atoms attached to oxygen or nitrogen, and thus useful compounds will include those having at least two of these groups (in any combination):



[152] The moieties attached to each group may be aliphatic, including cycloaliphatic, aromatic, or of a mixed type with aliphatic may be suitable.

[153] The active hydrogen-containing material may comprise from 2 to 4, such as 2 active hydrogens per molecule.

[154] Examples of such compounds include amines, which includes polyamines; aminoalcohols; mercapto-terminated derivatives; and alcohols, such as polyhydroxy materials (polyols) which may provide an easier reaction with a polyisocyanate, or combinations thereof. A polyol may give fewer side reactions, which may give higher yields of urethane product with lower by-product and/or the products may be hydrolytically stable. With regard to polyols, there are a wide variety of materials available which can be selected to give a wide spectrum of desired properties. In addition, a polyol may have a desirable reaction rate with polyisocyanates. Both saturated and unsaturated active hydrogen-containing compounds can be used, such as a saturated material, which may provide improved coating properties.

[155] The polyhydroxyl material or polyol may be a low or high molecular weight material and in general will have average hydroxyl values as determined by ASTM designation E-222-67, Method B, of 2000

and below, such as from 2000 and 10. As used herein, "polyol" means materials having an average of two or more hydroxyl groups per molecule.

[156] The polyol may comprise a low molecular weight diol, triol, a higher molecular weight polyol, a low molecular weight amide-containing polyol and a higher polymeric polyol, or a combination thereof, such as a polyester polyol, polyether polyol, polycarbonate polyol and hydroxy-containing (meth)acrylic polymer or a combination thereof. The polymer may have a hydroxyl value of from 10 to 180. The polymers may have number average molecular weight of from 96 to 10,000 Da.

[157] Suitable low molecular weight diol, triol and higher alcohol useful in the present invention will be known by a person skilled in the art. They may have a hydroxy value of 200 or above, such as within the range of from 200 to 2000. Such materials include aliphatic polyol, such as alkylene polyol containing from 4 to 18 carbon atoms. Examples include 1,4-butanediol and 1,6-hexanediol, or combinations thereof. The polyol may comprise an ether linkage such as diethylene glycol and tetraethylene glycol or combinations thereof.

[158] To form the polycarbodiimide, the polyisocyanate with or without the active hydrogen-containing compound may be condensed with the elimination of carbon dioxide to form the polycarbodiimide, that is, a polymer containing $[N=C=N]_n$ units where n with reference to the $[N=C=N] = 2$ to 20, such as 2 to 10.

[159] The condensation reaction may be conducted by taking the solution of the polyisocyanate and heating in the presence of suitable catalyst. Examples of catalyst include 1-ethyl-3-phospholine, 1-ethyl-3-methyl-3-phospholine-1-oxide, 1-ethyl-3-methyl-3-phospholine-1-sulfide, 1-ethyl-3-methyl-phospholidine, 1-ethyl-3-methyl-phospholidine-1-oxide, 3-methyl-1-phenyl-3-phospholine-1-oxide and bicyclic terpene alkyl or hydrocarbyl aryl phosphine oxide or camphene phenyl phosphine oxide or combinations thereof.

[160] The amount of catalyst used will depend to a large extent on the reactivity of the catalyst itself and the polyisocyanate being used. A concentration range of from 0.05-5 parts of catalyst per 100 parts of adduct is generally suitable.

[161] Further examples of suitable carbodiimide crosslinker materials are provided in WO2017/122171, the contents of which are incorporated herein by reference.

[162] The crosslinker material of the present invention may be substantially free, may be essentially free or may be completely free of formaldehyde. By "substantially free" we mean to refer to crosslinker material containing less than 1000 parts per million (ppm) of any of the compounds or derivatives thereof mentioned above. By "essentially free" we mean to refer to crosslinker material containing less than 100 ppm of any of the compounds or derivatives thereof mentioned above. By "completely free" we mean to refer to crosslinker material containing less than 20 parts per billion (ppb) of any of the compounds or derivatives thereof. The crosslinker material may comprise 0wt% of formaldehyde.

[163] The crosslinker material may comprise the reaction product of a reaction mixture comprising:

- (i) a cyclic unsaturated acid anhydride and/or diacid derivative thereof;
- (ii) an ethylenically unsaturated monomer; and
- (iii) an alcohol, amine, thiol and/or water,

wherein at least a portion of the cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with the alcohol, amine, thiol and/or water;

and wherein the crosslinker material has an acid number of at least 100 mg KOH/g.

[164] The crosslinker material may comprise the reaction product of a reaction mixture comprising:

- (i) $\geq 70\%$ by weight of a cyclic unsaturated acid anhydride and/or diacid derivative thereof by total solid weight of the monomers from which the crosslinker material is formed;
- (ii) optionally, an ethylenically unsaturated monomer;
- (iii) and optionally, an alcohol, amine, thiol and/or water, wherein at least a portion of the cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with the alcohol, amine, thiol and/or water, when present;

and wherein the crosslinker material has an acid number of at least 100 mg KOH/g.

[165] The cyclic unsaturated acid anhydride may be any suitable cyclic unsaturated acid anhydride. The cyclic unsaturated acid anhydride may be any suitable cyclic unsaturated acid anhydride that is able to undergo polymerisation, for example, free radical polymerisation, optionally with an ethylenically unsaturated monomer. Suitable cyclic unsaturated acid anhydrides will be known to a person skilled in the art. Examples of suitable cyclic unsaturated acid anhydrides include, but are not limited to, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, vinylhexahydrophthalic anhydride, chlorendic anhydride, methyl-endomethylenetetrahydrophthalic anhydride, itaconic anhydride, citraconic anhydride, alkenyl succinic anhydrides such as, for example, allyl succinic anhydride and dodecenyl succinic anhydride, norbornene anhydride and combinations thereof.

[166] The cyclic unsaturated acid anhydride may be maleic anhydride.

[167] 'Diacid derivative' of the cyclic unsaturated acid anhydride, and like terms as used herein, refers to the diacid derivative of the cyclic unsaturated acid anhydrides as defined herein that results from the hydrolysis of the anhydride group. A person skilled in the art will understand that the cyclic anhydride group will become non-cyclic upon hydrolysis.

[168] Thus, examples of suitable diacid derivatives of cyclic unsaturated acid anhydrides include, but are not limited to, maleic acid, tetrahydrophthalic acid, methyltetrahydrophthalic acid, vinylhexahydrophthalic acid, endomethylenetetra-hydrophthalic acid, chlorendic acid, itaconic acid, citraconic acid, alkenyl succinic acids such as, for example, allyl succinic acid and dodecenyl succinic acid, norbornene acid and combinations thereof.

[169] The diacid derivative of the cyclic unsaturated acid anhydride may be maleic acid.

[170] The ethylenically unsaturated monomer may comprise an acrylic monomer. Suitable acrylic monomers include, but are not limited to, alkyl (alk)acrylate, such as C_1 to C_6 alkyl (C_1 to C_6 alk)acrylate, for example, C_1 to C_6 alkyl (meth)acrylate, and (alk)acrylic acid, such as (C_1 to C_6 alk)acrylic acid. The acrylic monomers may comprise a functional group, such as an epoxy group. For example, the acrylic monomers may comprise glycidyl methacrylate.

[171] Examples of suitable acrylic monomers include, but are not limited to, acrylic acid, methacrylic acid, methyl acrylate; methyl methacrylate; ethyl acrylate; ethyl methacrylate; propyl acrylate; propyl

methacrylate; isopropyl methacrylate, isobutyl methacrylate, butyl acrylate; butyl methacrylate, pentyl acrylate, pentyl methacrylate, isoamyl acrylate, isoamyl methacrylate, hexyl acrylate, hexyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, decyl acrylate decyl methacrylate, isodecyl acrylate, isodecyl methacrylate, lauryl acrylate, lauryl methacrylate, octyl acrylate, octyl methacrylate, nonyl acrylate, nonyl methacrylate isobornyl acrylate, isobornyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate, phenoxy ethyl acrylate 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, glycidyl methacrylate; ethylene glycol diacrylate; ethylene glycol dimethacrylate; 1,6-hexanediol diacrylate; 1,6-hexanediol dimethacrylate; 4-hydroxybutyl acrylate; 4-hydroxybutyl methacrylate; allyl methacrylate; benzyl methacrylate; phosphate esters of 2-hydroxyethyl methacrylate; those sold under the trade name SIPOMER such as SIPOMER PAM-100, SIPOMER PAM-200 and SIPOMER PAM-300 (phosphate esters of polypropylene glycol monoacrylate commercially available from Solvay); acrylamides such as, for example, acrylamide methacrylamide, N,N-dimethylacrylamide, N-ethylacrylamide, N-hydroxyethyl acrylamide, diacetone acrylamide, N,N-diethylacrylamide, N-isopropylacrylamide and N-isopropylmethacrylamide; 2-acrylamido-2-methyl-1-propanesulfonic acid; and combinations thereof. Any other acrylic monomers known to those skilled in the art could also be used.

[172] The ethylenically unsaturated monomer may comprise a hydroxyl functional monomer, such as a hydroxyl functional acrylic monomer. The ethylenically unsaturated monomer may comprise a hydroxyl functional alkyl(alk)acrylate, for example, hydroxyl functional C₁ to C₆ alkyl (C₁ to C₆ alk)acrylate, such as hydroxyl functional C₁ to C₆ alkyl (meth)acrylate or hydroxyl functional C₁ to C₆ alkyl (C₁ to C₆ alk)acrylate. Examples of suitable hydroxyl functional acrylic monomer(s) include, but are not limited to, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxymethyl acrylate, hydroxymethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, hydroxypentyl acrylate, hydroxypentyl acrylate, hydroxyhexyl methacrylate, hydroxyhexyl methacrylate, methyl 2-(hydroxymethyl)acrylate and/or ethyl 2-(hydroxymethyl)acrylate. The ethylenically unsaturated monomer may comprise hydroxyethyl acrylate and/or hydroxyethyl methacrylate, such as hydroxyethyl acrylate.

[173] The hydroxyl functional ethylenically unsaturated monomer may comprise N-hydroxyethyl acrylamide, 2-hydroxyethyl vinyl ether, 4-hydroxybutyl vinyl ether, 2-(2-hydroxyethyl) ethyl vinyl ether, and/or hydroxystyrene.

[174] The hydroxyl functional ethylenically unsaturated monomer may comprise the reaction product of (meth)acrylic acid with an epoxy (such as Cardura E10) and/or the reaction product of glycidyl methacrylate with a carboxylic acid functional component (such as a benzoic acid, aliphatic acid).

[175] The crosslinker material may comprise $\geq 2.5\%$ hydroxyl functional ethylenically unsaturated monomer based on the total solid weight of the monomers from which the crosslinker material is formed, such as ≥ 5 wt%, or ≥ 7 wt%, or ≥ 10 wt%.

[176] The crosslinker material may comprise $\leq 50\%$ hydroxyl functional ethylenically unsaturated monomer based on the total solid weight of the monomers from which the crosslinker material is formed, such as ≤ 40 wt%, or ≤ 30 wt%, or ≤ 20 wt%.

[177] The ethylenically unsaturated monomer may comprise a vinyl ether monomer. Examples of suitable vinyl ether monomers include, but are not limited to, methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, t-butyl vinyl ether, pentyl vinyl ether, cyclopentyl vinyl ether, hexyl vinyl ether, cyclohexyl vinyl ether, 2-ethylhexyl vinyl ether, 2-hydroxyethyl vinyl ether, 4-hydroxybutyl vinyl ether, 1,4-butanediol divinyl ether, diethyleneglycol divinyl ether, triethyleneglycol divinyl ether, 1,4-cyclohexanedimethanol divinyl ether, 2-(2-hydroxyethyl) ethyl vinyl ether, octyl vinyl ether, benzyl vinyl ether, phenyl vinyl ether, phenethyl vinyl ether, allyl vinyl ether and combinations thereof.

[178] The ethylenically unsaturated monomer may comprise an additional ethylenically unsaturated monomer. Examples of suitable additional ethylenically unsaturated monomers include, but are not limited to, aryl substituted ethylenically unsaturated monomers such as, for example, styrene, α -methylstyrene, vinyltoluene, chloromethylstyrene, 4-hydroxystyrene, diglycidylloxymethylstyrene, 2,4-diglycidylloxymethylstyrene, 2,5-diglycidylloxymethylstyrene, 2,6-diglycidylloxymethylstyrene, 2,3,4-triglycidylloxymethylstyrene, 2,3,5-triglycidyl oxime styrene, 2,3,6-triglycidylloxymethylstyrene and 3,4,5-triglycidylloxymethylstyrene, 2,4,6-triglycidylloxymethylstyrene, ethylenically unsaturated nitriles such as, for example, acrylonitrile or methacrylonitrile, vinyl esters such as, for example, vinyl acetate and vinyl propionate, ethene, propene, 1-butene, 2-butene, 1-pentene, 2-pentene, 1-hexene, 2-hexene, 3-hexene, 1-heptene, 2-heptene, 3-heptene, 1-octene, 2-octene, 3-octene, 4-octene, isobutylene, vinyl chloride, butadiene, isoprene, chloroprene, N-vinyl monomers such as, for example, N-vinyl pyrrolidone, N-vinyl caprolactam and N-vinyl acetamide, unsaturated fatty acid ester; allyl glycidyl ether, allyl ethyl ether and combinations thereof. The additional ethylenically unsaturated monomer(s) may comprise monomers, oligomers and/or polymers of the aforementioned monomers. For example, butadiene may be in the form of a monomer or may be in the form of polybutadiene.

[179] The ethylenically unsaturated monomer(s) may comprise styrene, a vinyl ether monomer, vinyl acetate or combinations thereof.

[180] The ethylenically unsaturated monomer(s) may comprise styrene, isobutyl vinyl ether, vinyl acetate or combinations thereof.

[181] The unsaturated acid anhydride and/or diacid derivative thereof may comprise maleic anhydride and the ethylenically unsaturated monomer(s) may comprise styrene, isobutyl vinyl ether, vinyl acetate or combinations thereof.

[182] The unsaturated acid anhydride and/or diacid derivative thereof may comprise maleic anhydride and the ethylenically unsaturated monomer(s) may comprise styrene, isobutyl vinyl ether, vinyl acetate and/or a hydroxyl functional monomer (such as hydroxyethyl (meth)acrylate).

[183] The ethylenically unsaturated monomer(s) may comprise isobutyl vinyl ether.

[184] The unsaturated acid anhydride and/or diacid derivative thereof may comprise maleic anhydride and the ethylenically unsaturated monomer(s) may comprise isobutyl vinyl ether.

[185] The crosslinker material may comprise at least 75 wt% of cyclic unsaturated acid anhydride and/or diacid derivative thereof, such as maleic anhydride and/or maleic acid, such as at least 80 wt%, such as at least 85 wt%, such as at least 90 wt%, such as at least 95 wt% or at least 97 wt% or at least 98

wt% or at least 99 wt% or >99 wt%, or at least 99.1 wt%, or at least 99.5 wt% or at least 99.9wt% or 100wt% cyclic unsaturated acid anhydride and/or diacid derivative thereof, based on the total solid weight of the monomers from which the crosslinker material is formed.

[186] For the avoidance of doubt, by 'the total solid weight of the monomers from which the crosslinker material is formed' as used herein is meant the total solid weight of (i) a cyclic unsaturated acid anhydride and/or diacid derivative thereof, (ii) an ethylenically unsaturated monomer, when present, and any additional monomer(s) present and does not include (iii) an alcohol, amine and/or thiol, when present.

[187] The crosslinker material may be substantially free, may be essentially free or may be completely free of styrene. By substantially free in relation to styrene, is meant that the crosslinker material is formed from monomers which comprise less than 5 wt% of styrene based on the total weight of the monomers from which the crosslinker material is formed. By essentially free in relation to styrene, is meant that the crosslinker material is formed from monomers which comprise less than 1 wt% of styrene based on the total weight of the monomers from which the crosslinker material is formed. By completely free in relation to styrene, is meant that the crosslinker material is formed from monomers which comprise less than 0.01 wt% of styrene based on the total weight of the monomers from which the crosslinker material is formed. The crosslinker material may be formed from monomers which comprise no, i.e., 0 wt%, styrene based on the total weight of the monomers from which the crosslinker material is formed.

[188] The crosslinker material may comprise the reaction product of a reaction mixture comprising (iii) an alcohol, amine thiol and/or water, such as with alcohol, amine and/or thiol.

[189] The alcohol may be any suitable alcohol. Suitable alcohols will be known to a person skilled in the art. The alcohol may be an aliphatic or cycloaliphatic C₁-C₂₀ alkanol, an aryl alcohol or combinations thereof. The alcohol may be a monohydric alcohol or a polyol, such as a diol, triol, tetraol etc., for example.

[190] The alcohol may be methanol, ethanol, propanol, butanol, butoxy ethanol, methoxy propanol or combinations thereof.

[191] The alcohol may be an aryl alcohol. Examples of suitable aryl alcohols include, but are not limited to, phenol, benzyl alcohol, phenethyl alcohol, phenylpropyl alcohol, phenoxy ethanol, phenyl carbinol, methylphenyl carbinol, cresol, hydroxyalkylated bisphenols and combinations thereof.

[192] The amine may be any suitable amine. Suitable amines will be known to a person skilled in the art. The amine may be an aliphatic or cycloaliphatic C₁-C₂₀ amine, such as a C₁-C₁₀ amine, such as a C₁₋₆ amine, such as a C₁-C₄ amine, such as a C₁-C₃ amine, such as a C₁-C₂ amine, or even ethylamine. The amine may be an aryl amine. The amine may be a polyamine such as, for example, a diamine, triamine etc.

[193] Examples of suitable amines include, but are not limited to, methylamine, ethylamine, propylamine, isopropylamine, butylamine, isobutylamine, t-butylamine, benzylamine, polyetheramines such as, for example, those sold under the trade name JEFFAMINE (commercially available from Huntsman Corporation) or combinations thereof.

[194] The thiol may be any suitable thiol. Suitable thiols will be known to a person skilled in the art. Examples of suitable thiols include, but are not limited to, methanethiol, ethanethiol, 1-propanethiol, 2-propanethiol, 1-butanethiol, 2-butanethiol, beta-mercaptopropionic acids and/or esters, thioglycolic acids and/or esters, thiophenol and combinations thereof. The thiol may be a monothiol or a polythiol, such as a dithiol, trithiol, tetrathiol etc., for example.

[195] The alcohol, amine and/or thiol may have further functionality. For example, the alcohol may also have amine, acid, thiol, cyclic carbonate, hydroxy, epoxy or oxazoline functionality. For example, the amine may also have alcohol, acid, thiol, cyclic carbonate, hydroxy, epoxy or oxazoline functionality. For example, the thiol may also have amine, alcohol, acid, cyclic carbonate, hydroxy, epoxy or oxazoline functionality. It will be appreciated by a person skilled in the art that, for example, an alcohol also having amine functionality may be the same as an amine also having alcohol functionality. Examples of suitable alcohols, amines and/or thiols also having further functionality include, but are not limited to alkanolamines such as, for example, methanolamine, ethanolamine, methyl ethanolamine, ethyl ethanolamine, N-methyl ethanolamine, N-ethyl ethanolamine, 1-amino-2-propanol, 3-amino-1-propanol, 4-amino-1-butanol, 1-amino-2-butanol, 1-amino-3-butanol, dimethanolamine; diethanolamine, dipropanolamine, diisopropanolamine and methyl diethanolamine, hydroxyl and/or alkoxy-substituted oxazolines such as, for example, 2-propyl-4-methoxy oxazoline, glycerol carbonate, glycidol, mercaptoethanol, glycolic acid, lactic acid, malic acid, tartaric acid, thiomalic acid and combinations thereof.

[196] The amine and/or thiol may be a hydroxy functional amine and/or thiol. The hydroxy functional amine and/or thiol may comprise a hydroxyl group. The hydroxy functional amine may be an alkanolamine for example an aliphatic or cycloaliphatic C₁-C₂₀ alkanolamine, such as a C₁-C₁₀ alkanolamine, such as a C₁-C₆ alkanolamine, such as a C₁-C₄ alkanolamine, such as a C₁-C₃ alkanolamine, such as a C₁-C₂ alkanolamine, or even ethanolamine. The hydroxyl functional amine may be an alkanolamine comprising two or more hydroxyl groups. For example, the hydroxy functional amine may be a dialkanolamine or a trialkanolamine. Each alkanol group may independently comprise C₁-C₂₀ alkanol, such as C₁-C₁₀ alkanol, or C₁₋₆ alkanol, or C₁-C₃ alkanol, such as dimethanolamine; diethanolamine, dipropanolamine, diisopropanolamine, such as diisopropanolamine.

[197] The alcohol may comprise at least two hydroxyl groups.

[198] The crosslinker material may comprise the reaction product of the reaction mixture comprising (iii) an alcohol, amine and/or thiol wherein the amine and/or thiol comprises a hydroxy group and the alcohol comprises at least two hydroxy groups.

[199] The crosslinker material may comprise the reaction product of a reaction mixture wherein $\geq 10\%$, such as ≥ 25 mol%, such as ≥ 40 mol%, such as ≥ 50 mol% of the cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with an amine and/or thiol comprising a hydroxy group, and/or an alcohol comprising two or more hydroxy groups.

[200] The use of alcohols, amines and/or thiols also having further functionality can allow for the crosslinker material to be dual-curing due to the further functionality that remains available for

crosslinker, such that the crosslinker material may react with a suitable functional group of the binder and/or the suitable functional group of the crosslinker material.

[201] At least a portion of the cyclic unsaturated acid anhydride and/or diacid derivative thereof may be reacted with the alcohol, amine thiol and/or water, such as with alcohol, amine and/or thiol, when present. It will be appreciated by a person skilled in the art that reacting a cyclic unsaturated acid anhydride and/or diacid derivative thereof with an alcohol, amine and/or thiol results in the esterification, amidation and/or thioesterification of one or each of the acid groups of said cyclic unsaturated acid anhydride and/or diacid derivative thereof. When a cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with an alcohol, amine and/or thiol the monoester derivative may be formed. However, alternatively, the diester derivative is formed. By 'monoester derivative', and like terms as used herein, is meant that one of the acid groups of the cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with an alcohol, amine and/or thiol (to form an ester, amide and/or thioester group). By 'diester derivative', and like terms as used herein, is meant that both of the acid groups of the cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with an alcohol, amine and/or thiol (to form an ester, amide and/or thioester group). When a cyclic unsaturated acid anhydride is used, the reaction product may be obtained by reacting said alcohol, amine and/or thiol with the cyclic unsaturated acid anhydride under conditions which can affect the ring-opening reaction of the acid anhydride, but which do not substantially cause a polyesterification, polyamidation and/or thioesterification reaction and/or formation of the diester, diamide and/or dithioester derivative.

[202] The crosslinker material may have an acid number of at least 100 mg KOH/g.

[203] The crosslinker material may have an acid number of at least 200 mg KOH/g, such as at least 300 mg KOH/g, such as at least 400 mg KOH/g, such as at least 500 mg KOH/g, or even at least 600 mg KOH/g.

[204] The crosslinker material may have an acid number up to 1,000 mg KOH/g, such as up to 975 mg KOH/g, such as up to 950 mg KOH/g, such as up to 925 mg KOH/g, or even up to 900 mg KOH/g.

[205] The crosslinker material may have an acid number from 100 to 1,000 mg KOH/g, such as from 200 to 975 mg KOH/g, such as from 300 to 950 mg KOH/g, such as from 400 to 925 mg KOH/g or even from 500 to 900 mg KOH/g or from 600 to 900 mg KOH/g.

[206] The acid groups of the crosslinker material may be at least partially neutralised by contacting said crosslinker material with a neutraliser. Thus, the crosslinker material may comprise a neutraliser. Suitable neutralisers will be known to a person skilled in the art. Examples of suitable neutralisers include, but are not limited to, tertiary amines such as, for example, dimethylethanolamine (DMEA), trimethyl amine, N-methyl diethanol amine, N-ethyl N-methyl ethanol amine, N,N-dimethyl ethyl amine, N,N-dimethyl propyl amine, N,N-dimethyl 3-hydroxy-1-propyl amine, N,N-dimethylbenzyl amine, N,N-dimethyl 2-hydroxy-1-propyl amine, N,N-diethyl methyl amine, N,N-dimethyl 1-hydroxy-2-propyl amine, triethyl amine, tributyl amine, N,N-dimethyl dodecylamine, N-methyl morpholine; ammonia; hydrazine; metallic aluminium; metallic zinc; water-soluble oxides of the elements Li, Na, K, Mg, Ca, Fe(II) and Sn(II); water-soluble hydroxides of the elements Li, Na, K, Mg, Ca, Fe(II) and Sn(II); water-soluble carbonates of the elements Li, Na, K, Mg, Ca, Fe(II) and Sn(II); and combinations thereof. The

neutraliser may comprise a tertiary amine. The neutraliser may comprise dimethylethanolamine (DMEA).

[207] The crosslinker material may have a hydroxyl number of ≥ 2 mg KOH/g, such as of ≥ 5 mg KOH/g, or of ≥ 10 mg KOH/g.

[208] The crosslinker material may have a hydroxyl number of ≤ 230 mg KOH/g, such as ≤ 180 mg KOH/g, or ≤ 140 mg KOH/g.

[209] The crosslinker material may have a hydroxyl number from 2 to 230 mg KOH/g, such as from 5 to 180 mg KOH/g, such as from 10 to 140 mg KOH/g.

[210] The crosslinker material may have any suitable glass transition temperature (T_g). The crosslinker material may have a T_g of at least 0°C , such as at least 20°C , such as at least 30°C , such as at least 40°C , such as at least 50°C , such as at least 60°C , such as at least 70°C , such as at least 80°C , such as at least 90°C , or even at least 100°C . The crosslinker material may have a T_g of up to 300°C , such as up to 250°C , such as up to 225°C .

[211] The crosslinker material may have any suitable number average molecular weight (M_n). The crosslinker material may have an M_n of at least 300 Da ($\text{Da} = \text{g/mole}$), such as at least 400 Da, or at least 500 Da.

[212] The crosslinker material may have an M_n of up to 5,000 Da, such as up to 3,000 Da or up to 2,000 Da.

[213] The crosslinker material may have an M_n of from 300 to 5,000 Da, such as from 400 to 3,000 Da, such as from 500 to 2,000 Da.

[214] The crosslinker material may have an M_w of at least 450 Da ($\text{Da} = \text{g/mole}$), such as at least 600 Da, or at least 800 Da.

[215] The crosslinker material may have an M_w of up to 8,000 Da, such as up to 5,000 Da, or up to 4,000 Da.

[216] The crosslinker material may have an M_w from 450 to 8,000 Da such as from 600 to 5,000 Da, such as from 800 to 4,000 Da.

[217] The coating composition may comprise any suitable amount of the crosslinker material reaction product. The coating composition may comprise at least 2wt%, or at least 3wt%, such as at least 5 wt%, such as at least 8 wt% of the crosslinker material based on the total solid weight of the coating composition.

[218] The coating composition may comprise up to 90 wt%, such as up to 80 wt%, such as up to 70 wt%, such as up to 60 wt%, such as up to 50 wt%, such as up to 40 wt%, such as up to 30 wt%, or even 25 wt% of the crosslinker material based on the total solid weight of the coating composition.

[219] Further examples of such suitable crosslinker materials are provided in US application 16/832,108 and PCT application PCT/US2021/024078 the contents of each of which are incorporated herein by reference.

[220] The aqueous coating compositions of the present invention may comprise any suitable amount of crosslinker material operable to crosslink acid and/or hydroxyl functionality on the solution polymerised acrylic material.

[221] The aqueous coating composition may comprise from 0.5 to 50 wt%, such as from 1 to 40 wt%, such as from 1 to 30 wt%, such as from 1.5 to 20 wt%, such as from 1.5 to 10 wt%, such as from 2 to 8 wt%, or even from 2 to 6 wt% of crosslinker material based on the total solid weight of the aqueous coating composition.

[222] The aqueous coating composition may comprise from 0.5 to 50 wt%, such as from 1 to 50 wt%, such as from 1.5 to 50 wt%, or even from 2 to 50 wt% of crosslinker material based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.5 to 40 wt%, such as from 1 to 40 wt%, such as from 1.5 to 40 wt%, or even from 2 to 40 wt% of crosslinker material based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.5 to 30 wt%, such as from 1 to 30 wt%, such as from 1.5 to 30 wt%, or even from 2 to 30 wt% of crosslinker material based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.5 to 20 wt%, such as from 1 to 20 wt%, such as from 1.5 to 20 wt%, or even from 2 to 20 wt% of crosslinker material based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.5 to 10 wt%, such as from 1 to 10 wt%, such as from 1.5 to 10 wt%, or even from 2 to 10 wt% of crosslinker material based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.5 to 8 wt%, such as from 1 to 8 wt%, such as from 1.5 to 8 wt%, or even from 2 to 8 wt% of crosslinker material based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.5 to 6 wt%, such as from 1 to 6 wt%, such as from 1.5 to 6 wt%, or even from 2 to 6 wt% of crosslinker material based on the total solid weight of the aqueous coating composition.

[223] The aqueous coating compositions of the present invention may further comprise a solvent. The aqueous coating composition may comprise a single solvent or a mixture of solvents.

[224] The solvent suitably has sufficient volatility to essentially entirely evaporate from the aqueous coating composition during the curing process. As a non-limiting example, the curing process may be by heating at from 130-230 °C for from 1-15 minutes.

[225] Suitable organic solvents include, but are not limited to the following: aliphatic hydrocarbons such as mineral spirits and high flash point naphtha; aromatic hydrocarbons such as benzene; toluene; xylene; solvent naphtha 100, 150, 200; those available from Exxon-Mobil Chemical Company under the SOLVESSO (RTM) trade name; alcohols such as ethanol; n-propanol; isopropanol; and n-butanol; ketones such as acetone; cyclohexanone; methylisobutyl ketone; methyl ethyl ketone; esters such as ethyl acetate; butyl acetate; n-hexyl acetate; RHODIASOLV (RTM) RPDE (a blend of succinic and adipic esters commercially available from Rhodia); glycols such as butyl glycol; glycol ethers such as methoxypropanol; ethylene glycol monomethyl ether; ethylene glycol monobutyl ether and combinations thereof.

[226] The solvent, when present, may be used in the aqueous coating composition in amounts from 5 to 50 wt%, suitably from 6 to 40 wt%, such as from 7 to 30 wt%, or even from 8 to 25 wt% based on the total solid weight of the coating composition. The solvent, when present, may be used in the aqueous

coating composition in amounts from 10 to 20 wt% based on the total solid weight of the aqueous coating composition.

[227] The aqueous coating compositions of the present invention may further comprise a catalyst. Any catalyst typically used to catalyse crosslinking reactions between acrylic materials and crosslinker material may be used. Suitable catalysts will be well known to the person skilled in the art. The catalyst may be a non-metal or a metal catalyst or a combination thereof. Suitable non-metal catalysts include, but are not limited to the following: phosphoric acid; blocked phosphoric acid; phosphatised resins such as, for example, phosphatised epoxy resins and phosphatised acrylic resins; CYCAT (RTM) XK 406 N (commercially available from Allnex); sulfuric acid; sulfonic acid; CYCAT 600 (commercially available from Allnex); NACURE (RTM) 5076 or NACURE 5925 (commercially available from King industries); acid phosphate catalyst such as NACURE XC 235 (commercially available from King Industries); and combinations thereof. Suitable metal catalysts will be well known to the person skilled in the art. Suitable metal catalysts include but are not limited to the following: tin containing catalysts, such as monobutyl tin tris (2-ethylhexanoate); zirconium containing catalysts, such as KKAT (RTM) 4205 (commercially available from King Industries); titanate-based catalysts, such as tetrabutyl titanate TnBT (commercially available from Sigma Aldrich); and combinations thereof.

[228] The catalyst, when present, may be used in the aqueous coating composition in any suitable amount. The catalyst, when present, may be used in amounts from 0.001 to 10 wt%, such as from 0.001 to 5 wt%, such as from 0.01 to 5 wt%, such as from 0.05 to 3 wt%, such as from 0.1 to 2 wt%, or even from 0.1 to 1 wt% based on the total solid weight of the aqueous coating composition. The catalyst, when present, may be used in amounts from 0.1 to 0.5 wt% based on the total solid weight of the aqueous coating composition.

[229] The aqueous coating composition may comprise at least 0.001 wt%, such as at least 0.01 wt%, such as at least 0.05 wt%, or even at least 0.1 wt% of catalyst based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise up to 10 wt%, such as up to 5 wt%, such as up to 3 wt%, such as up to 2 wt%, such as up to 1 wt%, or even up to 0.5 wt% of catalyst based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 10 wt%, such as from 0.01 to 10 wt%, such as from 0.05 wt% to 10 wt%, or even from 0.1 to 10 wt% of catalyst based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 5 wt%, such as from 0.01 to 5 wt%, such as from 0.05 wt% to 5 wt%, or even from 0.1 to 5 wt% of catalyst based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 3 wt%, such as from 0.01 to 3 wt%, such as from 0.05 wt% to 3 wt%, or even from 0.1 to 3 wt% of catalyst based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 2 wt%, such as from 0.01 to 2 wt%, such as from 0.05 wt% to 2 wt%, or even from 0.1 to 2 wt% of catalyst based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 1 wt%, such as from 0.01 to 1 wt%, such as from 0.05 wt% to 1 wt%, or even from 0.1 to 1 wt% of catalyst based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001

to 0.5 wt%, such as from 0.01 to 0.5 wt%, such as from 0.05 wt% to 0.5 wt%, or even from 0.1 to 0.5 wt% of catalyst based on the total solid weight of the aqueous coating composition.

[230] The aqueous coating composition may comprise phosphoric acid or derivatives thereof. Derivatives of phosphoric acid include but are not limited to blocked phosphoric acid; phosphatised resins such as, for example, phosphatised epoxy resins and phosphatised acrylic resins; and combinations thereof. The aqueous coating composition may comprise phosphoric acid.

[231] The aqueous coating composition may comprise at least 0.001 wt%, such as at least 0.01 wt%, such as at least 0.05 wt%, or even at least 0.1 wt% of phosphoric acid or derivatives thereof based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise up to 10 wt%, such as up to 5 wt%, such as up to 3 wt%, such as up to 2 wt%, such as up to 1 wt%, or even up to 0.5 wt% of phosphoric acid or derivatives thereof based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 10 wt%, such as from 0.01 to 10 wt%, such as from 0.05 wt% to 10 wt%, or even from 0.1 to 10 wt% of phosphoric acid or derivatives thereof based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 5 wt%, such as from 0.01 to 5 wt%, such as from 0.05 wt% to 5 wt%, or even from 0.1 to 5 wt% phosphoric acid or derivatives thereof based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 3 wt%, such as from 0.01 to 3 wt%, such as from 0.05 wt% to 3 wt%, or even from 0.1 to 3 wt% of phosphoric acid or derivatives thereof based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 2 wt%, such as from 0.01 to 2 wt%, such as from 0.05 wt% to 2 wt%, or even from 0.1 to 2 wt% of phosphoric acid or derivatives thereof based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 1 wt%, such as from 0.01 to 1 wt%, such as from 0.05 wt% to 1 wt%, or even from 0.1 to 1 wt% of phosphoric acid or derivatives thereof based on the total solid weight of the aqueous coating composition. The aqueous coating composition may comprise from 0.001 to 0.5 wt%, such as from 0.01 to 0.5 wt%, such as from 0.05 wt% to 0.5 wt%, or even from 0.1 to 0.5 wt% of phosphoric acid or derivatives thereof based on the total solid weight of the aqueous coating composition.

[232] Advantageously, it has been found by the present inventors that the use of a catalyst, such as phosphoric acid or derivatives thereof, in combination with the crosslinker material (c) may provide better adhesion than would typically be expected.

[233] The aqueous coating compositions of the present invention may comprise a further resin material. Suitable further resin materials will be well known to a person skilled in the art. Suitable examples of further resin materials include but are not limited to the following: polyester resins; acrylic resins; polyvinyl chloride (PVC) resins; alkyd resins; polyurethane resins; polysiloxane resins; epoxy resins or combinations thereof.

[234] The aqueous coating compositions of the present invention may comprise other optional materials well known in the art of formulating coatings, such as colorants, plasticizers, abrasion-resistant particles, antioxidants, hindered amine light stabilizers, UV light absorbers and stabilizers, surfactants, flow control

agents, thixotropic agents, fillers, organic co-solvents, reactive diluents, catalysts, grind vehicles, lubricants, waxes and other customary auxiliaries.

[235] As used herein, the term "colorant" means any substance that imparts colour and/or other opacity and/or other visual effect to the composition. The colorant can be added to the aqueous coating compositions in any suitable form, such as discrete particles, dispersions, solutions and/or flakes. A single colorant or a mixture of two or more colorants can be used in the aqueous coatings of the present invention. Suitable colorants are listed in U.S. Patent No. 8,614,286, column 7, line 2 through column 8, line 65, which is incorporated by reference herein. Examples for packaging aqueous coatings are those approved for food contact, such as titanium dioxide; iron oxides, such as black iron oxide; aluminium paste; aluminium powder such as aluminium flake; carbon black; ultramarine blue; phthalocyanines, such as phthalocyanine blue and phthalocyanine green; chromium oxides, such as chromium green oxide; graphite fibrils; ferried yellow; quindo red; and combinations thereof, and those listed in Article 178.3297 of the Code of Federal Regulations, which is incorporated by reference herein.

[236] The colorant, when present, may be used in the aqueous coating composition in any suitable amount. The colorant, when present, may be used in the aqueous coating composition in amounts up to 90 wt%, such as up to 50 wt%, or even up to 10 wt% based on the total solid weight of the aqueous coating composition.

[237] Suitable lubricants will be well known to the person skilled in the art. Suitable examples of lubricants include but are not limited to the following: carnauba wax and polyethylene type lubricants. The lubricant, when present, may be used in the aqueous coating composition in amounts of at least 0.01 wt% based on the total solid weight of the aqueous coating composition.

[238] Surfactants may optionally be added to the aqueous coating composition in order to aid in flow and wetting of the substrate. Suitable surfactants will be well known to the person skilled in the art. Suitably the surfactant, when present, is chosen to be compatible with food and/or beverage container applications. Suitable surfactants include, but are not limited to the following: alkyl sulphates (e.g., sodium lauryl sulphate); ether sulphates; phosphate esters; sulphonates; and their various alkali, ammonium, amine salts; aliphatic alcohol ethoxylates; alkyl phenol ethoxylates (e.g. nonyl phenol polyether); salts and/or combinations thereof. The surfactants, when present, may be present in amounts from 0.01 wt% to 10 wt%, suitably from 0.01 to 5 wt%, such as from 0.01 to 2 wt% based on the total solid weight of the aqueous coating composition.

[239] The aqueous coating compositions of the present invention may be substantially free, may be essentially free or may be completely free of bisphenol A (BPA) and derivatives thereof. Derivatives of bisphenol A include, for example, bisphenol A diglycidyl ether (BADGE). The aqueous coating compositions of the present invention may also be substantially free, may be essentially free or may be completely free of bisphenol F (BPF) and derivatives thereof. Derivatives of bisphenol F include, for example, bisphenol F diglycidyl ether (BPFGE). The compounds or derivatives thereof mentioned above may not be added to the composition intentionally but may be present in trace amounts because of unavoidable contamination from the environment. "Substantially free" refers to coating compositions, or components thereof, containing less than 1000 parts per million (ppm) of any of the compounds or

derivatives thereof mentioned above. "Essentially free" refers to coating compositions, or components thereof, containing less than 100 ppm of any of the compounds or derivatives thereof mentioned above. By "completely free" refers to coating compositions, or components thereof, containing less than 20 parts per billion (ppb) of any of the compounds or derivatives thereof mentioned above.

[240] The aqueous coating compositions of the present invention may be substantially free, may be essentially free or may be completely free of dialkyltin compounds, including oxides or other derivatives thereof. Examples of dialkyltin compounds include but are not limited to the following: dibutyltindilaurate (DBTDL); dioctyltindilaurate; dimethyltin oxide; diethyltin oxide; dipropyltin oxide; dibutyltin oxide (DBTO); dioctyltin oxide (DOTO) or combinations thereof. By "substantially free" we mean to refer to coating compositions containing less than 1000 parts per million (ppm) of any of the compounds or derivatives thereof mentioned above. By "essentially free" we mean to refer to coating compositions containing less than 100 ppm of any of the compounds or derivatives thereof mentioned above. By "completely free" we mean to refer to coating compositions containing less than 20 parts per billion (ppb) of any of the compounds or derivatives thereof.

[241] The aqueous coating compositions of the present invention may be substantially free, may be essentially free or may be completely free of epoxy functional compounds. By "substantially free" we mean to refer to coating compositions containing less than 1000 parts per million (ppm) of any of the compounds or derivatives thereof mentioned above. By "essentially free" we mean to refer to coating compositions containing less than 100 ppm of any of the compounds or derivatives thereof mentioned above. By "completely free" we mean to refer to coating compositions containing less than 20 parts per billion (ppb) of any of the compounds or derivatives thereof. The aqueous coating compositions of the present invention may comprise 0wt% of epoxy material.

[242] The aqueous coating compositions of the present invention may be substantially free, may be essentially free or may be completely free of melamine crosslinker materials. By "substantially free" we mean to refer to coating compositions containing less than 1000 parts per million (ppm) of any of the compounds or derivatives thereof mentioned above. By "essentially free" we mean to refer to coating compositions containing less than 100 ppm of any of the compounds or derivatives thereof mentioned above. By "completely free" we mean to refer to coating compositions containing less than 20 parts per billion (ppb) of any of the compounds or derivatives thereof. The aqueous coating compositions of the present invention may comprise 0wt% of melamine crosslinker material.

[243] The aqueous coating compositions of the present invention may be substantially free, may be essentially free or may be completely free of formaldehyde. By "substantially free" we mean to refer to coating compositions containing less than 1000 parts per million (ppm) of any of the compounds or derivatives thereof mentioned above. By "essentially free" we mean to refer to coating compositions containing less than 100 ppm of any of the compounds or derivatives thereof mentioned above. By "completely free" we mean to refer to coating compositions containing less than 20 parts per billion (ppb) of any of the compounds or derivatives thereof. The aqueous coating compositions of the present invention may comprise 0wt% of formaldehyde.

[244] The aqueous coating compositions of the present invention may be substantially free, may be essentially free or may be completely free of styrene. By “substantially free” we mean to refer to coating compositions containing less than 1000 parts per million (ppm) of any of the compounds or derivatives thereof mentioned above. By “essentially free” we mean to refer to coating compositions containing less than 100 ppm of any of the compounds or derivatives thereof mentioned above. By “completely free” we mean to refer to coating compositions containing less than 20 parts per billion (ppb) of any of the compounds or derivatives thereof. The aqueous coating compositions of the present invention may comprise 0wt% of styrene.

[245] The aqueous coating compositions of the present invention may be substantially free, may be essentially free or may be completely free of ethyl acrylate. By “substantially free” we mean to refer to coating compositions containing less than 1000 parts per million (ppm) of any of the compounds or derivatives thereof mentioned above. By “essentially free” we mean to refer to coating compositions containing less than 100 ppm of any of the compounds or derivatives thereof mentioned above. By “completely free” we mean to refer to coating compositions containing less than 20 parts per billion (ppb) of any of the compounds or derivatives thereof. The aqueous coating compositions of the present invention may comprise 0wt% of epoxy material.

[246] The aqueous coating compositions of the present invention do not comprise an emulsion polymerised acrylic material. By the term “do not comprise” in this context is meant that the aqueous coating compositions contain less than 1wt% of emulsion polymerised acrylic material based on the total solid weight of the aqueous coating composition, such as less than 0.5wt% of emulsion polymerised acrylic material based on the total solid weight of the aqueous coating composition, such as less than 0.1wt% of emulsion polymerised acrylic material based on the total solid weight of the aqueous coating composition, such as less than 0.05wt% of emulsion polymerised acrylic material based on the total solid weight of the aqueous coating composition, such as less than 0.01wt% of emulsion polymerised acrylic material based on the total solid weight of the aqueous coating composition, such as less than 0.005wt% of emulsion polymerised acrylic material based on the total solid weight of the aqueous coating composition, such as less than 0.001wt% of emulsion polymerised acrylic material based on the total solid weight of the aqueous coating composition. The aqueous coating compositions of the present invention may comprise 0wt% of emulsion polymerised acrylic material based on the total solid weight of the aqueous coating composition.

[247] The aqueous coating composition of the present invention may be applied to a substrate, or a portion thereof, as a single layer or as part of a multi-layer system. The aqueous coating composition may be applied as a single layer. The aqueous coating composition may be applied to an uncoated substrate. For the avoidance of doubt an uncoated substrate extends to a surface that is cleaned prior to application. The aqueous coating compositions may be applied on top of another paint layer as part of a multi-layer system. For example, the aqueous coating composition may be applied on top of a primer. The aqueous coating compositions may form an intermediate layer or a topcoat layer. The aqueous coating composition may be applied as the first coat of a multi coat system. The second, third, fourth etc. coats may comprise any suitable paint such as those containing, for example, epoxy resins;

polyester resins; polyurethane resins; polysiloxane resins; hydrocarbon resins or combinations thereof. The second, third, fourth etc. coats may comprise polyester resins. The second, third, fourth etc. coats may be a liquid coating or a powder coating, suitably a powder coating. Suitably, the coating compositions may be applied on top of a primer.

[248] The aqueous coating compositions may be applied to a substrate once or multiple times.

[249] The aqueous coating compositions of the present invention may be applied to any suitable substrate. The aqueous coating compositions may be applied to a metal substrate. Examples of suitable metal substrates include, but are not limited to, food and/or beverage packaging, components used to fabricate such packaging or monobloc aerosol cans and/or tubes. Suitably, the food and/or beverage packaging may be a can. Examples of cans include, but are not limited to the following, two-piece cans, three-piece cans and the like. Suitable examples of monobloc aerosol cans and/or tubes include, but are not limited to, deodorant and hair spray containers. Monobloc aerosol cans and/or tubes may be aluminium monobloc aerosol cans and/or tubes. Suitably, the aqueous coating compositions may be applied to food and/or beverage packaging or components used to fabricate such packaging.

[250] The application of various pre-treatments and coatings to packaging is well established. Such treatments and/or coatings, for example, can be used in the case of metal cans, wherein the treatment and/or coating is used to retard or inhibit corrosion, provide a decorative coating, provide ease of handling during the manufacturing process, and the like. Coatings can be applied to the interior of such cans to prevent the contents from contacting the metal of the container. Contact between the metal and a food or beverage, for example, can lead to corrosion of a metal container, which can then contaminate the food or beverage. This can be true when the contents of the can are acidic in nature. The coatings applied to the interior of metal cans also help prevent corrosion in the headspace of the cans, which is the area between the fill line of the product and the can lid; corrosion in the headspace can be problematic with food products having a high salt content. Coatings can also be applied to the exterior of metal cans. Certain coating compositions of the present invention may be applicable for use with coiled metal stock, such as the coiled metal stock from which the ends of cans are made ("can end stock"), and end caps and closures are made ("cap/closure stock"). Since coatings designed for use on can end stock and cap/closure stock may be applied prior to the piece being cut and stamped out of the coiled metal stock, they may be flexible and extensible. For example, such stock may be coated on both sides. Thereafter, the coated metal stock is punched. For can ends, the metal is then scored for the "pop-top" opening and the pop-top ring is then attached with a pin that is separately fabricated. The end is then attached to the can body by an edge rolling process. A similar procedure is done for "easy open" can ends. For easy open can ends, a score substantially around the perimeter of the lid allows for easy opening or removing of the lid from the can, such as by means of a pull tab. For caps and closures, the cap/closure stock may be coated, such as by roll coating, and the cap or closure stamped out of the stock; it is possible, however, to coat the cap/closure after formation. Coatings for cans subjected to relatively stringent temperature and/or pressure requirements should also be resistant to popping, corrosion, blushing and/or blistering.

[251] Accordingly, the present invention is further directed to a food and/or beverage package coated at least in part with any of the aqueous coating compositions described above. In more detail, the present invention is further directed to a food and/or beverage package having a coating on at least a portion thereof, the coating being derived from any of the aqueous coating compositions described herein. A “package” is anything used to contain another item, such as for shipping from a point of manufacture to a consumer, and for subsequent storage by a consumer. A package will be therefore understood as something that is sealed so as to keep its contents free from deterioration until opened by a consumer. The manufacturer will often identify the length of time during which the food or beverage will be free from spoilage, which may range from several months to years. Thus, the present “package” is distinguished from a storage container or bakeware in which a consumer might make and/or store food; such a container would only maintain the freshness or integrity of the food item for a relatively short period. A package according to the present invention can be made of metal or non-metal, for example, plastic or laminate, and be in any form. An example of a suitable package is a laminate tube. Another example of a suitable package is metal can. The term “metal can” includes any type of metal can, container or any type of receptacle or portion thereof that is sealed by the food and/or beverage manufacturer to minimize or eliminate spoilage of the contents until such package is opened by the consumer. One example of a metal can is a food can; the term “food can(s)” is used herein to refer to cans, containers or any type of receptacle or portion thereof used to hold any type of food and/or beverage. The term “metal can(s)” specifically includes food cans and also specifically includes “can ends” including “E-Z open ends”, which may be stamped from can end stock and used in conjunction with the packaging of food and beverages. The term “metal cans” also specifically includes metal caps and/or closures such as bottle caps, screw top caps and lids of any size, lug caps, and the like. The metal cans can be used to hold other items as well, including, but not limited to, personal care products, bug spray, spray paint, and any other compound suitable for packaging in an aerosol can. The cans can include “two-piece cans” and “three-piece cans” as well as drawn and ironed one-piece cans; such one-piece cans often find application with aerosol products. Packages coated according to the present invention can also include plastic bottles, plastic tubes, laminates and flexible packaging, such as those made from PE, PP, PET and the like. Such packaging could hold, for example, food, toothpaste, personal care products and the like.

[252] The aqueous coating composition can be applied to the interior and/or the exterior of the package. The aqueous coating compositions and/or aqueous coating systems could also be applied as a rim coat to the bottom of the can. The rim coat functions to reduce friction for improved handling during the continued fabrication and/or processing of the can. The aqueous coating compositions can also be applied to caps and/or closures; such application can include, for example, a protective varnish that is applied before and/or after formation of the cap/closure and/or a pigmented enamel post applied to the cap, such as those having a scored seam at the bottom of the cap. Decorated can stock can also be partially coated externally with the aqueous coating described herein, and the decorated, coated can stock used to form various metal cans.

[253] The aqueous coating composition may be a post repair coating composition, such as a post repair spray coating composition. Such coating compositions are specifically designed to be applied to and thereby coat a score line of the package. During the scoring operation, which is often achieved by stamping with a punch, the external varnish layer is cut and therefore the corrosion resistance of the metal substrate is compromised. This can be particularly problematic in a context where:

- i) the metal has been stressed and therefore its resistance to corrosion is weakened
- ii) the tin layer of the tinplate (where this is the substrate) is also cut; and/or
- iii) the next treatment step of the packaging is sterilisation, where the presence of heat and high humidity will create high corrosion conditions
- iv) The container is at the beginning of its life cycle which has a minimum of two years.

The corrosion resistance of the metal substrate is restored by the application of a post repair coating (derived from a post repair coating composition) to the score line. This coating is often applied by spraying, such as by an airless spray process.

[254] The aqueous coating composition of the present invention may be a single component coating composition (often referred to as a 1K coating composition) or a multiple component coating composition, such as a two-component coating composition (often referred to as a 2K coating composition). Such terminology is well known in the art. In a multiple component coating composition, the components are provided separately but introduced to each other (by mixing, for example) prior to application. This could be hours before application, for example up to 24 hours before application, or up to 12 hours before application or up to 8 hours before application or up to 4 hours before application. In some instances, the multiple components may be introduced to each other (such as by mixing) during the application process, such as in line mixing, for example. If the aqueous coating composition is a multiple component coating composition, such as a 2-component coating composition, the solution polymerised acrylic material may be provided in a first component, while other materials may be provided in a further component, (such as a second component). For example, the crosslinker material may be provided in a further component (such as a second component).

[255] There is also provided a post repair coating composition comprising an aqueous coating composition as defined herein. The post repair coating composition may comprise a crosslinker agent, which may comprise carbodiimide.

[256] There is also provided a two-component post repair spray comprising an aqueous coating composition as defined herein, wherein the first component comprises a solution polymerized acrylic material and the second component comprises a crosslinker material, which crosslinker material may comprise carbodiimide.

[257] Metal coils, having wide application in many industries, are also substrates that can be coated according to the present invention. Coil coatings may comprise a colorant.

[258] The aqueous coating composition of the present invention may be applied to at least a portion of the metal substrate. For example, when the aqueous coating compositions are applied to a food and/or beverage can, the aqueous coating compositions may be applied to at least a portion of an internal and/or external surface of said food and/or beverage can. When the aqueous coating composition is

applied to a food and/or beverage can, the aqueous coating composition may be applied to at least a portion of an internal surface of said food and/or beverage can.

[259] The substrate may be formed from any suitable material. Suitable materials will be well known to a person skilled in the art. Suitable examples include, but are not limited to the following: steel; tinplate; tinplate pre-treated with a protective material such as chromium, titanium, titanate or aluminium; tin-free steel (TFS); galvanised steel, such as for example electro-galvanised steel; aluminium; aluminium alloy; and combinations thereof. Suitably, the substrate may be formed from steel, tinplate, tin-plate pre-treated with a protective material such as chromium, titanium, titanate or aluminium, tin-free steel (TFS), galvanised steel, such as for example electro-galvanised steel or combinations thereof.

[260] The aqueous coating composition of the present invention may be applied to the substrate by any suitable method. Methods of applying the aqueous coating compositions of the present invention will be well known to a person skilled in the art. Suitable application methods for the aqueous coating compositions of the present invention include but are not limited to the following: electrocoating such as electrodeposition; spraying; electrostatic spraying; dipping; rolling; brushing; and the like. The aqueous coating compositions of the present invention may be applied to the substrate by spraying. Thus, the aqueous coating composition of the present invention may be a spray composition. For the avoidance of doubt, by the term 'spray composition' and like terms as used herein is meant, unless specified otherwise, that the aqueous coating is suitable to be applied to a substrate by spraying, i.e. is sprayable. The aqueous coating compositions of the present invention may be applied to a metal substrate by lamination. For example, a film may be formed from the aqueous coating composition, which film may subsequently be applied to a metal substrate (such as a package, for example a food or beverage can) by lamination thereon.

[261] The aqueous coating composition of the present invention may be applied to any suitable dry film thickness. The aqueous coating composition of the present invention may be applied to a dry film thickness from 0.5 to 100 microns (μm), suitably from 0.5 to 75 μm , such as from 1 to 50 μm , or even from 1 to 40 μm .

[262] The term "alk" or "alkyl", as used herein unless otherwise defined, relates to saturated hydrocarbon radicals being straight, branched, cyclic or polycyclic moieties or combinations thereof and contain 1 to 20 carbon atoms, such as 1 to 10 carbon atoms, or 1 to 8 carbon atoms, or 1 to 6 carbon atoms, or 1 to 4 carbon atoms. These radicals may be optionally substituted with a chloro, bromo, iodo, cyano, nitro, OR^{19} , OC(O)R^{20} , C(O)R^{21} , C(O)OR^{22} , $\text{NR}^{23}\text{R}^{24}$, $\text{C(O)NR}^{25}\text{R}^{26}$, SR^{27} , C(O)SR^{27} , $\text{C(S)NR}^{25}\text{R}^{26}$, aryl or Het, wherein R^{19} to R^{27} each independently represent hydrogen, aryl or alkyl, and/or be interrupted by oxygen or sulphur atoms, or by silano or dialkylsiloxane groups or combinations thereof. Examples of such radicals may be independently selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, 2-methylbutyl, pentyl, iso-amyl, hexyl, cyclohexyl, 3-methylpentyl, octyl and the like.

[263] The term "alkenyl", as used herein, relates to hydrocarbon radicals having a double bond, such as up to 4, double bonds, being straight, branched, cyclic or polycyclic moieties or combinations thereof and containing from 2 to 18 carbon atoms, such as 2 to 10 carbon atoms, such as from 2 to 8 carbon

atoms, such as 2 to 6 carbon atoms, such as 2 to 4 carbon atoms. These radicals may be optionally substituted with a hydroxyl, chloro, bromo, iodo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$, $C(S)NR^{25}R^{26}$, or aryl, wherein R^{19} to R^{27} each independently represent hydrogen, aryl or alkyl, and/or be interrupted by oxygen or sulphur atoms, or by silano or dialkylsiloxane groups. Examples of such radicals may be independently selected from alkenyl groups include vinyl, allyl, isopropenyl, pentenyl, hexenyl, heptenyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, 1-propenyl, 2-butenyl, 2-methyl-2-butenyl, isoprenyl, farnesyl, geranyl, geranylgeranyl and the like. The term "alkenylene", as used herein, relates to a bivalent radical alkenyl group as defined above. For example, an alkenyl group such as ethenyl which would be represented as $-CH=CH_2$, becomes ethenylene, $-CH=CH-$, when represented as an alkenylene. Other alkenylene groups should be understood accordingly.

[264] The term "alkynyl", as used herein, relates to hydrocarbon radicals having a triple bond, such as up to 4, triple bonds, being straight, branched, cyclic or polycyclic moieties or combinations thereof and having from 2 to 18 carbon atoms, such as 2 to 10 carbon atoms, such as from 2 to 8 carbon atoms, such as from 2 to 6 carbon atoms, such as 2 to 4 carbon atoms. These radicals may be optionally substituted with a hydroxy, chloro, bromo, iodo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$, $C(S)NR^{25}R^{26}$, or aryl, wherein R^{19} to R^{27} each independently represent hydrogen, aryl or lower alkyl, and/or be interrupted by oxygen or sulphur atoms, or by silano or dialkylsiloxane groups. Examples of such radicals may be independently selected from alkynyl radicals include ethynyl, propynyl, propargyl, butynyl, pentynyl, hexynyl and the like. The term "alkynylene", as used herein, relates to a bivalent radical alkynyl group as defined above. For example, an alkynyl group such as ethynyl which would be represented as $-C\equiv CH$, becomes ethynylene, $-C\equiv C-$, when represented as an alkynylene. Other alkynylene groups should be understood accordingly.

[265] The term "aryl" as used herein, relates to an organic radical derived from an aromatic hydrocarbon by removal of one hydrogen, and includes any monocyclic, bicyclic, or polycyclic carbon ring of up to 7 members in each ring, wherein at least one ring is aromatic. These radicals may be optionally substituted with a hydroxy, chloro, bromo, iodo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$, $C(S)NR^{25}R^{26}$, aryl or Het, wherein R^{19} to R^{27} each independently represent hydrogen, aryl or lower alkyl, and/or be interrupted by oxygen or sulphur atoms, or by silano or dialkylsilicon groups or combinations thereof. Examples of such radicals may be independently selected from phenyl, p-tolyl, 4-methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-fluorophenyl, 4-chlorophenyl, 3-nitrophenyl, 3-aminophenyl, 3-acetamidophenyl, 4-acetamidophenyl, 2-methyl-3-acetamidophenyl, 2-methyl-3-aminophenyl, 3-methyl-4-aminophenyl, 2-amino-3-methylphenyl, 2,4-dimethyl-3-aminophenyl, 4-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, 1-naphthyl, 2-naphthyl, 3-amino-1-naphthyl, 2-methyl-3-amino-1-naphthyl, 6-amino-2-naphthyl, 4,6-dimethoxy-2-naphthyl, tetrahydronaphthyl, indanyl, biphenyl, phenanthryl, anthryl or acenaphthyl and the like.

[266] The term "Het", when used herein, includes four-to-twelve-membered, such as four-to-ten-membered ring systems, which rings contain a heteroatom selected from nitrogen, oxygen, sulphur and

mixtures thereof, and which rings may contain a double bond or be non-aromatic, partly aromatic or wholly aromatic in character. The ring systems may be monocyclic, bicyclic or fused. Each "Het" group identified herein is optionally substituted by a substituent selected from halo, cyano, nitro, oxo, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below) OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, SR²⁷, C(O)SR²⁷ or C(S)NR²⁵R²⁶ wherein R¹⁹ to R²⁷ each independently represent hydrogen, aryl or lower alkyl (which alkyl group itself may be optionally substituted or terminated as defined below). The term "Het" thus includes groups such as optionally substituted azetidiny, pyrrolidiny, imidazolyl, indolyl, furanyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, thiadiazolyl, triazolyl, oxatriazolyl, thiatriazolyl, pyridazinyl, morpholinyl, pyrimidinyl, pyrazinyl, quinolinyl, isoquinolinyl, piperidinyl, pyrazolyl and piperazinyl. Substitution at Het may be at a carbon atom of the Het ring or, where appropriate, at a heteroatom.

[267] "Het" groups may also be in the form of an N oxide.

[268] For the avoidance of doubt, the reference to alkyl, alkenyl, alkynyl, aryl or aralkyl in composite groups herein should be interpreted accordingly, for example the reference to alkyl in aminoalkyl or alk in alkoxyl should be interpreted as alk or alkyl above etc.

[269] As used herein, unless otherwise expressly specified, all numbers such as those expressing values, ranges, amounts or percentages may be read as if prefaced by the word "about", even if the term does not expressly appear. Also, the recitation of numerical ranges by endpoints includes all integer numbers and, where appropriate, fractions subsumed within that range (e.g. 1 to 5 can include 1, 2, 3, 4 when referring to, for example, a number of elements, and can also include 1.5, 2, 2.75 and 3.80, when referring to, for example, measurements). The recitation of end points also includes the end point values themselves (e.g. from 1.0 to 5.0 includes both 1.0 and 5.0). Any numerical range recited herein is intended to include all sub-ranges subsumed therein.

[270] Singular encompasses plural and vice versa. For example, although reference is made herein to "a" crosslinker material, "a" neutralizer, "an" isocyanate, "an" alkanol amine, "the" residue of "an", and the like, one or more of each of these and any other components can be used.

[271] As used herein, the term "polymer" refers to oligomers and both homopolymers and copolymers, and the prefix "poly" refers to two or more. "Including", "for example" and like terms means "including but not limited to".

[272] When ranges are given, any endpoints of those ranges and/or numbers within those ranges can be combined within the scope of the present invention.

[273] "Including" and like terms means "including but not limited to". Similarly, as used herein, the terms "on", "applied on/over", "formed on/over", "deposited on/over", "overlay" and "provided on/over" mean formed, overlay, deposited, or provided on but not necessarily in contact with the surface. For example, a coating layer "formed over" a substrate does not preclude the presence of another coating layer of the same or different composition located between the formed coating layer and the substrate."

[274] The terms "comprising", "comprises" and "comprised of" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. Additionally, although the present

invention has been described in terms of “comprising”, the coating compositions detailed herein may also be described as “consisting essentially of” or “consisting of”. For example, while the invention has been described in terms of a coating comprising a + b + c, a coating consisting essentially of and/or consisting of a + b + c is also within the present scope. In this context, ‘consisting essentially of’ means that any additional coating components will not materially affect the effectiveness of the coating.”

[275] All of the features contained herein may be combined with any of the above aspects and in any combination.

[276] For a better understanding of the invention, and to show how embodiments of the same may be carried into effect, reference will now be made, by way of example, to the following experimental data.

EXAMPLES

RESIN SYNTHESIS

[277] All polymerization was conducted in the solvent phase as discussed below. The resulting suspension polymer was then neutralized and dispersed in water to form an aqueous polymer.

[278] All parts and percentages mentioned herein are by weight unless otherwise indicated.

Example 1 – Preparation of Single-Stage Solution Polymerised Acrylic Dispersion (20-VK-007):

[279] 190 g glacial Acrylic Acid, 215 g Ethyl Acrylate, 70 g Styrene, 25 g Hydroxyethyl Methacrylate, 10 g t-butyl peroxy-3,5,5-trimethylhexanoate and 60 g butyl CELLOSOLVE™ were premixed in a conical flask. A 3-liter flask was equipped with a motor driven stainless steel stir blade, a water-cooled condenser, a nitrogen inlet, and a heating mantle with a thermometer connected through a temperature feedback control device. Added to the 3-liter flask was 121.13 g 1-pentanol and 275.87 g 2-butoxyethanol. The flask heated to 138°C. At 138°C the premix was added over two and a half hours. 6.25 g butyl CELLOSOLVE™ added as rinse. A second premix containing 6.15 g t-butyl peroxy-3,5,5-Trimethylhexanoate and 18.75 g butyl CELLOSOLVE™ was added in two halves, 30 minutes hold after the first half and one and a half hour hold after the second half addition. After the hold, the flask temperature reduced to <100 °C and neutralized with 117.52 g dimethylethanolamine, followed by 884.40 g Deionized water over 10 minutes. The batch was held for 10 minutes, heat discontinued, and the batch cooled for analysis and formulation.

Example 2 - Preparation of Two-Stage Solution Polymerised Acrylic Dispersion (3131-7):

[280] Polymer Stage-1: 78.68 g Hydroxyethyl Methacrylate and 500 g Glycidyl Methacrylate, 84.42 g Ethyl Acrylate and 127.74 g Styrene were premixed in a conical flask. A 2-liter flask was equipped with a motor driven stainless steel stir blade, a water-cooled condenser, a nitrogen inlet, and a heating mantle with a thermometer connected through a temperature feedback control device. Added to the 2-liter flask was 179 g Aromatic-100 ad then the flask was heated to 170°C. At 170°C, premixed solution of 18.25 g Di-Tert Amyl Peroxide and 38.34 g Aromatic-100, and monomer premix solution co-fed over 210 minutes. 11.66 g of Aromatic-100 used to rinse off the addition funnels. The batch held for 1 hour. After the hold, the flask temperature reduced to 129 °C and 429 g Benzoic Acid added to react off all epoxy functional groups. 4.48 g Aromatic-100 used as rinse, then the batch heated back to 170°C and held for

1 hour. After the hold, samples pulled out for epoxy equivalent weight and Infrared Spectroscopy (ASTM E168 and ASTM E1252) measurements to make sure epoxy reacted off. After epoxy consumed, heat discontinued, and the batch cooled for polymer stage-2.

[281] Polymer Stage-2 (3131-7): 86.4 g glacial Methacrylic Acid, 63.33 g Ethyl Acrylate, 30.09 Hydroxyethyl Methacrylate, 20.74 g Styrene, 21.39 g benzoyl peroxide (75%) and 35 g methylethylketone were premixed in a conical flask. A 2-liter flask was equipped with a motor driven stainless steel stir blade, a water-cooled condenser, a nitrogen inlet, and a heating mantle with a thermometer connected through a temperature feedback control device. Added to the 2-liter flask was 556 g polymer stage-1 and the flask was heated to 125°C. At 120 °C, premixed monomer solution added over 120 minutes. 3 g of t-butyl peroctoate added in two equal portions, after each portion the batch was held for 1 hour. 30 g of butyl CELLOSOLVE™ was used a rinse. After the hold, the flask temperature reduced to 95°C and neutralized with 71 g dimethylethanolamine, followed by 945.59 g De-ionized water. The batch was held for 15 minutes, heat discontinued, and the batch cooled for analysis and formulation.

Example 3 – Preparation of Two-Stage Solution Polymerised Acrylic Dispersion (3131-25):

[282] Polymer Stage-1: 154.74 g Hydroxyethyl Methacrylate, 5.44 g glacial Acrylic Acid, 300 g styrene, 221.42 Methyl Methacrylate, 115.45 g Butyl Acrylate and 73.19 g Hydroxyethyl Acrylate were premixed in a conical flask. A 3-liter flask was equipped with a motor driven stainless steel stir blade, a water-cooled condenser, a nitrogen inlet, and a heating mantle with a thermometer connected through a temperature feedback control device. The flask charged with 156.02 g DOWANOL™ DPM and 41.48 g of methylethylketone, then the flask was heated to 130°C. At 123°C, premixed solution of 30.38 g tert-butyl peroxy-3,5,5-trimethylhexanoate, 60.7 g DOWANOL™ DPM and 40.78 g methylethylketone was added over 185 minutes. Five minutes into 185 minutes, the monomer premix solution then co-fed over 180 minutes. The batch was held for 1 hour, after the hold proceeded with polymer stage-2.

[283] Polymer Stage-2 (3131-25): 41.56 g Hydroxyethyl Methacrylate, 40.67 g glacial Acrylic Acid, 72.67 g Styrene, 32.59 g Methyl Methacrylate, 38.96 g Butyl Acrylate, 8.37 g of Hydroxyethyl Acrylate, 34.21 g DOWANOL™ DPM, 17.13 g tert-butyl peroxy-3,5,5-trimethylhexanoate and 22.98 g methylethylketone were premixed in a conical flask. This premix added to the flask with the polymer stage-1 over 1 hour and the batch was held 1 hour at 130°C. 7.50 g DOWANOL™ DPM, 3.76 g tert-butyl peroxy-3,5,5-trimethylhexanoate and 5.04 g methylethylketone were premixed and added over 30 minutes. 17.82 g of DOWANOL™ DPM and 6.10 g of methylethylketone used as rinses. The batch was held for 1 hour. After the hold, the flask temperature reduced to 90°C and neutralized with 28.52 g dimethylethanolamine, followed by 1222.88 g Deionized water over 30 minutes. The batch was held for 15 minutes, heat discontinued, and the batch cooled for analysis and formulation.

Coating Examples

[284] The details of the coating examples are provided in Table 1. Each material in Table 1 was added under stirring. An MS 6002TS weighing balance available from the Mettler - Toledo Corporation was used to weigh each material. The coatings were stirred using a FAWCETT Model 103A air motor

equipped with a stir blade. The paints were allowed to equilibrate for 16 hours before the paints were coated onto flat aluminum cans.

Table 1
Paint Formulations

	Coating Example 1	Coating Example 2	Coating Example 3
Example 1 Acrylic Dispersion	52.8	0	0
Example 2 Acrylic Dispersion	0	55.3	0
Example 3 Acrylic Dispersion	0	0	62.5
Deionized Water	37.6	33.7	21.2
HRJ-13708 Phenolic	0	2.2	3.2
CURAPHEN 40-804 W75 Phenolic	1.8	0	0
Butanol	3.2	0	0
Amyl Alcohol	1.3	2.0	3.0
butyl CELLOSOLVE™	1.2	5.1	7.5
CYMEL 1123 melamine	1.3	1.6	2.4
NACURE 5925 catalyst	0.1	0.1	0.2
Dimethylethanolamine	0.7	0	0
Total	100.0	100.0	100.0

COATING SUBSTRATES

[285] Twelve-ounce aluminum beverage cans with no coating inside were obtained from the Metal Container Corporation production line located in Arnold, Missouri, USA. The cans as supplied were cut, flattened and attached by tape to an aluminum backing panel in order to have a flat surface for wire bar drawdowns.

[286] Wire drawdown bars were used to coat the flat aluminum cans. A DESPATCH LFC1-38-8 box oven was used for curing. The box oven was set at 215°C and the coated flat aluminum cans were baked for one minute and 45 seconds.

TESTING METHODS

Film Weight

[287] Average coating film weight was measured using a SENCON SI9600 Coating Thickness Gauge. The target film weight was 4 to 6 grams per meter squared. Commercial spray film weights can vary from 75 milligrams for Beer Weight per 12 oz. can up to 140 milligrams for Energy Weight per 12 oz. can.

Adhesion and Blush/Blistering

[288] The coated flat aluminum cans were cut into 6 cm by 11 cm panels and placed in a rack. Four hundred and fifty grams of a 1% JOY detergent solution made in deionized water was added to an 800 milliliter beaker. The solution of JOY detergent in the beaker was heated using a temperature-controlled CORNING PC-420D Hot Plate. The panels were added as soon as the solution of detergent reached 82° C and kept in the solution for forty-five minutes. The JOY detergent solution covered about the bottom half of the test panels. The panels removed and tested for adhesion and evaluated for defects such as blushing and /or blistering according to ISO 2409 and ASTM D714.

[289] A second set of 6 cm by 11 cm coated flat aluminum cans were tested using a 5% Acetic Acid solution made in deionized water. Four hundred and fifty grams of the 5% Acetic Acid solution was added to an 800 milliliter beaker. The solution of Acetic Acid in the beaker was heated using a temperature-controlled CORNING PC-420D Hot Plate. The panels were added as soon as the solution of Acetic Acid reached 100°C and kept in the solution for thirty minutes. The Acetic Acid detergent solution covered about the bottom half of the test panels. The panels removed, tested for tape adhesion as per ISO 2409, and evaluated for other defects such as blushing and /or blistering as per ASTM D714.

[290] The panels were tested for coating adhesion to the aluminum substrate using BYK Cross-Cut Tester Kit # 5127 with 1.5 mm blade. The adhesion rating scale is:

- 0 for zero loss of adhesion,
- 1 for <5% loss,
- 2 for 5% to 15% loss,
- 3 for 16% to 35% loss,
- 4 for 36% to 65% loss
- 5 for >65% loss.

[291] The loss percentage is in the area of the scribe. Visual references are available to rate the adhesion loss according to the above described percentages.

[292] MEK Resistance

The MEK resistance was determined using a two-pound ball hammer using MEK soaked gauze covering the ball end of the hammer. The number of double rubs until the coating failed to the substrate was recorded. The equipment used was a 2-pound ball-peen hammer, MEK solvent, an Aluminum guide, masking tape to adhere the test panel to a flat surface, rubber band and Gauze (Fisher Brand 4x4 12 ply).

[293] The MEK rub test method was as follows:

1. The test panel was placed on a flat surface.
2. A piece of Fisher Brand 4x4 12 ply gauze was arranged over the ball end of a two-pound ball-peen hammer. The gauze was snugly held in place with a rubber band in such a fashion that no wrinkles were formed.
3. The cloth was saturated with the appropriate solvent for the material being tested, the gauze was re-saturated every 25 double rubs.
4. The saturated gauze was immediately rubbed over the test area using a back-and-forth stroke of about 4 to 6 inches.
5. No downward or upward pressure was exerted on the hammer handle. The weight of the hammer controlled the downward pressure.
6. The back-and-forth action was continued counting one "double rub" for each forward and backward motion completed until bare substrate was exposed in the center of the strip where the rubs were performed.

7. The test result was recorded as the number of double rubs required to expose bare substrate in the center of the rub strip. During the test the start/stop points show failure early as they receive more force, it was important to monitor the center of the rub stroke for a correct failure reading.

TEST DATA

[294] The test results of the coating formulations from Table 1 are recorded in Table 2. As a comparative example, commercially available PPG 2012-820/C was used, which was a spray applied coating for Aluminum beverage cans sold by PPG Industries, Inc. and was based on emulsion polymerised acrylics.

Table 2
Coating Properties

Coating	MEK Rubs	Coating Weight grams/meter ²	Adhesion Rating to Aluminum Can after Test	
			1% Joy Detergent	5% Acetic Acid
Coating Example 1	35	4.5	0	0
Coating Example 2	100	3.8	0	0
Coating Example 3	45	5.2	0	0
PPG 2012-820 / C	35	6.1	0	0

[295] The coatings in Table 2 performed as well as the PPG 20120-820 / C commercially available coating for the inside of beverage cans in screening tests. No blushing and no other film defect were observed after the testing. The coatings maintained perfect adhesion after the JOY detergent and Acetic Acid testing. The MEK resistance of the coatings is equivalent or better than the commercially available coating.

Example 4 – Preparation of Two-Stage Solution Polymerised Acrylic Dispersion:

[296] Polymer Stage-1: 88.42 g Hydroxyethyl Methacrylate, 29.30 g NBMA (n-butoxymethyl acrylamide), 3.11 g Acrylic Acid, 215.85 g Methyl Methacrylate, 110.99 g n-Butyl Acrylate and 41.83 g Hydroxy Ethyl Acrylate were premixed in a conical flask. A 3-liter flask was equipped with a motor driven stainless steel stir blade, a water-cooled condenser, a nitrogen inlet, and a heating mantle with a thermometer connected through a temperature feedback control device. Added to the 3-liter flask was 317.72 g Dowanol DPM and 46.56 g MEK. The flask was heated to 94°C. At 94°C, premixed solution of 10.87 g T-Butyl Peroctoate, 34.69 g Dowanol DPM and 23.30 g MEK and monomer premix solution was co-fed over 185 minutes, after 5 minutes of the initiator mix. The batch was held for 1 hour.

[297] Polymer Stage-2: 23.79 g Hydroxyethyl Methacrylate, 7.10 g NBMA (n-butoxymethyl acrylamide), 23.24 g Acrylic Acid, 49.01 Methyl Methacrylate, 37.47 g n-Butyl Acrylate and 4.78 g Hydroxy Ethyl Acrylate were premixed in a conical flask. In a separate conical flask, 19.55g of Dowanol DPM, 3.09 g

T-Butyl Peroctoate and 13.13 g MEK was premixed. Both the monomer premix and initiator premixes were then co-fed into stage-1 polymer over 1 hour, rinsed with 10.18 g of Dowanol DPM. After the addition, the batch was held for 1 hour. 4.29 g of Dowanol DPM, 4.30 g of T-Butyl Peroctoate and 2.88 g MEK premixed, added over 30 minutes, rinsed with 3.49 g of MEK and held for 1 hour. After the hold, the flask temperature reduced to 90°C and neutralized with a mixture of 16.30 g dimethylethanolamine and 15.03 g of De-Ionized Water, followed by 964.59 g De-Ionized water over 30 minutes. The heat discontinued and the batch cooled for analysis and formulation.

Preparation of PMA crosslinker:

[298] A PMA crosslinker comprising a homopolymer of maleic acid was produced by the following method.

[299] **Synthesis of a homopolymer of maleic acid:** 520 g xylene and 520 g maleic anhydride were added to a four neck round bottom flask equipped with a mechanical stir blade, thermocouple and reflux condenser. The mixture was heated to a set point of 60°C under a nitrogen atmosphere. Once the maleic anhydride was dissolved, 2.6 g of octylamine was added and the mixture was held for 5 minutes. Next the mixture was heated to 140°C set point. At 140°C a solution of 434.3 g xylene and 52 g di-tertiary butyl peroxide was added over a time period of two hours via an addition funnel. After the addition was complete, the resin mixture was then held at 140°C for two hours. Next the mixture was cooled to 110°C to prepare the solution for vacuum distillation. At 110°C the xylene solvent was removed by vacuum distillation to obtain 263.9 g of distillate. After 2 hours the distillation process was stopped, and 131.4 g of DI water was added over 60 minutes. After this addition, the reactor was set up with a Dean-Stark apparatus to remove residual xylene. After 1 hour, 306.6 g of DI water was added over 60 min and the reaction was held at 110°C for 15 min.

[300] **Neutralization of the homopolymer of maleic acid with dimethylethanolamine:** The resin as prepared was heated to a set point of 70°C. Next 468 g of dimethylethanolamine was added over 60 min. After this addition, the mixture was held for 15 min then poured out into a suitable container.

[301] The resultant crosslinker material had a solids content of 64.5% as measured by 110°C solids test.

Coating Example 4

[302] The details of coating example 4 is provided in Table 3. Each material in Table 3 was added under stirring. An MS 6002TS weighing balance available from the Mettler - Toledo Corporation was used to weigh each material. The compositions were stirred using a FAWCETT Model 103A air motor equipped with a stir blade. The compositions were allowed to equilibrate for 16 hours before they were coated onto flat aluminum cans and ETP steel panels.

Table 3 – Coating composition

	Coating Example 4
Example 4 acrylic dispersion	32.88
Deionized Water	13.01
PMA crosslinker	1.12
Amyl Alcohol	3.03
Dimethylethanolamine	0.60
Total	50.64

COATING SUBSTRATES

[303] Twelve-ounce aluminum beverage cans with no coating inside were obtained from the Metal Container Corporation production line located in Arnold, Missouri, USA. The cans as supplied were cut, flattened and attached by tape to an aluminum backing panel in order to have a flat surface for wire bar drawdowns. Uncoated ETP steel panels were used cleaned and used for drawdown for wedge bend testing.

[304] Wire drawdown bars were used to coat the flat aluminum cans and ETP steep panels. A DESPATCH LFC1-38-8 box oven was used for curing. The box oven was set at 215° C and the coated flat aluminum cans were baked for one minute and 45 seconds.

TESTING METHODS

Film Weight

[305] Average coating film weight was measured using a SENCON SI9600 Coating Thickness Gauge. The target film weight was 2.5 to 3.0 milligram per square inches.

Wedge bend flex

[306] Coated ETP steel panels were used for the Wedge Bend test using a BYK-Garner “Coverall” Bend and Impact Tester. A 5x10 cm coated test panel was first bent double over the 1/8” rod so that the coated surface was on the outside. The bent panel was placed between the parts of the hinge. The impact tool, flat face down, was dropped from a height needed to deliver 48 inch-pounds of impact force onto the upper part of the hinge.

Adhesion and Blush/Blistering

[307] The coated flat Aluminum cans were cut into 6 cm by 11 cm panels and placed in a rack. Four hundred and fifty grams of a 1% JOY detergent solution made in deionized water was added to an 800 milliliter beaker. The solution of JOY detergent in the beaker was heated using a temperature-controlled CORNING PC-420D Hot Plate. The panels were added as soon as the solution of detergent reached 82°C and kept in the solution for ten minutes. The JOY detergent solution covered about the bottom

half of the test panels. The panels removed and tested for adhesion and evaluated for defects such as blushing and /or blistering according to ISO 2409 and ASTM D714.

[308] A second set of 6 cm by 11 cm coated flat aluminum cans were tested using a 3% Acetic Acid solution made in deionized water. Four hundred and fifty grams of the 3% Acetic Acid solution was added to an 800 milliliter beaker. The solution of Acetic Acid in the beaker was heated using a temperature-controlled CORNING PC-420D Hot Plate. The panels were added as soon as the solution of Acetic Acid reached 100°C and kept in the solution for thirty minutes. The Acetic Acid solution covered about the bottom half of the test panels. The panels removed, tested for tape adhesion as per ISO 2409, and evaluated for other defects such as blushing and /or blistering as per ASTM D714.

[309] The panels were tested for coating adhesion to the aluminum substrate using BYK Cross-Cut Tester Kit # 5127 with 1.5 mm blade. The adhesion rating is presented in % coating intact, rounded to nearest 10th with a higher number indicating better adhesion.

[310] The panels were tested for blush by visual inspection immediately after JOY detergent and Acetic Acid test using a scale of 1-10, where a rating of 10 indicates no blush and a rating of 0 indicates complete whitening of the film.

[311] The panels were tested for blistering by visual inspection immediately after Joy detergent and Acetic Acid test. A rating of no blisters, microblisters or blister is given based on the sizes of blister presents.

TEST DATA

[312] The test results of the coating formulations from Table 3 are recorded in Table 4. As a comparative example, commercially available PPG 2012-827/B was used, which was a spray applied coating for Aluminum beverage cans sold by PPG Industries, Inc. and was based on emulsion acrylic coating composition that contained resol-formaldehyde crosslinker technology. PPG 2012-827B was not formed from a monomer component containing acrylamide.

Table 4 - Coating Properties

Coating	Coating Weight mg per in ²	Wedge Bend Flex		1% Joy Test			3% Acetic Acid		
		Continuous	Peppering	Adhesion	Blush	Blister	Adhesion	Blush	Blister
Coating Example 4	3.00	31	42	100	9	none	100	8	none
PPG 2012-827 / B	3.00	26	38	100	8	none	100	8	none

[313] The coatings in Table 4 performed as well as the PPG 20120-827 / B commercially available coating for the inside of beverage cans in screening tests. No blushing and no other film defect were observed after the testing. The coatings maintained perfect adhesion after the JOY detergent and Acetic Acid testing. The wedge bend flex of the coating was equivalent to the commercially available coating.

[314] Attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

[315] All of the features disclosed in this specification (including any accompanying claims and abstract), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. Each feature disclosed in this specification (including any accompanying claims and abstract) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

[316] The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims and abstract), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A package coated on at least a portion thereof with a coating, the coating being derived from an aqueous coating composition, the aqueous coating composition comprising:
 - a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
 - b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material; and
 - c) a carrier comprising water,wherein the coating composition does not comprise an emulsion polymerised acrylic material; and wherein, when two or more different solution polymerised acrylic materials are present, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material.
2. A package coated on at least a portion thereof with a coating, the coating being derived from an aqueous coating composition, the aqueous coating composition being obtainable by a process comprising:
 - i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;
 - ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
 - iii) at least partially neutralising the acid functionality of the solution polymerised acrylic material with a neutraliser; and
 - iv) dispersing the solution polymerised acrylic material in water.
3. A package coated on at least a portion thereof with a coating, the coating being derived from an aqueous coating composition, the aqueous coating composition comprising:
 - a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
 - b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material;
 - c) a carrier comprising water; and
 - d) a further solution polymerised acrylic material, different from the at least one solution polymerised acid functional acrylic material "a)";wherein the coating composition does not comprise an emulsion polymerised acrylic material; and wherein, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material.
4. A package according to any preceding claim, wherein the package is a food or beverage can.

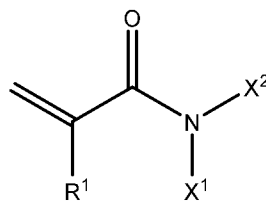
5. An aqueous coating composition, comprising:
- a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
 - b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material;
 - c) a carrier comprising water; and
 - d) a further solution polymerised acrylic material, different from the solution polymerised acid functional acrylic material "a)";
- wherein the coating composition does not comprise an emulsion polymerised acrylic material; and wherein, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material.
6. An aqueous coating composition, obtainable by a process comprising:
- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;
 - ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material;
 - iii) mixing a second monomer component comprising an acrylic monomer with the solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the solution polymerised acrylic material;
- wherein at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of solution polymerised acrylic material and/or the further solution polymerised acrylic material with a neutraliser; and
 - v) dispersing the solution polymerised acrylic material and the further solution polymerised acrylic material in water.
7. An aqueous coating composition obtainable by a process comprising:
- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier, which first monomer component comprises an epoxy functional monomer;
 - ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material; wherein the solution polymerised acrylic material comprises an epoxy group;

- iib) reacting the epoxy group on the solution polymerised acrylic material with an epoxy reactive material to form an epoxy reacted solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the epoxy reacted solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the epoxy reacted solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the epoxy reacted solution polymerised acrylic material;
wherein at least one of the epoxy reacted solution polymerised acrylic material and the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of the epoxy reacted solution polymerised acrylic material and/or the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the epoxy reacted solution polymerised acrylic material and the further solution polymerised acrylic material in water.

8. An aqueous coating composition obtainable by a process comprising:

- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier, which first monomer component comprises an epoxy functional monomer;
- ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material; wherein the solution polymerised acrylic material comprises an epoxy group;
- iib) reacting the epoxy group on the solution polymerised acrylic material with an epoxy reactive material to form an epoxy reacted solution polymerised acrylic material;
- iii) mixing a second monomer component comprising an acrylic monomer with the epoxy reacted solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the epoxy reacted solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic material, which further solution polymerised material is not covalently linked to the epoxy reacted solution polymerised acrylic material;
wherein the further solution polymerised acrylic material comprises acid functionality;
- iv) at least partially neutralising the acid functionality of the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the epoxy reacted solution polymerised acrylic material and the further solution polymerised acrylic material in water.

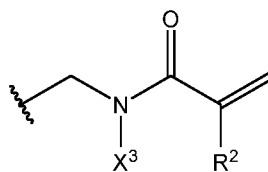
9. A package or aqueous coating composition according to any preceding claim, wherein the solution polymerised acrylic material and/or further solution polymerised acrylic material is formed from a monomer component comprising an acrylamide monomer of formula I:



Formula I

wherein R¹ represents a H or alkyl group; and

X¹ represents a linear or branched alkyl, a -Y-O-Z group; or is according to formula II;



Formula II

wherein

Y represents a bivalent linear or branched alkylene bridging group, and

Z represents linear or branched alkyl group, or is according to formula II, or H;

X³ represents a H or alkyl group;

R² represents a H or alkyl group;

wherein

Y represents a bivalent linear or branched alkylene bridging group, and

Z represents linear or branched alkyl group, or H;

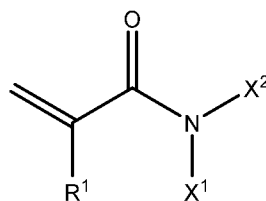
X² represents a linear or branched alkyl, H or a -Y-O-Z group;

wherein

Y represents a bivalent linear or branched alkylene bridging group, and

Z represents a linear or branched alkyl group, or H.

10. A package or aqueous coating composition according to any preceding claim, wherein the solution polymerised acrylic material and/or further solution polymerised acrylic material is formed from a monomer component comprising an acrylamide monomer of formula I:



Formula I

wherein R¹ represents a H or alkyl group; and

X¹ represents a linear or branched alkyl, or a -Y-O-Z group;

wherein

Y represents a bivalent linear or branched alkylene bridging group, and

Z represents linear or branched alkyl group, or H;

X² represents a linear or branched alkyl, H or a -Y-O-Z group;

wherein

Y represents a bivalent linear or branched alkylene bridging group, and

Z represents a linear or branched alkyl group, or H.

11. A package or an aqueous coating composition according to claim 10, wherein R¹ represents H or C₁-C₂₀ alkyl group, such as C₁-C₁₀ alkyl group, such as C₁-C₈ alkyl group, such as C₁-C₆ alkyl group, such as C₁-C₄ alkyl group, such as R¹ represents H, methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclohexyl or cycloheptyl group, or even such as, R¹ represents H or C₁-C₄ alkyl group, such as methyl, ethyl, propyl or butyl group and/or wherein X¹ represents a linear or branched C₁-C₂₀ alkyl group, such as C₁-C₁₀ alkyl group, such as C₁ to C₈ alkyl group, such as C₁-C₆ alkyl group, such as C₁-C₄ alkyl group; or X¹ represents a -Y-O-Z group; wherein Y represents a bivalent linear or branched alkylene bridging group, such as C₁-C₁₀ alkylene bridging group, such as C₁-C₈ alkylene bridging group, such as C₁-C₆ alkylene bridging group, such as C₁-C₄ alkylene bridging group, such as Y may represent methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene or decylene, or even such as Y represents methylene, ethylene or propylene, and Z represents a linear or branched C₁-C₂₀ alkyl group, such as C₁-C₁₀ alkyl group, such as C₁ to C₈ alkyl group, such as C₂-C₇ alkyl group, such as C₂-C₆ alkyl group, or H, such as Z represents H, methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclohexyl or cycloheptyl group, or even such as Z represents C₂-C₆ alkyl group, such as ethyl, propyl, butyl group, pentyl or hexyl; and/or wherein X² represents a linear or branched C₁-C₂₀ alkyl group, such as C₁-C₁₀ alkyl group, such as C₁ to C₈ alkyl group, such as C₁-C₆ alkyl group, such as C₁-C₄ alkyl group, or H, such as X² represents H, methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, cyclohexyl or cycloheptyl group, or even such as X² represents H or C₁-C₄ alkyl group, such as methyl, ethyl, propyl or butyl group.
12. A package or an aqueous coating composition according to claim 10 or 11, wherein R¹ represents H or C₁-C₄ alkyl group; X¹ represents a -Y-O-Z group wherein Y represents a C₁-C₄ alkylene bridging group and Z represents a C₂-C₇ alkyl group; and X² represents H.

13. A package or an aqueous coating composition according to any of claims 10 to 12, wherein R¹ represents H or methyl; X¹ represents a -Y-O-Z group wherein Y represents a methylene or ethylene bridging group and Z represents a C₂-C₆ alkyl group; and X² represents H.
14. A package or an aqueous coating composition according to claims 10 to 13, wherein the solution polymerised acrylic material and/or further solution polymerised acrylic material is formed from a monomer component comprising n-butoxymethyl acrylamide (NBMA).
15. A package or an aqueous coating composition according to any of claims 9 to 13, wherein the solution polymerised acrylic material and/or further solution polymerised acrylic material comprises at least 0.5 wt% acrylamide monomer of formula I based on the total weight of the monomers in the solution polymerised acrylic material and/or further solution polymerised acrylic material, such as at least 1 wt%, such as at least 1.5 wt%, such as at least 2 wt%, such as at least 5 wt%.
16. A package or an aqueous coating composition according to any of claims 9 to 15, wherein the further solution polymerised acrylic material comprises at least 1 wt% acrylamide monomer of formula I based on the total weight of the monomers in the further acrylic material, such as at least 2 wt%, such as at least 3 wt%, such as at least 4 wt%, such as at least 5 wt%.
17. A package or an aqueous coating composition according to any of claims 9 to 16, wherein the further solution polymerised acrylic material comprises at least 20 wt% acrylamide monomer of formula I based on the total weight of the monomers in the further acrylic material, such as at least 30 wt%, such as at least 40 wt%.
18. A package or an aqueous coating composition according to any preceding claim, wherein at least one of the solution polymerised acrylic material or the further solution polymerised acrylic material is formed from a monomer component comprising an optionally substituted styrene monomer or a styrene-mimicking ethylenically unsaturated monomer.
19. A package or an aqueous coating composition according to claim 18, wherein the substituted styrene monomer comprises a 2, 3, or 4- alkyl or aryl substituted styrene.
20. A package or an aqueous coating composition according to claim 18 or 19, wherein the substituted styrene monomer is selected from alpha-methyl styrene; 3,4-alpha-methyl styrene; methyl styrenes such as 2-methyl styrene, 4-methyl styrene (vinyl toluene) and the like; dimethyl styrenes such as 2,3-dimethyl styrene; 2-ethyl styrene; 4-tertbutylstyrene; 4-methoxystyrene; 4-phenylstyrene; 4-phenoxy styrene; 4-propyl styrene; 4-benzylstyrene; 4-cyclohexyl styrene; 4-dodecyl styrene; 4-(phenyl butyl)styrene; 2-methyl-4-isopropyl styrene; 2-ethyl-4-benzyl styrene;

halostyrenes such as 4-chlorostyrene, 2,5-dichlorostyrene, 3,4-dichlorostyrene, 2,6-dichlorostyrene, 4-fluorostyrene; divinylbenzene; isopropyl styrene, t-butyl styrene; trans-beta-styrene, or combinations thereof.

21. A package or an aqueous coating according to claim 18, wherein the styrene-mimicking ethylenically unsaturated monomers comprise an optionally saturated monocyclic group, for example, benzyl acrylate, benzyl methacrylate, cyclohexyl acrylate or cyclohexyl methacrylate.
22. A package or an aqueous coating composition according to any preceding claim, wherein at least one of the solution polymerised acrylic material or the further solution polymerised acrylic material is formed from a monomer component comprising terpene monomers or derivatives thereof, rosin monomers or derivatives thereof, cardanol monomers or derivatives thereof.
23. A package or an aqueous coating composition according to claim 22, wherein the terpene monomers or derivatives thereof are selected from at least one of monoterpenes such as α -pinene, β -pinene, camphene, sabinene, limonene and myrcene; sesquiterpenes such as bisabolene and nerolidol; diterpenes.
24. A package or an aqueous coating composition according to any preceding claim, wherein at least one of the acrylic material or the further acrylic material is formed from a monomer component comprising alkyl (alk)acrylate, alkyl (meth)acrylate, or (alk)acrylic acid; wherein the alkyl group is optionally cyclic, for example, isobornyl(methyl)acrylate or monomers derived from isosorbide and/or tetramethyl cyclobutene.
25. A package or an aqueous coating composition according to any preceding claim, wherein the solution polymerised acrylic material has an acid value from 30 mg KOH/g, such as from 40, or even from 50 mg KOH/g.
26. A package or an aqueous coating composition according to any preceding claim, wherein the further solution polymerised acrylic material has an acid value from 30 mg KOH/g, such as from 40 mg KOH/g, or even from 50 mg KOH/g.
27. A package or an aqueous coating composition according to any preceding claim, wherein the solution polymerised acrylic material and/or further solution polymerised comprise acrylic acid, methacrylic acid, ethyl acrylate, ethyl methacrylate, butyl methacrylate, butyl acrylate, hydroxyethyl methacrylate, hydroxyethyl acrylate or combinations thereof.
28. A package or an aqueous coating composition according to any preceding claim, wherein the amount of neutraliser is a suitable amount to neutralise at least 20%, such as at least 30%, such

as at least 40%, or even at least 50% of the acid functionality of the solution polymerised acrylic material and/or further solution polymerised acrylic material.

29. A package or an aqueous coating composition according to any preceding claim, wherein the aqueous coating composition further comprises a crosslinker material.
30. A package or an aqueous coating composition according to claim 29, wherein the crosslinker material comprises the reaction product of a reaction mixture comprising:
- (i) a cyclic unsaturated acid anhydride and/or diacid derivative thereof;
 - (ii) an ethylenically unsaturated monomer; and
 - (iii) an alcohol, amine, thiol and/or water,
- wherein at least a portion of the cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with the alcohol, amine, thiol and/or water;
- and wherein the crosslinker material has an acid number of at least 100 mg KOH/g.
31. A package or an aqueous coating composition according to claim 29, wherein the crosslinker material comprises the reaction product of a reaction mixture comprising:
- (i) $\geq 70\%$ by weight of a cyclic unsaturated acid anhydride and/or diacid derivative thereof by total solid weight of the monomers from which the crosslinker material is formed;
 - (ii) optionally, an ethylenically unsaturated monomer;
 - (iii) and optionally, an alcohol, amine, thiol and/or water, wherein at least a portion of the cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with the alcohol, amine, thiol and/or water, when present;
- and wherein the crosslinker material has an acid number of at least 100 mg KOH/g.
32. A package or an aqueous coating composition according to claim 30 or 31, wherein the cyclic unsaturated acid anhydride comprises maleic anhydride.
33. A package or an aqueous coating composition according to any of claims 30 to 32, wherein the ethylenically unsaturated monomer comprises a hydroxyl functional monomer.
34. A package or an aqueous coating composition according to any of claims 30 to 33, wherein the hydroxyl functional monomer comprises hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxymethyl acrylate, hydroxymethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, hydroxypentyl acrylate, hydroxypentyl methacrylate, hydroxyhexyl methacrylate, hydroxyhexyl methacrylate, methyl 2-(hydroxymethyl)acrylate and/or ethyl 2-(hydroxymethyl)acrylate.

35. A package or an aqueous coating composition according to claims 30 to 34, wherein the crosslinker material comprises $\geq 2.5\%$ hydroxyl functional ethylenically unsaturated monomer based on the total solid weight of the monomers from which the crosslinker material is formed.
36. A package or an aqueous coating composition according to any of claims 30 to 35, wherein the unsaturated acid anhydride and/or diacid derivative thereof comprises maleic anhydride and the ethylenically unsaturated monomer(s) comprises a hydroxyl functional monomer with styrene, isobutyl vinyl ether and/or vinyl acetate.
37. A package or an aqueous coating composition according to any of claims 29 to 36, wherein the crosslinker material has a Tg of at least 50°C .
38. A package or an aqueous coating composition according to any of claims 29 to 37, wherein the crosslinker material has a Tg of at least 100°C .
39. A package or an aqueous coating composition according to any of claims 30 to 38, wherein the reaction mixture comprises an alcohol, amine, and/or thiol, wherein at least a portion of the cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with the alcohol, amine, and/or thiol.
40. A package or an aqueous coating composition according to any of claims 30 to 39, wherein the amine and/or thiol is hydroxy functional.
41. A package or an aqueous coating composition according to claim 40, wherein the hydroxy functional amine comprises dimethanolamine; diethanolamine, dipropanolamine and/or diisopropanolamine.
42. A package or an aqueous coating composition according to any of claims 30 to 41, wherein the alcohol comprises ethanol.
43. A package or an aqueous coating composition according to any of claims 30 to 42, wherein the crosslinker material comprises the reaction product of a reaction mixture wherein $\geq 10\%$ of the cyclic unsaturated acid anhydride and/or diacid derivative thereof is reacted with an amine and/or thiol comprising a hydroxy group, and/or an alcohol comprising at least two hydroxy groups.
44. A package or an aqueous coating composition according to any of claims 30 to 43, wherein the crosslinker material comprises at least 75 wt% of cyclic unsaturated acid anhydride and/or diacid derivative thereof based on the total solid weight of the monomers from which the crosslinker material is formed.

45. A package or an aqueous coating composition according to any of claims 30 to 44, wherein the crosslinker material comprises at least 90 wt% of cyclic unsaturated acid anhydride and/or diacid derivative thereof based on the total solid weight of the monomers from which the crosslinker material is formed.
46. A package or an aqueous coating composition according to any of claims 30 to 45, wherein the crosslinker material comprises at least 99 wt% of cyclic unsaturated acid anhydride and/or diacid derivative thereof based on the total solid weight of the monomers from which the crosslinker material is formed.
47. A package or an aqueous coating composition according to any of claims 29 to 46, wherein the crosslinker material has an acid number of at least 200 mg KOH/g.
48. A package or an aqueous coating composition according to any of claims 29 to 47, wherein the crosslinker material has an acid number of at least 500 mg KOH/g.
49. A package or an aqueous coating composition according to any of claims 29 to 48, wherein the crosslinker material has a hydroxyl number of ≥ 2 mg KOH/g.
50. A package or an aqueous coating composition according to any of claims 29 to 49, wherein the crosslinker material has a hydroxyl number of ≥ 10 mg KOH/g.
51. A package or an aqueous coating composition according to any of claims 29 to 50, wherein crosslinker material has an Mn of at least 300 Da.
52. A package or an aqueous coating composition according to any of claims 29 to 51, wherein the crosslinker material has a Mn of up to 5,000 Da.
53. A package or an aqueous coating composition according to any of claims 29 to 52, wherein the crosslinker material is substantially free of formaldehyde.
54. A package coated on at least a portion thereof with a coating, the coating being derived from an aqueous coating composition of any of claims 5 to 53.
55. A package or aqueous coating composition according to any preceding claim, wherein the aqueous coating composition is a spray composition.

56. A post repair coating composition comprising an aqueous coating composition the aqueous coating composition comprising:
- a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
 - b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material; and
 - c) a carrier comprising water,
- wherein the coating composition does not comprise an emulsion polymerised acrylic material; and wherein, when two or more different solution polymerised acrylic materials are present, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material.
57. A post repair spray coating composition according to claim 56, wherein the aqueous coating composition is a two-component composition, wherein the first component comprises:
- a) a solution polymerised acrylic material, which solution polymerised acrylic material comprises acid functionality;
 - b) a neutraliser operable to at least partially neutralise the acid functionality of the solution polymerised acrylic material; and
 - c) a carrier comprising water,
- wherein the coating composition does not comprise an emulsion polymerised acrylic material; and wherein, when two or more different solution polymerised acrylic materials are present, there is no covalent linkage between one solution polymerised acrylic material and another different solution polymerised acrylic material;
- and wherein the second component comprises a crosslinker material, which crosslinker material may comprise carbodiimide.
58. A post repair spray coating composition comprising an aqueous coating composition of any of claims 5 to 53.
59. A method of making a coating composition, the method comprising:
- i) mixing a first monomer component comprising an acrylic monomer with a non-aqueous carrier;
 - ii) polymerising the first monomer component in the non-aqueous carrier to form a solution polymerised acrylic material;
 - iii) mixing a second monomer component comprising an acrylic monomer with the solution polymerised acrylic material and non-aqueous carrier; polymerising said second monomer component, in the presence of the solution polymerised acrylic material and non-aqueous carrier, to form a further solution polymerised acrylic

material, which further solution polymerised material is not covalently linked to the solution polymerised acrylic material;

wherein at least one of the solution polymerised acrylic material and the further solution polymerised acrylic material comprises acid functionality;

- iv) at least partially neutralising the acid functionality of the solution polymerised acrylic material and/or the further solution polymerised acrylic material with a neutraliser; and
- v) dispersing the solution polymerised acrylic material and the further solution polymerised acrylic material in water.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/015111

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C08F2/04	C08F212/08
	C08L33/12	C09D125/06
	C08F220/14	C09D133/06
	C08F220/18	C09D133/08
	C08F220/32	C09D133/12
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
B65D C09D C08F C08G C09J C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2020/084409 A1 (PPG IND OHIO INC [US]) 30 April 2020 (2020-04-30) paragraph [0082]; tables 6-7 -----	1, 2, 4, 29, 56-59
X	US 2020/190352 A1 (YOULTON ANTHONY C [US]) ET AL) 18 June 2020 (2020-06-18) examples 1-2, 4-5 -----	1-8
X	US 2012/302690 A1 (CUNNINGHAM SARAH [US]) ET AL) 29 November 2012 (2012-11-29)	6, 9-18, 24-28, 54, 55
Y	example 2B ----- -/-	19-23, 41, 42, 44-46, 48
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
13 April 2022		25/04/2022
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Jegou, Gwénaëlle

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2022/015111

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 833 869 A1 (AKZO NOBEL COATINGS INT BV [NL]) 19 September 2007 (2007-09-19)	6, 18, 29
Y	polyacrylate polyol 1; paragraphs [0023], [0071] - [0075] -----	19-23
X	JP 2015 196812 A (TOYO INK SC HOLDINGS CO LTD) 9 November 2015 (2015-11-09)	1, 2, 4, 30-40, 43, 47, 49-54
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