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54 **Removable, biodegradable coating**

57 The present invention relates to a functional coating obtained from an aqueous coating composition, which composition comprises a pigment and a polymeric binder, wherein the binder has a weight average molecular weight of from 2000 to 50000 g/mole, and an acid value of 40 to 250, and wherein the binder is a polyester comprising a side group introduced by a Diels-Alder and/or pericyclic Ene-reaction, wherein the side group contains an ionic group and/or an ion-forming group.

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Title: Removable, biodegradable coating

The present invention relates to an aqueous coating composition  
5 suitable for providing a functional coating which is removable with a  
removing agent comprising a strong base.

In horticulture, many plants are grown in greenhouses. Thus, they  
can benefit from optimized conditions, such as temperature, amount of light,  
humidity and the like. However, a problem with greenhouses is that the  
10 plants being grown in them are exposed, under warm, sunny weather  
conditions, to a large amount of radiation, which might disturb the living  
conditions and growth of the plants, and might even cause them to burn. To  
obviate this problem, it is customary in horticulture to protect the plants  
during the spring and the summer against the adverse effect of undue  
15 radiation by providing the transparent surfaces of the greenhouse with a  
functional coating.

One of the chief requirements to be met by such a functional  
coating is that sufficient protection from light and/or heat is achieved. To  
meet this requirement, the functional coating should contain a pigment,  
20 such as chalk or titanium oxide. The functional coating may also be used to  
scatter light, which can also be achieved using pigments. A further  
important requirement is that the functional agent from which the  
functional coating is formed exhibits sufficient adhesion to the surface of a  
greenhouse. When its adhesive strength is too low, the coating will not be  
25 sufficiently resistant to weather influences and it will be necessary to  
restore the coating several times per season or to replace it. When adhesion  
is too strong, it requires too much effort to remove the coating at the end of  
the season.

EP 0 999 736 describes aqueous coating compositions which are  
30 able to provide coatings on the transparent surfaces of greenhouses to  
protect plants during spring and summer against the adverse effect of

undue radiation which may disturb the living conditions and growth of the plants and might even cause them to burn. The protective coating comprises a polymeric binder which has a weight-average molecular weight of 10,000 – 100,000 g/mole and an acid value of 40-250 mg KOH/g. Such a binder  
5 provides for sufficient adhesion of the coating to a surface, while the coating can be easily removed at any desired time. The protective coating is removable from the surface of the greenhouse by treating the coating with a removing agent comprising a strong base and a complex former. The removing agent renders the binder in the protective coating water-soluble or  
10 water-dispersible.

A disadvantage of EP 0 999 736 is that the binder used in the protective coating is not biodegradable. As those coatings are removed by applying an alkaline solution onto the coating and subsequently rinsing with water (*e.g.* with rain), all coating components, although not necessarily  
15 harmful, accumulate into the waste water. Accordingly, there is a need for functional coatings with a biodegradable binder, which binder is capable of degrading within the waste water to non-toxic components, and preferably still satisfies the requirements described in EP 0 999 736.

Although biodegradable polymers are known in the art, not every  
20 biodegradable polymer can be suitably used as the polymeric binder in functional coatings for horticulture. In addition to being biodegradable, the binder should have a good stability. Further, the binder should be capable of forming a coating composition with good stability that is easy to apply and (after drying) has a good adhesive strength and a good removability.

25 An object of the invention is to solve at least one of the above-mentioned problems.

In particular, it is an object of the present invention to provide a stable aqueous coating composition suitable for providing a functional coating which is removable with a removing agent comprising a strong base

(in particular sodium and/or potassium hydroxide) and which composition contains a polymeric binder having an increased biodegradability.

As used herein, a stable aqueous coating composition does not phase separate when being stored at 21 °C and atmospheric pressure  
5 without agitating for at least 4 weeks, preferably 6 weeks and more preferably 10 weeks. Preferably, the aqueous coating composition of the present invention does not phase separate when being stored at 40 °C and atmospheric pressure without agitating for at least 4 weeks, preferably 6 weeks and more preferably 10 weeks. Phase separation in aqueous coating  
10 compositions may occur mainly as a result of excessive hydrolysis of the polymeric binder.

The object of the invention has surprisingly been achieved by providing an aqueous coating composition comprising a pigment and a polymeric binder, wherein the binder has a weight average molecular  
15 weight of from 2000 to 50000 g/mole, and an acid value of from 40 to 250 mg KOH/g polymeric binder, and wherein the binder is a polyester comprising a side group introduced by a Diels-Alder and/or pericyclic Ene-reaction, wherein the side group contains an ionic group.

The inventors found that the coating composition according to the  
20 invention can be suitably used as a functional coating on greenhouses. The polymeric binder used in the coating composition is biodegradable, is stable in water and provides for a stable coating composition (*e.g.* a stability of at least 6 weeks when being stored at 40 °C and atmospheric pressure without agitating). Furthermore, the coating composition can be easily applied to a  
25 surface of a greenhouse, forms a wear and weather resistance coating after drying and is easily removable from the surface when treating the coating with a removing agent comprising water, a strong base and preferably a complex former.

WO-A-2013123314 describes an aqueous coating composition for  
30 use in forming a food-contact coating, which composition contains a water

dispersible binder polymer obtained by effecting a Diels-Alder reaction and/or pericyclic Ene-reaction between an unsaturated polyester and an unsaturated compound(s) containing ionic groups or ion-forming groups. This publication however does not disclose or teach to use the binder  
5 polymer in an aqueous coating composition suitable for providing a functional coating which is removable with a removing agent comprising a strong base. Further, this publication is silent about the biodegradability of the polymeric binder.

10           The binder present in the coating composition according to the invention may be obtained by at least the following steps :

- (a)           preparing an unsaturated polyester,
- (b)           effecting a Diels-Alder reaction and/or pericyclic Ene-  
15 reaction between the unsaturated polyester and an unsaturated compound containing an ionic group and/or an ion-forming group to obtain a polymer with side groups containing an ionic group and/or an ion-forming group, and
- (c)           optionally converting at least part of the ion-forming  
20 groups present in the polymer to ionic groups. Step (c) must be effected in case the polymer obtained in step (b) contains no ionic groups. Step (c) is preferably effected in case the polymer obtained in step (b) contains both ionic groups and ion-forming groups.

In particular, the binder may be obtained by at least the following steps :

- (a)           preparing an unsaturated polyester,
- 25           (b)           effecting a Diels-Alder reaction and/or pericyclic Ene-  
reaction between the unsaturated polyester and an unsaturated compound containing an ion-forming group to obtain a polymer with side groups containing an ion-forming group, and
- (c)           converting at least part of the ion-forming groups present  
30 in the polymer to ionic groups.

Steps (a) to (c) are described in more detail below.

In step (a), an unsaturated polyester is prepared. The unsaturated polyester may be prepared by methods known in the prior art. For example, the unsaturated polyester may be prepared by polycondensation,  
5 transesterification or reaction between an epoxide and an anhydride.

The unsaturated polyester is typically prepared from at least one unsaturated monomer and at least one, preferably at least two saturated monomers. The unsaturated monomer may for example be an unsaturated dicarboxylic acid, diol, anhydride or epoxide. The saturated monomer may  
10 be a saturated dicarboxylic acid, diol, anhydride or epoxide.

As the unsaturated monomer, an unsaturated dicarboxylic acid or anhydride can be used. The unsaturated dicarboxylic acid (anhydride) is preferably selected from the group consisting of maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid,  
15 citraconic anhydride and any mixture thereof. More preferably, the unsaturated dicarboxylic acid (anhydride) is selected from the group consisting of maleic acid, maleic anhydride, fumaric acid and any mixture thereof.

An unsaturated diol or epoxide can also be used as the unsaturated  
20 monomer. The unsaturated diol may for example be selected from 2-butene-1,4-diol, cis-3-hexenol and allyl alcohol. The unsaturated epoxide may for example be selected from limonene oxide and vinylcyclohexeneoxide.

Preferably, at least one of the saturated monomers used to prepare the unsaturated polyester is a saturated diol. The diol is preferably selected  
25 from the group consisting of ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, hexanediol, cyclohexanedimethanol, trimethylolpropane, pentaerythritol, glycerol, butane diol, neopentylglycol, and any mixture thereof.

Preferably, at least one of the saturated monomers used to prepare  
30 the unsaturated polyester is a dicarboxylic acid or anhydride. The saturated

dicarboxylic acid or anhydride thereof is preferably selected from the group consisting of adipic acid, isophthalic acid, tetrahydrophthalic acid, terephthalic acid, hexahydrophthalic acid, decanedicarboxylic acid, dimer fatty acid, succinic acid, and anhydrides thereof, and any mixture thereof.

5           Optionally an aromatic dicarboxylic acid may be used as a saturated monomer, for example as a second saturated monomer in addition to the saturated monomers mentioned above.

          Preferably, at least two different saturated monomers are used, *i.e.* a first saturated monomer and a second saturated monomer different from  
10   the first. The first saturated monomer is typically a saturated diol or epoxide (*e.g.* the saturated diol or epoxide specified above), while the second saturated monomer is typically a saturated dicarboxylic acid or anhydride (*e.g.* the saturated dicarboxylic acid or anhydride specified above).

          Optionally monocarboxylic acids may be used as a saturated  
15   monomer, which may function as a chain stopper in the polymerization reaction. Non-limited example of monocarboxylic acid is benzoic acid, para-*t*-butyl benzoic acid, stearic acid and fatty acid.

          The molar ratio between the amount of unsaturated monomers and the amount saturated monomers used to prepare the unsaturated polyester  
20   is in the range of 1:1 to 1:100, preferably in the range of 1:2 to 1:10, more preferably in the range of 1:3 to 1:6. Such a ratio results in a polymer with an acceptable amount of side groups. In order to satisfy the preferred ratio, at least two saturated monomers are typically used in order to limit the  
25   total amount of ionic and ion forming side groups that are produced by the Diels-Alder reaction and/or pericyclic Ene-reaction.

          The polymerization reaction to prepare the unsaturated polyester is preferably conducted at a temperature of 180 to 220 °C. Water present in the reaction mixture, such as reaction formed during the reaction, is preferably removed from the reaction mixture, *e.g.* by evaporation, typically  
30   by distillation. The reaction may be conducted in the presence of a

polymerization catalyst. The polymerization may be conducted in a single or in multiple steps. The polymerization reaction may be conducted for at least one hour, preferably until a sufficiently low acid value is obtained, *e.g.* below 5 mg KOH/g.

5           The unsaturated polyester may for example be prepared from at least one unsaturated dicarboxylic acid or anhydride thereof, at least one saturated dicarboxylic acid, and at least one diol, preferably in the presence of esterification catalyst(s) and a free radical polymerisation inhibitor(s) at a temperature of from 180 to 220 °C.

10           The reaction of step (a) results in an unsaturated polyester. The unsaturated polyester is preferably a linear or substantially linear unsaturated polyester. Substantially linear unsaturated polyesters means unsaturated polyesters in which substantially (*i.e.* at least 95 wt.%, preferably at least 98 wt.%, more preferably at least 99 wt.% and even more preferably at least 99.5 wt.%) of the monomers used to form the unsaturated  
15           polyester are mono-functional or di-functional monomers. Accordingly, substantially linear unsaturated polyesters include less than 5 wt.%, preferably less than 2 wt.%, more preferably less than 1 wt.% and even more preferably less than 0.5 wt.% of tri-functional or higher functional  
20           monomers (relative to the total amount of monomers used to form the unsaturated polyester). Since no further polymerization steps are conducted after step (a), the above features on linearity of the unsaturated polyester may also apply to the final (typically saturated) polyester obtained in steps (b) and (c). In this respect, the addition of the side groups may be considered  
25           as not adding additional branching, but rather as modification of the side groups of the monomers already present in the polymer backbone.

The unsaturated polyester preferably contains one or more double carbon-carbon bounds introduced in the backbone of the unsaturated polyester by the unsaturated diol, the unsaturated dicarboxylic acid, the

unsaturated anhydride, the unsaturated epoxide or a mixture thereof, as *e.g.* described above for step (a).

In step (b), the unsaturated polyester obtained in step (a) is reacted with at least one unsaturated compound containing an ionic or ion-forming group. This reaction is a Diels-Alder reaction and/or pericyclic Ene-reaction. The reaction results in a polymer (*viz.* a polyester) comprising a side group introduced by the Diels-Alder and/or pericyclic Ene-reaction,

The unsaturated compound with an ionic group and/or an ion-forming group contains one or more double bonds. The unsaturated compound with an ionic group and/or ion-forming group preferably contains one or more carbon-carbon double bonds, more preferably one or more conjugated carbon-carbon double bonds and even more preferably one conjugated carbon-carbon double bond.

The unsaturated compound containing an ionic group and/or ion-forming group preferably comprises a conjugated diene with a carboxylic acid ionic group and/or a carboxylate forming group. More preferably, the unsaturated compound is a conjugated diene with carboxylic acid ionic groups and/or carboxylate forming groups.

Non-limiting examples of unsaturated compounds with an ionic group or an ion-forming group include sorbic acid, muconic acid, 2,4-pentadienoic acid, furoic acid, vinyl acetic acid, (meth)acrylic acid, the carboxylates of any of these acids, 1-amino-1,3-butadiene and the protonated amine of 1-amino-1,3-butadiene. The unsaturated compound with ionic groups and/or ion-forming groups preferably comprises sorbic acid and/or the carboxylate of sorbic acid (sorbate). More preferably, the unsaturated compound is selected from the group consisting of sorbic acid, sorbate and any mixture thereof.

The reaction of step (b) may be conducted at a temperature in the range of 120 to 190 °C, preferably 140 to 170 °C. The molar ratio between the amount of unsaturated compound and amount of unsaturated monomer

used to prepare the unsaturated polyester is in the range of 1:2 to 2:1, preferably in the range of about 1:1. The reaction may be conducted in the presence of a catalyst. The reaction may be conducted for at least one hour.

In step (c), at least part of the ion-forming groups of the side chain  
5 of the polymer obtained in step (b) are converted to ionic groups. This may be done by reacting the polymer with a neutralizing agent. The neutralizing agent is typically a volatile base, preferably a volatile amine, such as ammonia. After the reaction of step (c), the neutralizing agent will be converted to its ionic, typically cationic form. The cationic form of the  
10 neutralizing agent may be a protonated version of the neutralizing agent, *e.g.*  $\text{NH}_4^+$  in case ammonia was used as the neutralizing agent. The ionic form of the neutralizing agent may act as a counter ion to the ionic groups of the polymeric binder.

The ion-forming groups may be converted to an ionic group selected  
15 from the group consisting of carboxylate ( $-\text{COO}^-$ ), sulphate ( $-\text{OSO}_3^-$ ), phosphate ( $-\text{OPO}_3^-$ ), sulphonate ( $-\text{SO}_2\text{O}^-$ ), phosphinate ( $-\text{POO}^-$ ), phosphonate ( $-\text{PO}_2\text{O}^-$ ). This is typically done by reaction with a base, which deprotonates the ion-forming group. The ion-forming group typically corresponds to the protonated version of the ionic group. For example, a carboxylic acid group  
20 may be converted to a carboxylate.

Preferred neutralizing agents to be used in step (c) include amines, in particular volatile inorganic and organic amines selected from the group consisting of tertiary amines, ammonia, and mixtures thereof. Non-limiting examples of suitable tertiary amines include trimethyl amine,  
25 dimethylethanol amine (also known as dimethylamino ethanol), methylethanol amine, triethanol amine, ethyl methyl ethanol amine, dimethyl ethyl amine, dimethyl propyl amine, dimethyl 3-hydroxy-1-propyl amine, dimethylbenzyl amine, dimethyl 2-hydroxy-1-propyl amine, diethyl methyl amine, dimethyl 1-hydroxy-2-propyl amine, triethyl amine, tributyl

amine, N-methyl morpholine, and mixtures thereof. Ammonia is the most preferred neutralizing agent.

The reaction of step (c) is conducted by adding the reaction product obtained in step (b) to an aqueous solution comprising the neutralizing agent. The aqueous solution preferably has a temperature of 20-100 °C, more preferably 70-80 °C. The product of step (b) may have a temperature of 120-190 °C, typically 150-160 °C. The amount of neutralizing agent used should be sufficient such that the polymeric binder will be soluble or dispersible in water. Accordingly, the amount of neutralizing agent will depend on the acid value of the polymeric binder, with the amount being larger for a polymeric binder with a lower acid value. The molar ratio between the amount of acid groups and the amount of neutralizing agent is in the range of 1000:1 to 10:13, preferably in the range of about 10:8 to 10:11. After neutralization, the reaction mixture may be cooled and additional aqueous solution of the neutralizing agent may be added to obtain a desirable pH and additional water may be added to obtain a desirable viscosity.

The polymeric binder used in the coating composition of the invention, *e.g.* as obtained in steps (a)-(c) described above, has the following properties.

The polymeric binder is a polyester comprising a side group introduced by a Diels-Alder and/or pericyclic Ene reaction, wherein the side group contains an ionic group.

The polymeric binder may comprise two or more different monomer residues. These correspond to the unsaturated and the saturated monomers that are typically used in the polymerization reaction to obtain the unsaturated polyester, as described above for step a). The preferred monomer residues of the polymeric binder can be derived from the reaction compounds used for reaction steps (a), (b) and (c), which compounds are described in detail above. The percentage of the number of monomeric

residues in the polymeric binder that comprises a side group with an anionic group may be 5-50%, preferably 10-30%, based on the total number of monomeric residues in the polymeric binder.

The ionic groups of the polymeric binder are typically anionic groups, *e.g.* carboxylate groups. Preferably, the anionic groups are selected from the group consisting of carboxylate groups ( $-\text{COO}^-$ ), sulphate groups ( $-\text{OSO}_3^-$ ), phosphate groups ( $-\text{OPO}_3^-$ ), sulphonate groups ( $-\text{SO}_2\text{O}^-$ ), phosphinate groups ( $-\text{POO}^-$ ), phosphonate groups ( $-\text{PO}_2\text{O}^-$ ) and any combination thereof. The polymeric binder preferably comprises carboxylate ( $-\text{COO}^-$ ) groups. The polymeric binder may also comprise a cationic group, *e.g.* a protonated amine group.

Due the presence of the ionic groups in the side group, the polymeric binder will typically have a net charge. The polymeric binder can be considered a polysalt or a polyelectrolyte, *i.e.* a polymer with at least one monomeric residue that bears a charged group. In addition to the charged groups, the polymeric binder may further comprise counter ions. These counter ions balance the charge provided by the ionic groups of the polymeric binder. The counter ion is preferably a protonated volatile amine, more preferably ammonium. Examples of suitable volatile amines are described above with respect to the neutralizing agent.

The polymeric binder present in the coating composition of the invention comprises ionic groups in such an amount that the polymeric binder is water-dispersible or water-soluble at 40 °C and atmospheric pressure. Preferably, the polymeric binder present in the coating composition of the invention comprises ionic groups in such an amount that the polymeric binder is water-dispersible or water-soluble at 21 °C and atmospheric pressure. The polymeric binder typically comprises side groups containing ionic groups in an amount of at least 1 wt.%, preferably at least 3 wt.%, more preferably at least 5 wt.%, based on the weight of the polymeric binder. The polymeric binder typically comprises side groups containing

ionic groups in an amount of at most 50 wt.%, typically less than 25 wt.%, based on the total weight of the polymeric binder.

The polymeric binder has a weight average molecular weight of from 2000 to 50000 g/mole. The weight-average molecular weight of the binder may influence the biodegradability and stability of the binder. Taking these parameters into account, the following preferred ranges can be defined for the weight-average molecular weight of the binder. Preferably, the polymeric binder has a weight average molecular weight of at least 3000 g/mole, more preferably at least 4000 g/mole and most preferably at least 5000 g/mole. Preferably, the polymeric binder has a weight average molecular weight of at most 40000 g/mole, more preferably at most 30000 g/mole and most preferably at most 20000 g/mole. Most preferably, the polymeric binder has a weight average molecular weight of from 5000 to 20000 g/mole. Furthermore, a low weight-average molecular weight is normally indicative of short polymer chains, which may entail a poorer binding effect in the coating to be used. Moreover, the degradation of the binder under the influence of (UV) radiation has more effect when short chains are broken than when long chains are broken. Too high a weight-average molecular weight also entails disadvantages. Often, the viscosity of the coating composition will be too high when the chains of the binder are too long. The agent is then difficult to apply to a surface. As used herein, the weight average molecular weight may be determined as described in the experimental part of the description.

The polymeric binder preferably has a number average molecular weight of from 1000 to 10000 g/mole. Preferably, the polymeric binder has a number average molecular weight of at least 2000 g/mole. Preferably, the polymeric binder has a number average molecular weight of at most 8000 g/mole, more preferably at most 6000 g/mole and most preferably at most 5000 g/mole. Most preferably, the polymeric binder has a number average molecular weight of from 2000 to 5000 g/mole. As used herein, the number

average molecular weight may be determined as described in the experimental part of the description.

The polymeric binder preferably has a polydispersity of a value of 1 to 20, preferably of 2 to 15. The term 'polydispersity' used herein means the ratio between the weight-average and the number-average molecular weight ( $M_w/M_n$ ).

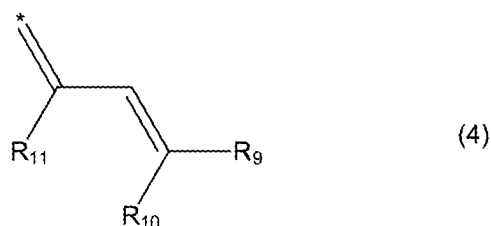
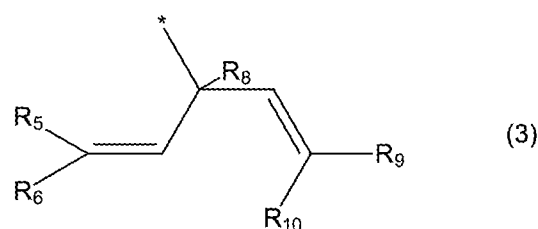
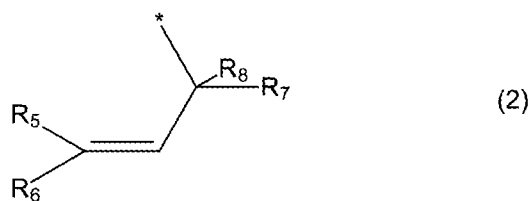
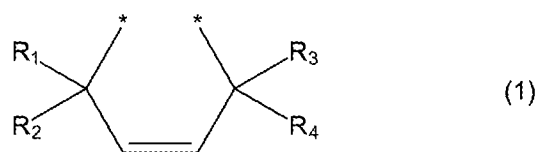
The polymeric binder has an acid value of from 40 to 250 mg KOH/g polymeric binder. Preferably, the polymeric binder has an acid value from 40 to 160 mg KOH/g polymeric binder. More preferably, the polymeric binder has an acid value from 60 to 130 mg. Such acid values are advantageous with respect to the removability of the coating from the surface. As used herein, the acid value is determined as described in the experimental part of the description.

The polymeric binder preferably has a glass transition temperature from 10 to 80 °C. More preferably, the glass transition temperature of the polymeric binder is from 20 to 70 °C. A coating with a binder with such glass transition temperature may exhibit good adhesion to the surface of a greenhouse. A polymeric binder having such glass transition temperature also yields a coating composition that has good handling properties and is easy to apply to form the functional coating. As used herein, the glass transition temperature is determined as described in the experimental part of the description.

The polymeric binder comprises one or more side groups. The side group may for example be attached to a carbon atom of a monomeric residue selected from a dicarboxylic acid residue, a diol residue, an anhydride residue and an epoxide residue. The side group may be attached to a carbon atom of the backbone of the polyester.

The side group of the polymeric binder may be represented by any one of structures (1) – (4):

30



or any isomer thereof, wherein  $R_1$  to  $R_{11}$  are defined as follows:

- $R_1$  is selected from the group of anionic groups, which group consists of  
 5 carboxylate ( $-\text{COO}^-$ ), sulphate ( $-\text{OSO}_3^-$ ), phosphate ( $-\text{OPO}_3^-$ ), sulphonate ( $-\text{SO}_2\text{O}^-$ ), phosphinate ( $-\text{POO}^-$ ), phosphonate ( $-\text{PO}_2\text{O}^-$ ) and substituted alkyl, alkenyl, aryl and alkylaryl groups of the formula  $-\text{R}_{12}-\text{A}^-$ ,

wherein  $R_{12}$  is linear or branched alkyl, alkenyl, aryl or alkylaryl moiety, which moiety preferably has 1-12 carbon atoms, even more  
 10 preferably 1-6 carbon atoms, *e.g.* a  $-\text{C}_x\text{H}_{2x}-$  group with  $x$  is 1, 2, 3 or 4. Thus, the  $-\text{R}_{12}-\text{A}^-$  is effectively a linear or branched alkyl, alkenyl, aryl or alkylaryl group to which the ionic ( $\text{A}^-$ ) group is substituted.

The asterisk (\*) in formulas (1)-(4) indicate the position at which the side group is attached to the polyester. The side group is typically attached to a carbon atom of the polyester, *e.g.* a carbon atom of the backbone of the polyester, via a covalent bond. In case of structure (1), the side group is attached to the polyester at two different positions, typically at two adjacent carbon atoms, *e.g.* two covalently bound carbon atoms that may be part of the backbone of the polyester.

wherein A<sup>-</sup> is an anionic group selected from carboxylate, sulphate, phosphate, sulphonate, phosphinate and phosphonate, preferably a carboxylate;

- R<sub>2</sub>-R<sub>11</sub> may each be individually chosen from either the group of anionic groups defined for R<sub>1</sub> or from the group consisting of hydrogen, alkyl, alkenyl, aryl and alkylaryl, preferably from the group of H, alkyl and alkenyl.

The -R<sub>12</sub>-A<sup>-</sup> may for example be a methyl, ethyl, propyl, butyl, ethenyl, 1-propenyl, 2-propenyl, 1-butenyl, 2-butenyl, phenyl or tolyl group substituted with an A<sup>-</sup> group, preferably with a -COO<sup>-</sup> group.

In case R<sub>2</sub>-R<sub>11</sub> is an alkyl group or alkenyl group, the group may be linear or branched. The group may have 1-12 carbon atoms, preferably 1-6 carbon atoms, for example methyl, ethyl, propyl, butyl, ethenyl, 1-propenyl, 2-propenyl, 1-butenyl or 2-butenyl. In case R<sub>2</sub>-R<sub>12</sub> is an aryl or alkylaryl group, it preferably is or comprises a phenyl ring, which may be substituted with an alkyl or alkylene group, *e.g.* methyl. The aryl or alkylaryl group may have 1-12 carbon atoms. Alternatively, though less preferred, the aryl or alkylaryl group is a naphthalene moiety or an anthracene moiety, optionally substituted with an alkyl or alkylene group, *e.g.* methyl.

For structure (1), R<sub>2</sub> and/or R<sub>4</sub> are preferably H. R<sub>1</sub> preferably is or comprises a carboxylate group (*i.e.* is -COO<sup>-</sup> or -R<sub>12</sub>COO<sup>-</sup>), for example a linear -C<sub>x</sub>H<sub>2x</sub>COO<sup>-</sup> group with *x* = 1-5. R<sub>3</sub> is as defined above for R<sub>2</sub>-R<sub>12</sub> in general and preferably is methyl, ethyl or propyl.

In one embodiment of structure (1), each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are part of a naphthalene or anthracene moiety substituted with an anionic group, preferably a carboxylate or -R<sub>12</sub>COO<sup>-</sup> group.

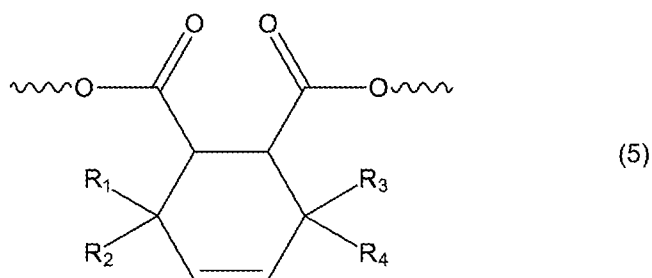
5 For structure (2), at least one of R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> must be an anionic group. R<sub>5</sub> and R<sub>8</sub> are preferably hydrogen, while R<sub>6</sub> and R<sub>7</sub> are both individually selected from the general group defined for R<sub>2</sub>-R<sub>11</sub> above.

For structure (3), at least one of R<sub>5</sub>, R<sub>6</sub>, R<sub>8</sub>, R<sub>9</sub> and R<sub>10</sub> must be an anionic group. R<sub>5</sub>, R<sub>8</sub> and R<sub>10</sub> are preferably hydrogen, while R<sub>6</sub> and R<sub>11</sub> are both individually selected from the general group defined for R<sub>2</sub>-R<sub>11</sub> above.

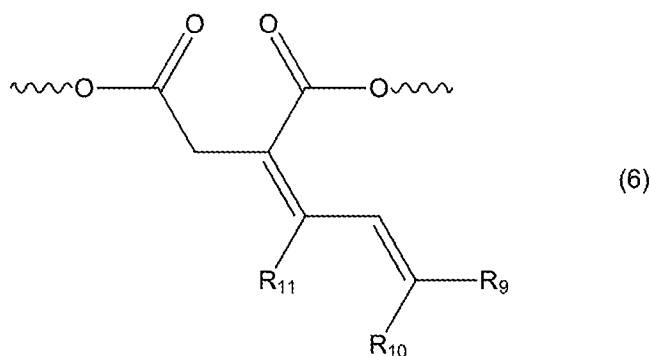
10 For structure (4), at least one of R<sub>9</sub>, R<sub>10</sub> and R<sub>11</sub> must be an anionic group. R<sub>10</sub> is preferably hydrogen, while R<sub>9</sub> and R<sub>11</sub> are both individually selected from the general group defined for R<sub>2</sub>-R<sub>11</sub> above.

The side group may also be an isomer of any of structures (1) – (4), in particular an isomer obtained as a result of repositioning of one or more  
15 of the double bonds in the structure. The side group of the polymeric binder, for example those depicted in structures (1) – (4), may comprise a conjugated system. Therefore, one or more isomers of the side group may exist.

In a preferred embodiment, the polymeric binder comprises a unit  
20 according to formula (5) or (6):



(5)



(6)

or any isomer thereof. Herein,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_9$ ,  $R_{10}$  and  $R_{11}$  are as defined above. The molecular structure depicted in formula (5) or (6) may result from introducing an unsaturated compound in an unsaturated polyester containing unsaturated dicarboxylic acid units based on fumaric acid, maleic acid or maleic anhydride. Such a configuration may be in particular stable due to the formation of a conjugate system comprising the ene groups and the ester group.

In a particular preferred embodiment, the polymeric binder comprises at least one of the structural units according to formula (5) and (6), and/or any isomer thereof, wherein  $R_1$  and  $R_9$  are  $\text{COO}\cdot\text{B}^+$ ,  $R_2$ ,  $R_4$  and  $R_{10}$  are H,  $R_3$  is ethyl and  $R_{11}$  is ethyl. Herein, the  $\text{COO}\cdot\text{B}^+$  group represents an ionic group obtained by neutralizing a  $\text{COOH}$  group with neutralizing agent B. Such units can for example be obtained when sorbic acid is used as unsaturated compound in step (b) and fumaric acid, maleic acid and/or maleic anhydride were used as monomers in step (a).

The coating composition according to the invention comprises the polymeric binder described above, a pigment and a number of optional ingredients. The components and composition are described in detail below.

The amount of the polymeric binder present in the coating composition of the present invention may be from 4 to 95, preferably from 5 to 60 wt.%, more preferably from 10 to 45, based on the dry weight of the coating composition. For example, the amount of polymeric binder may be from 15 to 90 wt.%.

The amount of pigment present in the coating composition of the present invention is preferably from 5 to 95 wt.%, more preferably from 10 to 85 wt.%, based on the dry weight of the coating composition. For example, the amount of pigment may be from 40 to 95 wt.%. The amount may depend on the type of pigment used. In case of calcium carbonate or titanium dioxide, In case the pigment is selected from the group of calcium carbonate, titanium dioxide and silicate, gypsum, baryte, and combinations thereof, the pigment is generally present in the coating composition in an amount of preferably 20-95 wt.%, more preferably 40-85 wt.%, based on the dry weight of the coating composition. In case the pigment is selected from the group consisting of mica, mica based pigments and boehmite, the amount of the pigment in the coating composition is preferably 5-75 wt.%, more preferably 10-50 wt.%, based on the dry weight of the coating composition.

The term "dry weight" of the coating composition, as used herein, refers to the total weight of the aqueous coating composition minus the weight of the water present in the aqueous coating composition.

The pigment may be selected from the group of calcium carbonate, titanium dioxide, boehmite (such as nano boehmite), mica (such as synthetic mica), mica based pigments, a silicate, such as magnesium or aluminum silicate, gypsum, baryte, and combinations thereof. As pigment, any substance can be used that can be suitably dispersed in the aqueous coating composition from which the coating according to the invention is

formed, and which imparts the coating with desired properties. For example, certain pigments can provide protective action against (solar) radiation. Such pigments preferably yield a white protective coating. Suitable pigments may be selected from the group of calcium carbonate, titanium dioxide, a silicate, such as magnesium or aluminum silicate, gypsum, baryte, and combinations thereof. Pigments are also known that can scatter light when present in the coating, resulting in diffuse light inside the greenhouse. This may be desirable for plants that need lots of light. An example of such a pigment is nano boehmite. Yet other pigments are known that can reflect certain types of light, such as mica (*e.g.* synthetic mica) and mica based pigments. Depending on the desired properties of the functional coating, the skilled person will be able to suitably select the pigment. Generally, a pigment is typically used that selectively absorbs, reflects, transmits and/or scatters certain types of light, in particular light of a particular wavelength.

The weight ratio of polymeric binder to pigment may be in the range of 20:1 to 1:15, preferably in the range of 15:1 to 1:5. Typically, the weight ratio of polymeric binder to pigment may be 2:1 or smaller, generally 1:1 or smaller. The specific ratio may depend on the type of pigment used. Titanium oxide has a very high covering power, so that only a relatively small quantity thereof is needed. As a consequence, the ratio between binder and pigment will be relatively larger for this pigment. When much binder with respect to the pigment can be used, the weather resistance of the coating will be better. The advantage of the use of calcium carbonate is that a coating based thereon becomes slightly transparent in damp weather, so that the light intensity within a greenhouse adjusts itself to the weather conditions. Further, calcium carbonate is an economically attractive natural product and upon removal gives little, if any, visual or other contamination of the environment.

To optimize the viscosity of the aqueous coating composition according to the invention, a thickener can be included. Suitable thickeners may be xanthan gum, acrylic thickeners, cellulose derived thickeners such as carboxymethylcellulose and hydroxyethylcellulose, and sodium starch glycolate. The optimum viscosity of the coating composition depends on the method by which the coating is applied to a surface. If a surface is brushed with the coating composition, a higher viscosity will be desirable than when a surface is sprayed with a coating composition. Further, the viscosity must be sufficient to obtain a thick coating. On the basis of his common professional knowledge, the skilled person will be able to determine which viscosity is most suitable in any given case. Examples of thickeners comprise organic and inorganic thickeners, such as hydroxyethyl cellulose, magnesium aluminum silicate and combinations thereof. A preferred thickener is xanthan gum. The amount of the thickener will be tuned to the desired viscosity and may be between 0.1 and 5 wt.%, preferably between 0.5 and 3 wt.%, based on the dry weight of the coating composition.

The coating composition may further comprise a weak base in addition to the neutralizing agent possibly present in the polymeric binder. A weak base can provide for neutralization of free acid groups present in one or more components of the coating composition. It has also been found that the presence of the weak base leads to improved film formation of the coating composition upon drying, when a functional coating is being formed. Preferably, the weak base is selected from the group of ammonia, mono-, di- and trialkylamines, with the alkyl group containing from 1 to 8 carbon atoms. Particularly preferred is ammonia ( $\text{NH}_3$ ), which can be suitably dissolved in the aqueous coating composition. The weak base is preferably present in an amount of 0.2-5 wt.%, more preferably of 0.4-3 wt.%, based on the dry weight of the coating composition.

Preferably, the coating composition further comprises an adhesion promoter. The adhesion of the coating to a surface will be improved by the

presence of an adhesion promoter, while the ease of removing the functional coating is hardly, if at all, affected. The presence of such a substance may also prevent aggregation of pigment upon drying of the aqueous coating composition. Depending on the material of the surface on which a functional coating is to be provided, the skilled person will be able to select a suitable adhesion promoter. Preferably, the adhesion promoter is water-soluble and contains an amino group. For use on glass surfaces, it is recommended to use a silane, such as  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -aminopropyltrimethoxy silane,  $\gamma$ -(methylamino)propyltrimethoxy silane,  $\gamma$ -aminopropylmethyldiethoxy silane,  $\gamma$ -(2-aminoethyl-3-aminopropyl)triethoxy silane and  $\gamma$ -(2-aminoethyl-3-aminopropyl)methyldimethoxy silane. An adhesion promoter will typically be present in the functional coating in an amount of 0.05 to 1% by weight, preferably from 0.1 to 0.3% by weight, based on the dry weight of the coating composition.

Another constituent that may advantageously be present in the coating composition is a pigment divider. The presence of such a substance prevents aggregation of pigment upon drying of the coating composition when forming the functional coating. A pigment divider can be present in amounts of from 0.1 to 0.5 wt.%, based on the dry weight of the coating composition. The nature of the pigment divider depends on the nature of the pigment present in the coating composition. Thus, sodium hexametaphosphate is highly suitable when calcium carbonate is used as pigment. When titanium dioxide is used as pigment, for instance a polymeric multifunctional surfactant, such as Ser-Ad FA 607<sup>®</sup> (available from the firm of Elementis) can be used excellently as a pigment divider.

The coating composition may further comprise a defoamer, which may be present in an amount of 0.1-2 wt.%, based on the dry weight of the coating composition.

The coating composition further comprises water. The coating

composition may comprise 25-95 wt.% water, preferably 40-80 wt.% water, typically about 45-70 wt.% water, based on the total weight of the coating composition. A composition with such an amount of water is in particular suitable for distribution. However, before such a coating composition can be suitably used to form a functional coating on a surface, the coating composition is typically diluted with water by a factor 1.5 – 15, preferably a factor 2 – 12. If the coating composition comprises calcium carbonate as pigment, the coating composition may be diluted with water 1.5-5 times. If titanium oxide is used as pigment, that dilution is a factor of 5-12 times.

10           The present invention further relates to the use of the coating composition as described herein to obtain a functional coating on an outside wall and/or roof of a greenhouse and which coating is removable with a removing agent comprising a strong base.

15           The present invention further relates to a method for forming a functional coating on a surface, *e.g.* on an outside wall and/or roof of a greenhouse, wherein the method comprises (1) applying the coating composition as described herein to the surface and (2) drying the coating composition.

20           The coating composition according to the invention can be suitably applied to surfaces of different materials. Preferably, the surface is a substantially transparent surface, such as an outside surface of a greenhouse, for instance a horticultural greenhouse. Typically, the surface will be made of glass or plastic. Conventionally used plastics are, for instance, polycarbonates, polyolefins, polyethylene terephthalate and  
25           polyesters.

          The application of the coating composition can occur in different ways. Possible ways include spraying, brushing and the like. The functional action of the coating will be hardly, if at all, affected by the manner of application.

The inventors found that the coating composition can be easily applied, forming a smooth layer and drying quickly.

After drying of the coating composition, a functional coating will have been formed. The binder in the coating is no longer soluble in water after drying. Typically, the neutralizing agent will evaporate during drying. As a result, the ionic groups of the binder will be converted to their neutral states and the polymeric binder will no longer be a salt, such that it is no longer soluble in water.

Accordingly, the invention further relates to a functional coating. The functional coating has good resistance to wear under different weather types. When applied to a greenhouse or other surface, the functional coating can perform its function for several weeks or even months.

The term “functional coating” as used herein refers to a coating that comprises a pigment that selectively absorbs, reflects, transmits and/or scatters certain types of light, in particular light of a certain wavelength. The function of the coating is mainly determined by the type of pigment used. The functional coating may be a protective coating, which provides protection against light and/or heat. For example, the coating may be used to reflect infrared light. The functional coating may also be used to scatter light and/or to make the light that passes through the coating diffuse. Such a coating may be referred to as an light enhancing coating. Examples of pigments that provide the protective or light enhancing function are mentioned above for the coating composition.

It will be clear that the functional coating according to the invention will have a similar composition as the coating composition, except that water will no longer be present. Water will have been evaporated during the drying step.

When in the course of time, for instance at the end of the season, the functional coating is to be removed, the coating according to the invention is treated with a removing agent, comprising a strong base and

preferably a complex former, which renders the binder in the functional coating water-soluble.

Accordingly, the present invention further relates to a method for removing a functional coating as described herein from a surface, *e.g.* from an outside wall and/or roof of a greenhouse, wherein the method comprises  
5 treating the functional coating with a removing agent comprising water, a strong base and preferably a complex former.

The strong base is preferably present in an amount of from 1 to 10 wt.%, preferably 2 to 5 wt.%, based on the weight of the removing agent.  
10 Suitable strong bases are, for instance, alkali metal hydroxides such as sodium hydroxide, potassium hydroxide and lithium hydroxide. Preferably, sodium hydroxide or potassium hydroxide is used.

Preferably, a complex former is present in the removing agent. A complex former improves the ability of the removing agent to remove the  
15 functional coating. The complex former is preferably present in an amount of from 2 to 10 wt.%, based on the weight of the removing agent. For example, tetrasodium N,N-bis(carboxylatomethyl)-L-glutamate or the trisodium salt of alanine, N,N-bis(carboxylmethyl) can be used as a complex former. These substances are properly and rapidly biodegradable.

Especially when a functional coating provided on a plastic is to be removed, it is found to be of great advantage to use a removing agent that further comprises an organic solvent. It is also possible to use an organic solvent separately, in addition to the removing agent. The latter option is advantageous in that the organic solvent used does not necessarily need to  
20 be alkali-resistant. A great many solvents are eligible for use as a separate component. Examples include benzyl alcohol, tetrahydrofuran, 1,4-dioxane, dimethyl sulfoxide, higher alcohols, such as butanol, pentanol, hexanol, cyclohexanol and isomers thereof, and cyclohexanone. The organic solvent effects a still easier removal of the functional coating.

It is preferred to use the organic solvent in the removing agent. This is beneficial in particular to the simplicity of the procedure of removing the functional coating. In that case, an alkali resistant organic solvent should be used. The amount of organic solvent is preferably 10-30% by weight, more preferably 15-25% by weight, based on the weight of the removing agent. Particularly preferred is the use of benzyl alcohol. Benzyl alcohol is little volatile, little toxic to man and animals and hardly combustible, so that the health of those working with the removing agent is not put at risk. When benzyl alcohol ends up in the environment after the removal of the functional coating, this does not yield unacceptable contamination.

In addition to the constituents mentioned, the removing agent may further contain a thickener, such as xanthan gum. Xanthan gum renders the removing agent highly pseudoplastic, so that it is thin when being applied and thick after being applied. This property prevents the agent from flowing off the surface too fast. Further, the removing agent may contain a substance reducing the surface tension, or an emulsifier. For instance, the sodium salt of dodecylbenzenesulfonic acid is suitable.

An example of a suitable removing agent is ReduClean (available from Mardenkro, the Netherlands)

To remove the functional coating, the coating is treated with the above-described removing agent. This treatment comprises applying the removing agent onto the coating to be removed, for example by spraying or pouring. Typically, the removing agent is used in a 5 to 10-fold dilution. After application of the removing agent, the surface can be rinsed with water. It is also possible to allow the rain to wash things off. Thereafter, virtually all traces of the functional coating will be gone.

The present invention is now illustrated by reference to the following examples. Unless otherwise specified, all parts, percentages and ratios are on a weight basis.

5            EXAMPLES

Test methods

Stability of aqueous solutions

10            Samples were put in 30 ml jars and sealed air-tight. All samples were clear, indicating good solubility in water. They were placed in an oven at 40°C. Biweekly the samples were checked for clarity. When the samples became hazy this indicated that the solubility in water is limited. From that moment, the sample is called unstable.

15

Biodegradability

              Biodegradability is measured according OECD 301 F: Manometric Respirometry. Instrument used was Aqualytic BOD-System AL606. Reference material is sodium acetate, which is assumed to be 100%  
20 biodegradable.

Weight average molecular weight  $M_w$  and number average  
molecular weight  $M_n$

              The weight average molecular weight can be measured using size  
25 exclusion chromatography (SEC). The SEC analyses in these experiments were performed on an Advance Polymer Chromatography system (Waters APC), including a pump, auto injector, degasser, and column oven. The eluent was tetrahydrofuran (THF) to which 0.8 vol% acetic acid was added, based on the total volume of THF. The injection volume was 10  $\mu$ l. The flow  
30 was established at 1.0 ml/min. Three Acquity APC columns of 15 cm with

different pore sizes: 450 Å, 125 Å and 45 Å were applied in series at a temperature of 40°C. The detection was performed with a differential refractive index detector (Waters Acquity Refractive Index detector). The sample solutions were prepared with a concentration of 50 mg solids in 5 ml eluent (THF + 0.8 vol% acetic acid, based on the total volume of THF), and the samples were dissolved for a period of 24 hours. Calibration is performed with 21 polystyrene standards (Agilent EasiCal), ranging from 162 to 3,000,000 g/mole. The calculation was performed with Empower 3 software (Waters) with a fourth order calibration curve. The obtained molar masses are polystyrene equivalent molar masses (g/mole).

#### Acid value

The acid value may be calculated using a method based on ISO 2114. Sample (approximately 1,5 g, weighed to nearest 0.01g) is dissolved in tetrahydrofuran (50 ml) and water (2 ml). The solution is titrated with 0.1 N potassium hydroxide in ethanol using o-cresolphthalein as indicator. Pink colour should persist for 10 seconds. Acid value (AV) is calculated by:

$$AV = (\text{ml KOH solution} * 0.1 * 56.11) / \text{sample weight in grams.}$$

The acid value is expressed by mg KOH/g polymeric binder.

20

#### Glass transition temperature $T_g$

The  $T_g$  was measured by DSC using the Mettler Toledo 821 using ME-26763 alumina cups of 40 µl. The flow rate was 50 ml/min of nitrogen and the sample was loaded at a temperature range of 20-25°C. The sample was first heated to 150°C using a rate of 20°C/min. At 150°C the sample was cooled to 0°C at a rate of -10°C/min. At 0°C the sample was heated to 80°C at a rate of 5°C/min. The reported  $T_g$  is the measured inflection point.

### Solids content

Solids content is measured on a Mettler Toledo HR73 Halogen Moisture Analyser. Sample (0.9 – 1.1 grams) is spread out in a spiral shape on the fluffy side of a  $\Phi$  90 mm Macherey-Nagel MN85/90 filter paper held in a  $\Phi$  100 mm Schuett-biotec aluminium weighing / IR sample dish. Drying temperature is 160°C and automatic switch-off criterion set to 4 (medium – slow drying). The instrument shows the solids content in weight %.

### Example 1: Preparation of polymeric binders 1-7

In this example, polymeric binders 1-7 were prepared as described below.

#### Polymeric binder 1 – polymerization (step a)

Neopentylglycol (39.7 g), adipic acid (13.8 g), isophthalic acid (3.2 g), fumaric acid (22.4 g), benzoic acid (13.3 g), butyl stannic acid (400 ppm) and hydroquinone monomethylether (300 ppm) were heated in a reactor with a flow of nitrogen gas to a temperature of 210°C. Water was removed using a vigreux column maintaining a maximum top temperature of 100°C. Once the top temperature of the column dropped below 80°C the column was removed and the product was kept at atmospheric pressure for 1 hour. Using vacuum distillation, the reaction was continued until an acid number of <5 mg KOH/g was obtained. Then the mixture was cooled to 150°C.

#### Polymeric binder 1 – introducing side group (step b)

At 150°C sorbic acid (21.6 g) was added under stirring and reacted for 2 hours, keeping the temperature at 150°C - 160°C, to yield a solid polymer after cooling.

Polymeric binders 2-7 – polymerization and introducing side group

Polymeric binders 2-7 were prepared in the same manner as polymeric binder 1, but with different compositions which are shown in Table 1. The test results are also reported in Table 1.

5

Table 1:

	1	2	3	4	5	6	7
Neopentyl-glycol (g)	39.7	40.8	41.2	41.5	43.3	43.9	42.5
Adipic acid (g)	13.8	13.8	13.8	13.8	13.8	21.9	
Isophthalic acid (g)	3.2	9.7	12.4	14.2	26.8	12.9	35.6
Fumaric acid (g)	22.3	22.3	22.3	22.3	14.5	18.5	18.5
Benzoic acid (g)	13.3	6.1	3.0	1.0	2.8	--	--
Butyl stannic acid (ppm)	400	400	400	400	400	400	400
Hydro-quinone monomethyl ether (ppm)	300	300	300	300	300	300	300
Sorbic acid (g)	21.6	21.6	21.6	21.6	14.0	17.7	17.9
Measured Mn	1383	2166	2711	3794	3109	3650	4151
Measured Mw	3372	7327	10480	36028	10905	28026	38655
Measured Acid Value (mg KOH/g)	110	109	111	108	73	87	89
Tg (°C)	15	-	29	41	29	18	66

Polymeric Binder 1 – side group conversion (step c)

Polymeric binder 1 (30 g) was discharged in a mixing vessel containing water (66.7 g), preheated to 80°C, containing a 25% ammonia solution (3.3 g) to be able to neutralise approximately 80% of the acid groups of the polymer, and mixed until completely dissolved. After cooling additional ammonia was dosed to the final product, till a pH of 9.0 was reached and additional water was added to obtain a viscosity below 500 mPa.s. The final polymeric binder solution had a solid content of 30% and was stable for at least 6 weeks at 40°C.

10

Polymeric Binders 2-7 – side group conversion (step c)

In the same manner as polymeric binder 1, polymeric binders 2-7 were discharged in water and an ammonia solution to yield polymeric binder solutions 2-7 with solid content and pH as indicated in Table 2.

15

Table 2:

Binder Solution	1	2	3	4	5	6	7
Polymeric binder	1	2	3	4	5	6	7
Solid Content (%)	30	31	29	31	27	31	25
pH	9.0	9.0	9.1	9.1	9.1	9.0	9.0
Stability (wks at 40°C)	>10	>10	>10	>10	>10	>10	-
Biodegradability (%)	83	48	46	23	27	41	-

Example 2: Preparation of Polymeric binder 8 (comparative example)

Neopentylglycol (43.1 g), adipic acid (25.0 g), isophthalic acid (33.3 g) and butyl stannic acid (400 ppm) were heated in a stirred reactor with a flow of nitrogen gas to a temperature of 240°C. Water was removed using a vigreux column maintaining a maximum top temperature of 100°C. Once

20

the top temperature of the column dropped below 80°C the column was removed and, using vacuum distillation, the reaction was continued until an acid number of <5 mg KOH/g was obtained. Then the mixture was cooled to 180°C. At 180°C trimellitic anhydride (12.8 g) was added and reacted for 1  
5 hour, keeping the temperature at 180°C. The reaction product had an acid value of 74.9 mg KOH/g and was diluted with acetone to obtain a solids content of 64.9%.

The obtained reaction product (65.3 g) and 25% ammonia solution (2.6 g, to neutralise 68% of the acid value) were heated to a temperature of  
10 40°C in a stirred reactor. Water (420 g) was added in 8 minutes. Acetone and part of water was removed from the resulting emulsion by vacuum distillation at a temperature of 30 - 40°C to obtain a solids content of 45.2%.

This emulsion was stable for less than 2 weeks at 40°C.

### 15 Example 3: Preparation of the Coating Composition

Aqueous coating composition with the following composition were prepared:

- 23.4 wt.% of polymeric binder solution;
- 49 wt.% CaCO<sub>3</sub> pigment
- 20 - less than 1 wt.% additives such as ammonia, an adhesion promoter, antifoam and dispersant.

The coating compositions were prepared for each of polymeric binder solutions 1-7 described above by mixing each binder solution with a CaCO<sub>3</sub> pigment slurry and the additives.

25

### Example 4: Preparation of the Coating

A coating was prepared from the coating composition. First, the coating composition was diluted using 5 weight parts of water on 1 weight part of the aqueous coating composition. The diluted coating composition  
30 was applied to the surface of a glass plate. The coated glass plates were

subjected for 24 hours to UV radiation in a UV chamber. Subsequently, the coated glass plates were subjected for 7 days to UV radiation in a climate chamber. While in the climate chamber, the coated glass plates were further subjected every 8 hours to 15 minutes of artificial rain (simulated using a water sprinkler).

The wear resistance of the coating was determined by measuring the transmission of the coating using a spectrograph, both before and after subjecting the coatings to UV and climate chambers. An increase in transmission is an indication of wear.

The removability of the coating was determined by applying the removing agent ReduClean 1:7 (comprising a strong base and a complex former) to a strip of 5 cm of coating of the coated glass. After drying, the plate was analyzed for any remaining coating residue.

The results of the wear resistance and removability test are shown in Table 3. All coatings showed acceptable removability and wear resistance. Coating composition V and VII showed the best wear resistance, although composition V scored a little lower than the rest on removability.

Table 3:

Coating Composition	I	II	III	IV	V	VI	VII
Polymeric Binder	1	2	3	4	5	6	7
Removability	+	+	+	+	+	+ -	
Wear Resistance	+ -	+	+	+	++	++	

20

#### Example 5: Application of Coating Composition on Greenhouse

An experiment was conducted wherein a coating composition according to the present invention comprising a biodegradable binder (coating composition A) was compared to a coating composition comprising a

non-biodegradable binder, as described in EP 0 999 736 and available from Mardenkro under the name ReduSol (coating composition B).

Coating composition A comprised the following ingredients:

- about 50 wt.% pigment ( $\text{CaCO}_3$ );
- 5 - about 7 wt.% of polymeric binder 3; and
- less than 1 wt.% other additives, such as ammonia, an adhesion promoter, antifoam and dispersant. The weight amounts are based on the total weight of coating composition A.

As the binder in coating composition A, a polyester prepared  
10 according to the method given above for polymeric binder 3 was used. The polymeric binder had a Mw of 10480 and an acid value of 111.

The coating composition B comprised about 50 wt.% of an acrylic binder, the same amount and type of pigment used in coating composition A and less than 1 wt.% of other additives, such as ammonia, an adhesion  
15 promoter, antifoam and dispersant.

The coating compositions were diluted with water by a factor of about 10. The resulting composition were applied to the roof surface of a greenhouse.

Both coating compositions had desirable properties, such that it  
20 could be applied evenly on the surface of the greenhouse. The coating composition dried quickly, thereby forming a functional coating.

After six weeks, the coatings were analyzed for any wear. There were no big differences observed for the two coatings. Although some wear of the coatings had taken place, both coatings were still in good condition.

25 To test the removability of the coating, a removing agent based on sodium hydroxide (ReduClean, available from Mardenkro) was used by spraying the outside surface of the greenhouse. After 15 minutes, the surface was sprayed with water, which removed the coatings.

Based on this Examples, it can be concluded that a coating  
30 composition comprising a biodegradable polymeric binder according to the

present invention works just as well as the commercially available coating composition comprising an acrylic binder. Both coating compositions could be easily and evenly applied, were resistant to wear and were removable by a strong base.

5

## Conclusies

1. Een waterige coatingsamenstelling geschikt voor het verschaffen van een functionele coating die verwijderbaar is met een verwijderingsmiddel dat een sterke base omvat, waarbij de coatingsamenstelling een pigment en een polymere binder omvat, waarbij de binder een gewichtsgemiddeld  
5 molecuulgewicht heeft van 2000 tot en met 50000 g/mol, en een zuurgetal van 40 tot en met 250, waarbij de binder een polyester omvattende een zijgroep geïntroduceerd door een Diels-Alder en/of pericyclische Een-reactie is, waarbij de zijgroep een iongroep bevat.
2. De coatingsamenstelling volgens conclusie 1, waarbij de binder is  
10 verkregen door ten minste de volgende stappen:
  - (a) het bereiden van een onverzadigd polyester,
  - (b) het bewerkstelligen van een Diels-Alder reactie en/of pericyclische Een-reactie tussen het onverzadigd polyester en een onverzadigde verbinding die een iongroep en/of ionvormende groep bevat  
15 zodat een polymeer word verkregen met zijgroepen die iongroepen en/of ionvormende groepen bevat,
  - (c) optioneel, het omzetten van ten minste deel van de ionvormende groepen aanwezig in het polymeer naar iongroepen.
3. De coatingsamenstelling volgens conclusie 1 of 2, waarbij de binder  
20 een gewichtsgemiddeld molecuulgewicht heeft van ten minste 5000 g/mol.
4. De coatingsamenstelling volgens één van de voorgaande conclusie, waarbij de binder een gewichtsgemiddeld molecuulgewicht heeft van ten hoogste 40000 g/mol, bij voorkeur ten hoogste 30000 g/mol en bij grootste voorkeur ten hoogste 20000 g/mol.
- 25 5. De coatingsamenstelling volgens één van de voorgaande conclusies, waarbij de zuurgetal van de binder van 60 tot en met 160 mg KOH/g polymere binder is.

6. De coatingsamenstelling volgens één van de voorgaande conclusies, waarbij de zuurgetal van de binder van 60 tot en met 130 mg KOH/g polymere binder is.
7. De coatingsamenstelling volgens één van de voorgaande conclusies, 5 waarbij de glas-transitietemperatuur van 10 tot en met 80 °C, bij voorkeur van 20 tot en met 70 °C, is.
8. De coatingsamenstelling volgens één van conclusies 2-7, waarbij de onverzadigde verbinding een conjugaat dieen met carbonzuur-iongroepen en/of carbonzuur-ionvormende groepen is.
- 10 9. De coatingsamenstelling volgens één van conclusies 2-8, waarbij de onverzadigde verbinding gebruikt in stap (b) een onverzadigde verbinding(en) met ionvormende groepen is zodat een polymeer met zijgroepen die ionvormende groepen bevat wordt verkregen.
- 15 10. De coatingsamenstelling volgens één van conclusies 2-9, waarbij de onverzadigde verbinding een geconjugeerd dieen met carboxylaatformende groepen is zodat een polymeer met zijgroepen die carbonzuur-ionvormende groepen wordt verkregen.
- 20 11. De coatingsamenstelling volgens conclusie 9 of 10, waarbij de polymeer met zijgroepen die ionvormende groepen bevatten wordt omgezet zodat een polymeer met zijgroepen die iongroepen bevatten wordt verkregen.
12. De coatingsamenstelling volgens één van conclusies 2-11, waarbij de onverzadigde verbinding sorbinezuur is.
- 25 13. De coatingsamenstelling volgens één van de voorgaande conclusies, waarbij de polymere binder in water dispergeerbaar of in water oplosbaar is.
14. De coatingsamenstelling volgens één van conclusies 2-13, waarbij de onverzadigde polyester een lineaire of in wezen lineaire onverzadigde polyester is.
- 30 15. De coatingsamenstelling volgens één van conclusies 2-14, waarbij de onverzadigde polyester één of meer dubbele koolstof-koolstof bindingen bevat die in de hoofdgroep van het onverzadigde polyester zijn

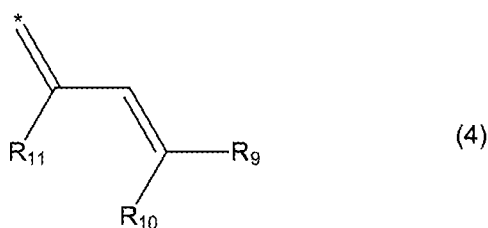
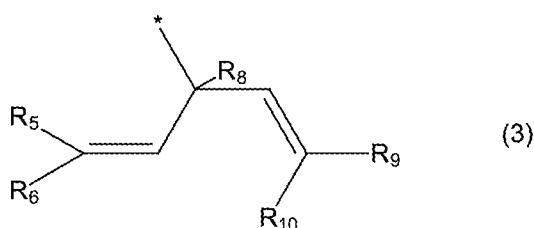
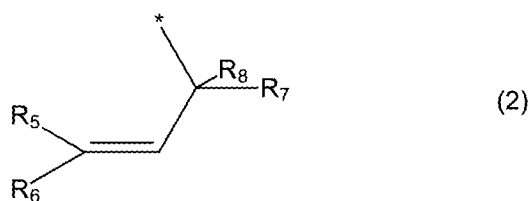
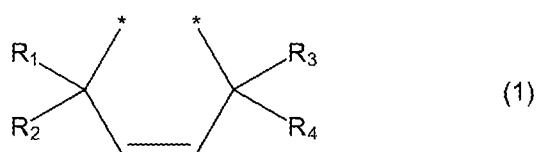
geïntroduceerd door gebruik van een onverzadigde diol, een onverzadigde dicarbonzuur, een onverzadigde dicarbonzuuranhydride of een mengsel daarvan.

16. De coatingsamenstelling volgens één van conclusies 2-15, waarbij de  
5 onverzadigde polyester wordt bereid door polycondensatie van ten minste één onverzadigd dicarbonzuur of anhydride daarvan, ten minste één verzadigde dicarbonzuur en ten minste één diol.

17. De coatingsamenstelling volgens conclusie 16, waarbij de  
10 onverzadigde dicarbonzuur(anhydride) is gekozen uit de groep die bestaat uit maleïnezuur, maleïnezuuranhydride, fumaarzuur en enig mengsel daarvan.

18. De coatingsamenstelling volgens één van de voorgaande conclusies, waarbij de zijgroep van de polymere binder wordt weergegeven door één van de volgende structuren

15



of enig isomeer daarvan, waarbij:

R1 gekozen is uit de groep van anione groepen, welke groep bestaat  
 5 uit carboxylaar (-COO-), sulfaat (-OSO<sub>3</sub>-), fosfaat (-OPO<sub>3</sub>-), sulfonaat (-SO<sub>2</sub>O-),  
 fosfinaat (-POO-), fosfonaat (-PO<sub>2</sub>O-) and gesubstitueerd alkyl, alkenyl,  
 aryl en alkylaryl groepen met de formule -R<sub>12</sub>-A-,

waarbij R<sub>12</sub> een lineaire of vertakte alkyl, alkenyl, aryl of alkylaryl  
 eenheid is, welke eenheid bij voorkeur 1-12 koolstofatomen heeft, bij grotere  
 10 voorkeur 1-6 koolstofatomen, *e.g.* een -C<sub>x</sub>H<sub>2x</sub>- groep met x is 1, 2, 3 or 4.  
 Zodoende is de -R<sub>12</sub>-A- effectief een lineaire of vertakte alkyl, alkenyl, aryl of  
 alkylaryl groep waaraan de ione (A-) groep is gesubstitueerd.

waarbij A- een anione group is gekozen uit carboxylaar, sulfaat,  
 fosfaat, sulfonaat, fosfinaat en fosfonaat, bij voorkeur een carboxylaar;

waarbij  $R_2$ - $R_{11}$  elk individueel gekozen kunnen worden uit de groep van anione groepen gedefinieerd voor  $R_1$  of uit de groep die bestaat uit waterstof, alkyl, alkenyl, aryl en alkylaryl, bij voorkeur uit de groep van H, alkyl en alkenyl;

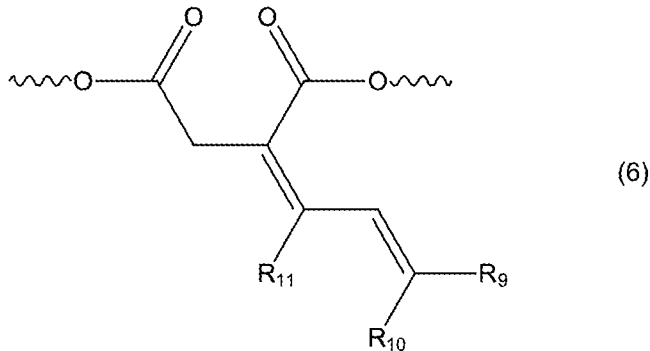
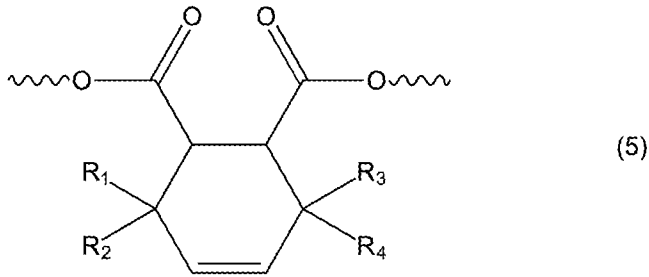
5           waarbij \* een koolstofatoom van het polyester weergeeft waaraan de zijgroep is verbonden, en;

          waarbij voor structuur (2), ten minste één van  $R_5$ ,  $R_6$ ,  $R_7$  en  $R_8$  een anione groep moet zijn;

          waarbij voor structuur (3), ten minste één van  $R_5$ ,  $R_6$ ,  $R_8$ ,  $R_9$  en  $R_{10}$  een  
10 anione groep moet zijn;

          waarbij voor structuur (4), ten minste één van  $R_9$ ,  $R_{10}$  en  $R_{11}$  een anione groep moet zijn.

19. De coatingsamenstelling volgens één van de voorgaande conclusies, waarbij de polymere binder ten minste één van de volgende  
15 structureenheden (1) en (2) bevat:



waarbij  $R_1$  is gekozen uit  $\text{COO}^-$ ;  $R_2$  en  $R_3$  zijn H; en  $R_4$  is methyl; en  
 waarbij  $R_{11}$  is ethyl;  $R_9$  is  $\text{COO}^-$ ; en  $R_{10}$  is H; en/of enig isomeer daarvan.

20. De coatingsamenstelling volgens één van de voorgaande conclusies,  
 5 waarbij de hoeveelheid binder van 5 tot en met 45 gew.% is en de  
 hoeveelheid pigment van 55 tot en met 95 gew.% is, gebaseerd op het  
 drooggewicht van de waterige coatingsamenstelling.

21. De coatingsamenstelling volgens één van de voorgaande conclusies,  
 waarbij het pigment is gekozen uit de groep van calciumcarbonaat,  
 10 titaandioxide, een silicaat, zoals magnesium- of aluminiumsilicaat, gips,  
 bariet en combinaties daarvan.

22. De coatingsamenstelling volgens één van de voorgaande conclusies,  
 waarbij de coatingsamenstelling verder een adhesiepromotor omvat gekozen  
 uit de groep die bestaat uit silanen.

15 23. De coatingsamenstelling volgens één van de voorgaande conclusies,  
 waarbij de coatingsamenstelling verder een pigmentscheider omvat.

24. De coatingsamenstelling volgens één van de voorgaande conclusies,  
 waarbij de coatingsamenstelling verder een verdikkingsmiddel omvat.

25. Toepassing van de coatingsamenstelling volgens één van de voorgaande conclusies om een functionele coating te verkrijgen op een buitenwand en/of dak van een broeikas en welke coating verwijderbaar is met een verwijderingsmiddel dat een sterke base omvat.
- 5 26. Een werkwijze voor het vormen van een functionele coating op een buitenwand en/of dak van een broeikas, waarbij de werkwijze (1) het aanbrengen van een coatingsamenstelling volgens één van conclusies 1-24 en (2) het drogen van de coatingsamenstelling omvat.
27. Een functionele coating die verwijderbaar is met een  
10 verwijderingsmiddel dat een sterke base omvat, welke functionele coating een pigment en een polymere binder omvat, waarbij de binder een gewichtsgemiddeld molecuulgewicht van 2000 tot en met 50000 g/mol heeft, en een zuurgetal van 40 tot en met 250 mg KOH/g polymere binder heeft, waarbij de binder een polyester is die een zijgroep omvat geïntroduceerd  
15 door een Diels-Alder en/of pericyclische Een-reactie, waarbij de zijgroep een iongroep bevat.
28. Een functionele coating volgens conclusie 27, waarbij het pigment calciumcarbonaat of titaandioxide is.
29. Een oppervlak voorzien van een functionele coating volgens conclusie  
20 27 of 28.
30. Een oppervlak volgens conclusie 29, waarbij het oppervlak een buitenwand en/of dak van een broeikas is.
31. Een werkwijze voor het verwijderen van een functionele coating op een buitenwand en/of dak van een broeikas, welke coating een coating  
25 verkregen door de werkwijze volgens conclusie 26 of een coating volgens conclusie 27 of 28 is, waarbij de werkwijze het behandelen van de functionele coating met een verwijderingsmiddel dat water, een sterke base en bij voorkeur een complexvormer omvat omvat, waarbij de sterke base aanwezig is in een hoeveelheid van 1 tot en met 10 gew.%, en waarbij de  
30 complexvormer, indien aanwezig, aanwezig is in een hoeveelheid van 2 tot en met 10 gew.%, op basis van het gewicht van het verwijderingsmiddel.

32. Een werkwijze volgens conclusie 31, waarbij de sterke base natriumhydroxide en/of kaliumhydroxide is.

Title: Removable, biodegradable coating

Abstract

The present invention relates to a functional coating obtained from an aqueous coating composition, which composition comprises a pigment and a polymeric binder, wherein the binder has a weight average molecular weight of from 2000 to 50000 g/mole, and an acid value of 40 to 250, and wherein the binder is a polyester comprising a side group introduced by a Diels-Alder and/or pericyclic Ene-reaction, wherein the side group contains an ionic group and/or an ion-forming group.

## SAMENWERKINGSVERDRAG (PCT)

### RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE
	<b>P114530NL00</b>
Nederlands aanvraag nr.	Indieningsdatum
<b>2018543</b>	<b>17-03-2017</b>
	Ingeroepen voorrangdatum
Aanvrager (Naam)	
<b>Mardenkro Holding B.V.</b>	
Datum van het verzoek voor een onderzoek van internationaal type	Door de instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr.
<b>06-05-2017</b>	<b>SN68905</b>
<b>I. CLASSIFICATIE VAN HET ONDERWERP</b> (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)	
Volgens de internationale classificatie (IPC)	
<b>C08G63/91;C09D167/00;C09D167/06;A01G9/14</b>	
<b>II. ONDERZOCHE GEBIEDEN VAN DE TECHNIEK</b>	
Onderzochte minimumdocumentatie	
Classificatiesysteem	Classificatiesymbolen
<b>IPC</b>	<b>C08G;C09D;A01G</b>
Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen	
<b>III.</b>	<input type="checkbox"/> <b>GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES</b> <span style="float: right; font-size: small;">(opmerkingen op aanvullingsblad)</span>
<b>IV.</b>	<input type="checkbox"/> <b>GEBREK AAN EENHEID VAN UITVINDING</b> <span style="float: right; font-size: small;">(opmerkingen op aanvullingsblad)</span>

**ONDERZOEKSRAPPORT BETREFFENDE HET  
RESULTAAT VAN HET ONDERZOEK NAAR DE STAND  
VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE**

Nummer van het verzoek om een onderzoek naar  
de stand van de techniek

NL 2018543

<p>A. CLASSIFICATIE VAN HET ONDERWERP INV. C08G63/91 C09D167/00 C09D167/06 A01G9/14 ADD.</p>								
<p>Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.</p>								
<p>B. ONDERZOCHE GEBIEDEN VAN DE TECHNIEK</p> <p>Onderzochte minimum documentatie (classificatie gevolgd door classificatiesymbolen) C08G C09D A01G</p> <p>Onderzochte andere documentatie dan de minimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen</p> <p>Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden) EPO-Internal, WPI Data</p>								
<p>C. VAN BELANG GEACHTE DOCUMENTEN</p> <table border="1"> <thead> <tr> <th>Categorie *</th> <th>Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages</th> <th>Van belang voor conclusie nr.</th> </tr> </thead> <tbody> <tr> <td>X,D A</td> <td> <p>WO 2013/123314 A1 (VALSPAR SOURCING INC [US]) 22 augustus 2013 (2013-08-22) in de aanvraag genoemd</p> <p>* conclusies *</p> <p>* voorbeelden *</p> <p>* alinea's [0059] - [0067] *</p> <p>* alinea's [0069] - [0071] *</p> <p>* alinea's [0094], [0096], [0097] *</p> <p>* alinea's [0128], [0131] *</p> <p>-----</p> <p>-/--</p> </td> <td> <p>1-24, 27-29</p> <p>25, 26, 30-32</p> </td> </tr> </tbody> </table>			Categorie *	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.	X,D A	<p>WO 2013/123314 A1 (VALSPAR SOURCING INC [US]) 22 augustus 2013 (2013-08-22) in de aanvraag genoemd</p> <p>* conclusies *</p> <p>* voorbeelden *</p> <p>* alinea's [0059] - [0067] *</p> <p>* alinea's [0069] - [0071] *</p> <p>* alinea's [0094], [0096], [0097] *</p> <p>* alinea's [0128], [0131] *</p> <p>-----</p> <p>-/--</p>	<p>1-24, 27-29</p> <p>25, 26, 30-32</p>
Categorie *	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.						
X,D A	<p>WO 2013/123314 A1 (VALSPAR SOURCING INC [US]) 22 augustus 2013 (2013-08-22) in de aanvraag genoemd</p> <p>* conclusies *</p> <p>* voorbeelden *</p> <p>* alinea's [0059] - [0067] *</p> <p>* alinea's [0069] - [0071] *</p> <p>* alinea's [0094], [0096], [0097] *</p> <p>* alinea's [0128], [0131] *</p> <p>-----</p> <p>-/--</p>	<p>1-24, 27-29</p> <p>25, 26, 30-32</p>						
<p><input checked="" type="checkbox"/> Verdere documenten worden vermeld in het vervolg van vak C. <input checked="" type="checkbox"/> Leden van dezelfde octrooifamilie zijn vermeld in een bijlage</p>								
<p>* Speciale categorieën van aangehaalde documenten</p> <p>* "A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft</p> <p>* "D" in de octrooiaanvraag vermeld</p> <p>* "E" eerdere octrooi(aanvraag), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven</p> <p>* "L" om andere redenen vermelde literatuur</p> <p>* "O" niet-schriftelijke stand van de techniek</p> <p>* "P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur</p> <p>* "T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvraag, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding</p> <p>* "X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur</p> <p>* "Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht</p> <p>* "Z" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie</p>								
<p>Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid</p> <p>28 november 2017</p>		<p>Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type</p>						
<p>Naam en adres van de instantie</p> <p>European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040 Fax: (+31-70) 340-3016</p>		<p>De bevoegde ambtenaar</p> <p>Schlicke, Benedikt</p>						

**ONDERZOEKSRAPPORT BETREFFENDE HET  
 RESULTAAT VAN HET ONDERZOEK NAAR DE STAND  
 VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE**

Nummer van het verzoek om een onderzoek naar  
 de stand van de techniek

NL 2018543

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN		
Categorie *	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	DE 22 51 745 A1 (BASF AG) 2 mei 1974 (1974-05-02)	1-7, 9-11, 13-16, 20-24, 27-29
A	* conclusies 1-4 * * voorbeelden 1,3-5,7 * * bladzijde 5, regels 18,19 * * bladzijde 7, regels 1-7 * -----	8,12, 17-19, 30-32
A	WO 99/22588 A1 (RAADGEVEND CHEMIEBUREAU RSB V [NL]; ROSSUM ANTOON JOHANNES GERARDU [NL] 14 mei 1999 (1999-05-14) * conclusies *	1-32

**ONDERZOEKSRAPPORT BETREFFENDE HET  
RESULTAAT VAN HET ONDERZOEK NAAR DE STAND  
VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE**

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar  
de stand van de techniek

NL 2018543

In het rapport genoemd octrooigescrift	Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
WO 2013123314	A1	22-08-2013	CA 2864122 A1 22-08-2013
			CN 104114453 A 22-10-2014
			EP 2814746 A1 24-12-2014
			JP 6184424 B2 23-08-2017
			JP 2015514639 A 21-05-2015
			KR 20140125788 A 29-10-2014
			RU 2014131130 A 10-04-2016
			US 2014076768 A1 20-03-2014
			US 2017313473 A1 02-11-2017
			WO 2013123314 A1 22-08-2013
DE 2251745	A1	02-05-1974	DE 2251745 A1 02-05-1974
			FR 2203839 A1 17-05-1974
			NL 7314361 A 23-04-1974
WO 9922588	A1	14-05-1999	AT 199205 T 15-03-2001
			BR 9814107 A 03-10-2000
			CA 2302738 A1 14-05-1999
			DE 69800536 D1 29-03-2001
			DE 69800536 T2 27-09-2001
			DK 0999736 T3 11-06-2001
			EP 0999736 A1 17-05-2000
			ES 2156447 T3 16-06-2001
			JP 5066312 B2 07-11-2012
			JP 2001521944 A 13-11-2001
			KR 100419165 B1 18-02-2004
			NL 1007433 C2 04-05-1999
			US 2002168472 A1 14-11-2002
			US 2004197586 A1 07-10-2004
WO 9922588 A1 14-05-1999			

## WRITTEN OPINION

File No. SN68905	Filing date (day/month/year) 17.03.2017	Priority date (day/month/year)	Application No. NL2018543
International Patent Classification (IPC) INV. C08G63/91 C09D167/00 C09D167/06 A01G9/14			
Applicant Mardenkro Holding B.V.			

This opinion contains indications relating to the following items:

- Box No. I      Basis of the opinion
- Box No. II      Priority
- Box No. III      Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- Box No. IV      Lack of unity of invention
- Box No. V      Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- Box No. VI      Certain documents cited
- Box No. VII      Certain defects in the application
- Box No. VIII      Certain observations on the application

	Examiner Schlicke, Benedikt
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## WRITTEN OPINION

Application number  
NL2018543

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### Box No. I Basis of this opinion

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1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:
  - a. type of material:
    - a sequence listing
    - table(s) related to the sequence listing
  - b. format of material:
    - on paper
    - in electronic form
  - c. time of filing/furnishing:
    - contained in the application as filed.
    - filed together with the application in electronic form.
    - furnished subsequently for the purposes of search.
3.  In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

---

### Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

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#### 1. Statement

Novelty	Yes: Claims	25, 26, 30-32
	No: Claims	1-24, 27-29
Inventive step	Yes: Claims	25, 26, 30-32
	No: Claims	1-24, 27-29
Industrial applicability	Yes: Claims	1-32
	No: Claims	

#### 2. Citations and explanations

**see separate sheet**

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1 Reference is made to the following documents:

D1 WO 2013/123314 A1 (VALSPAR SOURCING INC [US]) 22 augustus 2013, in de aanvraag genoemd

D2 DE 22 51 745 A1 (BASF AG) 2 mei 1974

2 Document D1 discloses (see claims; examples; paragraphs [0059] - [0067]; [0069] - [0071]; [0094], [0096], [0097] an aqueous coating composition, said composition comprising a water-dispersible polyester binder and optionally a pigment. The binder has a number average molecular weight of preferably from 5000 to 10000 g/mole (resulting in a weight average molecular weight of between 2000 and 50000 g/mole), an acid value of preferably from 40 to 100 mg KOH/g, and a glass transition temperature of preferably 10° to 100°C. The polyester binder is obtained by subjecting an unsaturated polyester to a Diels-Alder- or pericyclic Ene-reaction reaction with a functionalized diene, such as sorbic acid, or an olefin. The side groups contain acid functionalities and can be transformed in ionic groups through reaction with a base.

The subject-matter of independent claims 1, 27 and 29 lacks novelty in view of this teaching.

3 Document D2 shows in its examples an aqueous coating composition comprising a water-dispersible polyester binder. The polyester binder is obtained by subjecting a polyester resin having conjugated double bonds to a Diels-Alder reaction with an acid substituted unsaturated dienophile. The acid functionalities are transformed into ionic groups by reaction with a base. The compositions of D2 may contain a pigment (page 7, first full paragraph) and have a molecular weight of 2000 to 40000 (page 5, first full paragraph).

Document D2 further discloses the use of these aqueous compositions as protective coatings for e.g. wood or concrete (see claim 4, page 7, first full paragraph).

The subject-matter of independent claims 1, 27 and 29 differs from this prior art teaching only in that the polyester binder is required to have an acid number of between 40 and 250.

In absence of suitable comparative examples, the objective problem underlying the present invention in view of D2 may be regarded as to provide an alternative coating composition.

It is a routine practice of the skilled person to adapt the acid number of a polyester resin to its particular needs. Acid numbers of above 40 are normal features of polyester resins as disclosed in the present application, see for example document D1, paragraph 94. It therefore would have been obvious at the time of filing of the present application to modify the acid number in order to provide alternative polyesters.

For these reasons, the subject-matter of independent claims 1, 27 and 29 lacks inventive step

- 4 The subject-matter of dependent claims 2-24, 28 and 29 is either disclosed in, or rendered obvious by the disclosure of D1 and/or D2, see passages cited in the search report.
- 5 The available prior art fails to disclose or to suggest the application and removal of a coating composition as defined in claims 1 and 27 on file to the outside wall or the roof of a greenhouse.

The present application does not meet the criteria of patentability, because the subject-matter of claim(s) [...] does not involve an inventive step.

[insert document] is regarded as being the prior art closest to the subject-matter of claim [...], and discloses [insert references applying to this document].

The subject-matter of claim [...] therefore differs from this known [...] in that [...] and is therefore new.

The problem to be solved by the present invention may therefore be regarded as [...]

The solution proposed in claim [...] of the present application cannot be considered as involving an inventive step for the following reasons: [insert reasoning].

---- [other independent claims] ----

The same reasoning applies, mutatis mutandis, to the subject-matter of the corresponding independent claim(s) [...], which therefore is/are also considered not new/inventive.

----- [dependent claims, negative assessment] -----

Dependent claim(s) [...] does/do not contain any features which, in combination with the features of any claim to which it/they refers/refer, meet the requirements of novelty and/or inventive step, see [insert document(s) and references applying to this document(s) cited in the search report].

----- [dependent claims, positive assessment] -----

The combination of the features of dependent claim(s) [...] is neither known from, nor rendered obvious by, the available prior art. The reasons are as follows: [insert reasoning].