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(54) **Title**: MODIFIED EPOXY PRIMER FOR IMPROVED ADHESION OF RMA CROSSLINKABLE COATING COMPOSITIONS

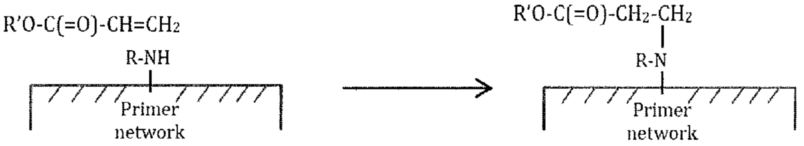

Figure 1

(57) **Abstract**: The invention relates to a method for applying a RMA crosslinked coating with improved adhesion, comprising the steps of applying on the substrate surface a layer of a modified epoxy primer comprising an epoxy functional polymer binder and a crosslinker, wherein adhesion of the RMA crosslinked coating to the epoxy primer layer is improved by said primer comprising after curing functional groups X reactable with crosslinkable components of the RMA crosslinkable composition or a precursor of functional groups X, preferably a moisture deblockable precursor. The invention also relates to modified epoxy primers, compositions for improving adhesion of epoxy primers and use thereof to improve adhesion of RMA crosslinkable coatings.

MODIFIED EPOXY PRIMER FOR IMPROVED ADHESION OF RMA CROSSLINKABLE COATING COMPOSITIONS

[0001] The invention relates generally to a method for applying a RMA crosslinked coating with improved adhesion. The invention further relates to a primer composition for use in the method, a composition for use in an epoxy primer for improving adhesion of a RMA crosslinkable coating to the epoxy primer.

[0002] RMA crosslinkable compositions are compositions comprising at least one crosslinkable component comprising reactive components A and B each comprising at least 2 reactive groups wherein the at least 2 reactive groups of component A are acidic protons (C-H) in activated methylene or methine groups *(RMA donor group)*, and the at least 2 reactive groups of component B are activated unsaturated groups (C=C) *(RMA acceptor group)*. These reactive groups react to achieve crosslinking by Real Michael Addition (RMA) reaction between said at least one crosslinkable components in the presence of a base catalyst (C).

[0003] Such RMA crosslinkable compositions are described in EP2556108. Herein a special catalyst C is described which is a substituted carbonate catalyst which decomposes in a coating layer to generate carbon dioxide which evaporates from the applied curing coating layer and a strong base which starts the RMA crosslinking reaction. The catalyst provides long pot-life and at the same time a high reactivity when applied as a coating layer where CO2 can escape.

[0004] The problem underlying the invention is that the RMA crosslinkable compositions may show undesirably poor adhesion properties in particular to polar surfaces for example in direct to metal applications unless the metal surface has been pretreated with a primer layer or with known metal pretreatments like silane treatment.

[0005] In the General Industrial, Marine, Protective, and ACE markets, topcoats are usually applied over an epoxy-amine primer. Adhesion studies of coatings based on RMA crosslinkable compositions were carried out over many different types of commercially available epoxy primers used in a wide field of end use applications including general industry, ACE and protective coatings. However, known epoxy primers do not always give good adhesion results for coatings based on RMA crosslinkable compositions.

[0006] Therefore the desire remains to more adequately improve the adhesion of RMA crosslinkable compositions, in particular coating compositions, in particular in pigmented coating compositions comprising the crosslinkable composition as the binder system for the coating and there is a need for adhesion promotors for improving the adhesion of RMA crosslinkable compositions

BRIEF SUMMARY OF THE INVENTION

[0007] According to the invention this problem has been solved by a method for applying a RMA crosslinked coating with improved adhesion, comprising the steps of

I. providing an RMA crosslinkable composition comprising
    a) one or more crosslinkable components comprising a reactive component A with at least two acidic protons C-H in activated methylene or methine groups,
    b) a reactive component B with at least two activated unsaturated C=C groups and
    c) a catalyst C for catalyzing the RMA crosslinking reaction between components A and B,
    d) optional reactivity moderator D and
    e) optional organic solvent T,
II. applying on the substrate surface a layer of an epoxy primer comprising an epoxy functional polymer binder and a crosslinker, wherein adhesion of the RMA crosslinked coating to the epoxy primer layer is improved by said primer comprising after curing functional groups X reactable with crosslinkable component A or B of the RMA crosslinkable composition or a precursor of functional groups X, preferably a moisture deblockable precursor,
III. at least partial curing of the primer layer,
IV. applying, over the at least partially cured primer layer, a coating layer of the RMA crosslinkable composition and
V. curing the coating layer.

[0008] The inventors have found significant improvement of the adhesion to the epoxy primer layer and believe that to some extent crosslinkable components of the RMA crosslinkable composition will diffuse into the epoxy primer and react with functional groups X present in the modified epoxy primer creating a firm bond between the primer layer and the RMA crosslinked coating.

[0009] The epoxy primer can be formulated with excess amount of amine crosslinking groups relative to epoxy functional groups of the epoxy functional polymer and/or said epoxy primer is modified by addition of polyfunctional amine components or precursors thereof so that said primer layer after curing has free primary or secondary amine functional groups X or precursors thereof.

[0010] A preferred RMA crosslinkable composition comprises a crosslinkable component with components A being predominantly malonate or an acetoacetate and a crosslinkable component with components B being an acryloyl and the one or more functional groups X in the modified primer are reactable with malonate or acetoacetate and/or with the acryloyl, and preferably are primary or secondary amine.

[0011] The primer can be modified by addition to the primer of a polyfunctional compound comprising one or more functional groups X reactable with component A or component B of the RMA crosslinkable composition and also one or more groups chemically or physically binding with the epoxy functional binder or its crosslinker during or after curing, said one or more functional groups X being a primary or secondary amine, a thiol, isocyanate, epoxy or a RMA reactable component A' or B' or oligomers or polymers of components A' or B' which are same or different from the reactive components A and/or B in the RMA crosslinkable components.

[0012] In one embodiment the method comprises adding a RMA crosslinkable component comprising reactive component A, preferably malonate to the primer, preferably having a molecular weight Mw of at least 400, more preferably at least 700, 1000 or even 2000 dalton.

[0013] The polyfunctional compound comprising one or more functional groups X is preferably reactable both with component A or component B of the RMA crosslinkable composition and also chemically binding with the epoxy functional binder or its crosslinker.

[0014] In a particular preferred embodiment the epoxy primer is an epoxy resin modified with a polyfunctional moisture deblockable primary or secondary amine, preferably ketimine, aldimine or oxazolidine. These compounds react with water to form an amine. This has a further advantage that water present in the primer, RMA composition or adsorbed from the ambient is bound and cannot interfere with the curing reaction of both epoxy primer and RMA crosslinkable compositions.

[0015] The epoxy primer composition is modified by addition of polyfunctional compound in an amount not exceeding 20, 15, 10 or preferably 5 wt% relative to the total solids weight of the primer composition.

[0016] The primer can suitably be modified by a RMA crosslinkable component comprising reactive components A or B, preferably malonate or acetoacetate, most preferably a malonate, for example an adduct of TMP with acetoacetate or malonate triacetoacetate/malonate and/or a polyfunctional compound comprising a free primary or secondary amine functional group or precursor thereof, preferably moisture deblockable precursors thereof, preferably a polyfunctional ketimine, aldimine or oxazolidine or combinations or reaction products thereof.

[0017] The invention also relates to a primer composition for use in the method according to the invention comprising an epoxy functional binder, a crosslinker and a polyfunctional component as described above as adhesion promotor. Said polyfunctional component being reacted or reactable with the epoxy binder or its crosslinker in the primer curing conditions or is a separate non reacted component which is physically bonded in the cured primer.

[0018] The invention also relates to a composition for use in an epoxy primer for improving adhesion of a RMA crosslinkable coating on an epoxy primer layer, said composition comprising one or more primer adhesion improvers selected from a RMA crosslinkable component comprising reactive components A and or B, for example tri- or tetra-acetoacetate- or malonate or a crosslinkable component comprising reactive component B, in particular a tri- or tetraacrylate, a polyfunctional component comprising two or more free primary or secondary amine functional group or precursor thereof, preferably moisture deblockable precursors thereof, preferably a polyfunctional ketimine, aldimine or oxazolidine or combinations or reaction products thereof. The invention also relates to the use of the above composition for improving adhesion of a RMA crosslinkable coating on an epoxy primer layer.

BRIEF DESCRIPTION OF THE DRAWING

[0019] Figure 1 illustrates chemical adhesion of RMA crosslinkable resins comprising acryloyl groups on epoxy-amine primers.

DETAILED DESCRIPTION OF THE INVENTION

[0020] Reference is made to EP2556108 and EP2764035 for detailed description of all components in the RMA crosslinkable composition A, B, C or D, their preparation, the amounts used in the RMA crosslinkable composition as well as for measurement methods and definitions and the description thereof is hereby incorporated by reference and applicable unless described otherwise herein. Most important features are described below in summary.

[0021] It is preferred that reactive component A is malonate or acetoacetate, preferably dominantly a malonate, and reactive component B is acryloyl. It is preferred that the one or more reactive components A in the crosslinkable component predominantly comprise one type of reactive components, predominantly meaning preferably more than 50, 75, 90 and most preferably 100 % of the C-H reactive groups in crosslinkable component A are from one type of reactive component A, preferably from malonate or acetoacetate and most preferably consisting predominantly of malonate and acetoacetate or acetylacetone as the remainder component A. The most preferred component B is an acryloyl.

[0022] The reactive components A and B are preferably build into a polymer chain or pending or terminal pending on a polymer chain. Preferably, the one or more crosslinkable components are one or more polymers chosen from the group of polyesters, alkyds, polyurethanes, polyacrylates, epoxy resins, polyamides and polyvinyl resins which contain components A or B in the main chain, pendant, terminal or combinations thereof.

[0023] The one or more RMA crosslinkable components can be monomeric but preferably at least one crosslinkable component is a polymeric component with a weight average molecular weight Mw of at least 250 g/mol, preferably a polymer having Mw between 250, 300 and 5000, more preferably between 400 and 4000 or 500 and 3000 g/mol (as determined by GPC).

[0024] The relative amounts of the crosslinkable components in the RMA crosslinkable composition are chosen such that the molar ratio of activated unsaturated reactive group C=C in reactive component B to the activated acidic reactive groups C-H in reactive component A is between 0.5 and 2 and preferably between 0.75 – 1.5 or 0.8 – 1.2.

[0025] In case components D or P or both are present that comprise reactive groups X-H and can react with B, the molar ratio of activated unsaturated reactive group C=C in reactive component B to the total number of reactive groups C-H in reactive component

A and reactive groups X-H in component D and P is between 0.3 and 3, preferably 0.5 – 2 and even more preferably 0.75 – 1.5 or 0.8 – 1.2.

[0026] In case a reactive solvent is present having 2 C-H reactive groups (for example malonate) then these are also included in the total amount of C-H in the above ratio as they are crosslinkable components. The total amount of monofunctional material should be limited otherwise it will negatively affect coating properties. Preferably the total amount monofunctional reactive solvent is less than 10, preferably less than 5, 3 or even 2 wt%.

[0027] The RMA crosslinkable composition preferably further comprises a reactivity moderator D comprising an X-H group that is also a Michael addition donor reactable with component B under the action of catalyst C, wherein X is C, N, P, O or S or an alcohol with 2 to 12 carbon atoms or both for improving open time and hence working time of application of the floor coating composition on a floor.

[0028] The X-H group in component D, preferably an N-H group containing component, has a pKa (defined in aqueous environment) of at least one unit, preferably two units, less than that of the C-H groups in predominant component A, preferably the pKa of the X-H group in component D is lower than 13, preferable lower than 12, more preferably lower than 11, most preferably lower than 10; it is preferably higher than 7, more preferably 8, more preferably higher than 8.5.

[0029] The component D preferably comprises a molecule containing the N-H as part of a group -(C=O)-NH-(C=O)-, or of a group -NH-(O=S=O)- or a heterocycle in which the nitrogen of the N-H group is contained in a heterocyclic ring preferably chosen from the group of a substituted or unsubstituted succinimide, glutarimide, hydantoin, triazole, pyrazole, immidazole or uracil, preferably chosen from the group of succinimides, benzotriazoles and triazoles.

[0030] The component D is present in an amount between 0.1 and 10 wt%, preferably 0.2 and 7 wt%, 0.2 and 5 wt%, 0.2 and 3 wt%, more preferably 0.5 and 2 wt% relative to the total amount of the crosslinkable components A or B and component D. The component D is present in such amount that the amount of X-H groups in component D is no more than 30 mole%, preferably no more than 20, more preferably no more than 10, most preferably no more than 5 mole% relative to C-H donor groups from component A present in the crosslinkable polymer.

[0031] The catalyst C can be preferably a carbon dioxide blocked strong base catalyst, more preferably a quaternary alkyl ammonium bi- or alkylcarbonate (as described in

EP2556108). As this catalyst generates CO2 it is preferred for use in coating layers with a thickness up to 500, 400, 300, 200 or 150 micrometer.

[0032] A homogeneous base catalyst C, which is more suitable for thicker coating layers, are described in EP0326723 which is a catalyst consisting of the combination of a tertiary amine and an epoxide.

[0033] A preferred homogeneous catalyst C is a salt of a basic anion X- from an acidic X-H group containing compound wherein X is N, P, O, S or C, and wherein anion X- is a Michael Addition donor reactable with component B and anion X- is characterized by a pKa(C) of the corresponding acid X-H of more than two units lower than the pKa(A) of the majority component A and being lower than 10.5. Details of this catalyst are described in PCT/EP2014/056953, which is hereby incorporated by reference.

[0034] Other catalysts C that are especially useful in applications in which there is no large surface available for allowing C02 to evaporate such as in the case of thick films applications, have been described in WO2014166880A1.

[0035] In view of the fact that the RMA crosslinking reaction is base catalyzed, acidic components should not be used in the composition such that the acid base reaction between catalyst C and A and optionally D is not interfered. Preferably the composition is free of acidic components.

[0036] The RMA composition may comprise one or more organic solvents T required for dissolving certain components or for adjusting the RMA composition to an appropriate handling viscosity (eg for spraying application). Organic solvents for use in RMA crosslinkable compositions are common coating solvents that do not contain acid impurities like alkylacetate (preferably butyl or hexyl acetate), alcohol (preferably C2 – C6 alcohol), N alkylpyrrolidine, glycolether, Di-propylene Glycol Methyl Ether, Dipropylene Glycol Methyl Ether, Propylene Glycol Methyl Ether Acetate, ketones etc.

[0037] The amount of volatile solvent can be between 0 and 60, 50 or 40 wt% but in view of QESH preferably the composition has a low volatile organic compounds (VOC) content and therefore the amount of volatile organic solvent is preferably less than 20, 15, 10, 5 and most preferably less than 2 or even 1 wt% relative to the total of the crosslinkable components A and B.

[0038] In particular where a low viscosity and a low VOC is required it is preferred that the RMA crosslinkable composition comprises one or more reactive solvents which react with crosslinkable components A or B. The one or more reactive solvents are preferably selected from the group of monomeric or dimeric components A, monomeric or dimeric components B, compounds A’ having only 1 reactive acidic proton (C-H) in activated methylene or methine groups, compounds B’ having only 1 reactive unsaturated groups (C=C), most preferably alkylacetoacetates, dialkylmalonates, mono- or diacrylates of limited molecular weight. The total amount of volatile organic solvent plus reactive solvents is between 0 and 30 wt% and the volatile organic solvent is less than 5wt% relative to the total weight of the RMA composition.

[0039] The modified epoxy primer suitable for use in the method of the invention is an epoxy primer which is modified to have, after curing, free amine groups. Good to excellent adhesion was found with these primers, which may be explained by chemical bond formation between remaining free amine groups on the primer substrate and acryloyl groups from the paint (see Figure 1).

EXAMPLES

[0040] The following is a description of certain embodiments of the invention, given by way of example only.

Adhesion test:

[0041] The results of adhesion stated in the following examples are based on the cross cut adhesion test following the ISO/DIN 2409, ASTM D3359 protocol. The ranking is briefly summarized as follows:

0: The edges of the cuts are completely smooth; none of the squares of the lattice is detached.

1: Detachment of small flakes of the coating at the intersection of the cuts. A cross-cut area not significantly greater than 5% is affected.

2: The coating has flaked along the edges and/or at the intersection of the cuts. A cross-cut area significantly greater than 5%, but not significantly greater than 15% is affected.

3: The coating has flaked along the edges partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area significantly greater than 15%, but not significantly greater than 35%, is affected.

4: The coating has flaked along the edges of the cuts in large ribbons and/or same squares have detached partly or wholly. A cross-cut area significantly greater than 335%, but not significantly greater than 65% is affected.

5: Any degree of flaking that cannot even be classified by classification 4.

Metal substrate:

[0042] To test the adhesion of given examples and comparative examples films were applied on two types of metal substrates Gardobond 26S 6800 OC and Gardobond C. Gardobond© is a trade name of the German producer "Chemetall". Some example use aluminium substrates (Q-panel Al-46).

General procedure for mixing of the formulations used for the comparative examples:

[0043] A malonate containing polyester as described below (paint A) was mixed with the DiTMPTA and the thinner n-propanol and stirred till a homogenous sample was obtained.

[0044] Prior to use all mentioned formulations were activated by adding the stated amount of initiator which is a tetrabutylammoniumhydroxide TBAH solution reactively blocked with diethylcarbonate, with a base concentration of 0.928 meq/g solution (see procedure for preparation of initiator solutions). The initiator is also referred to herein as catalyst CAT4.

Component	**Catalyst CAT4**
Aqueous TBAH (55%)	100
Diethylcarbonate	45.1
n-propanol	181

MPE1 malonated polyester

[0045] This resin is prepared as follows: into a reactor provided with a distilling column filed with Raschig rings were brought 382 g of neopentyl glycol, 262.8 g of hexahydrophthalic anhydride and 0.2 g of butyl stannoic acid. The mixture was polymerised at 240° C under nitrogen to an acid value of 0.2 mg KOH/g. The mixture was cooled down to 130° C and 355 g of diethylmalonate was added. The reaction mixture was heated to 170° C and ethanol was removed under reduced pressure. Part the resin was modified by addition of succinimide as reactivity moderator; when the viscosity at 100°C reached 0.5 Pa.s the material was cooled down to 140° and 11.2 grams of solid succinimide were added (MPE1S). This mixture was stirred until all succinimide was dissolved. Both resins were diluted with butyl acetate to 85% solids, to yield a material with OH value 16 mg KOH/g, GPC Mn 1750, and a malonate equivalent weight of 350 (active C-H EQW 175).

[0046] MA9 is a malonated alkyd using coconut oil as the oil component, an oil length of 30%, an OH value of 108 mg KOH/g, a GPC Mn of 1800 and a Mw of 4350. The malonate equivalent weight of this material is 360 (active C-H equivalent weight 180).

Paint preparation

[0047] Paint D was prepared by mixing the components as described in Table 7 below. Paint D is based on MPE1, further comprising malonated TMP but no adhesion improver, and was tested on a primer of a ketimine modified epoxy primer paint (Ex 17).

[0048] Table 7: paint compositions

Component	**Paint D**
MPE1	45.33
Acetoacetate functional TMP	1.89
Miramer M300	18.17
Acrylate functional IPDI trimer	15.56
Methyl amyl ketone	18.89
Silmer ACR-D2**	0.09

** Silmer ACR-D2 is reactive silicone comprising multi-functional or linear-difunctional silicone pre-polymers with reactive terminal end groups being acrylates.

Catalyst preparation examples:

[0049] Catalyst compositions were prepared by mixing components specified in Table 8.

Table 8: Catalyst compositions

Component	**Catalyst 1**	**Catalyst 4a**
Aqueous TBAH (55%)	100	0
Methanolic TBAH 1M	0	51.18
Diethylcarbonate	45.1	
Dimethylcarbonate	0	8.6
n-propanol	181	0
Geniosil GF 93	0	**0**
Silquest A1120	0	0

TBAH is tetrabutyl ammonium hydroxide

Example 17.

[0050] An epoxy paint, Aquapon 97-137 was activated with hardener 97-1200 at the volume ratio suggested by the producer (PPG) with an excess of epoxy groups and therefore no free amine groups. Then Setalux 10-1440, which is a ketimine functional resin, was added at a level of 5% by volume to the epoxy paint and thoroughly mixed and then applied onto a metal panel and dried for 24 hours. 18 grams of Paint D (having no adhesion improver) was mixed with 0.53 grams of Catalyst 1 and then sprayed onto the day-old primed panels, flashed for 10 minutes at room temperature and then baked for 15 minutes at 66°C. After cooling, adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be very good.

Example 18.

[0051] An epoxy paint, Aquapon 97-137 was activated with hardener 97-1200 at the volume ratio suggested by the producer (PPG) with an excess of epoxy groups and therefore no free amine groups. Then a ketimine prepared from reacting 1 mole of diethylenetriamine with 2 moles of methyl isobutyl ketone, was added at a level of 5% by volume to the epoxy paint and thoroughly mixed and then applied onto a metal panel and dried for 24 hours. 18 grams of Paint D was mixed with 0.53 grams of Catalyst 1 and then sprayed onto the day-old primed panels, flashed for 10 minutes at room temperature and then baked for 15 minutes at 66°C. After cooling, adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be very good.

Comparative example 13.

[0052] An epoxy paint, Aquapon 97-137 was activated with hardener 97-1200 at the volume ratio suggested by the producer (PPG) with an excess of epoxy groups and therefore no free amine groups. The primer was then applied onto a metal panel and dried for 24 hours. 18 grams of Paint D was mixed with 0.53 grams of Catalyst 1 and then sprayed onto the day-old primed panels, flashed for 10 minutes at room temperature and then baked for 15 minutes at 66°C. After cooling, adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be very bad. It shows that a paint without adhesion improver on this standard epoxy primer does not show sufficient adhesion, whereas modifying the epoxy primer according to the invention does result in good adhesion.

Example AA1.

[0053] 100g of a commercially available epoxy primer was mixed with 10g of TMPTAA (TMP triacetoacetate). Next 6.6g of part B (crosslinker) of the epoxy primer was added and mixed. The primer was spray applied to 2 phosphated steel panels. One panel was cured for 3 hours and the second panel was cured at 66°C for 30 minutes. The primed panels were top coated with Paint B, which was catalyzed with CAT4. The panels were allowed to air dry for 7 days and then adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good. The test panels were then exposed in a condensing humidity cabinet set at 40°C for 3 days and again adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good.

Example MAA1.

[0054] 100g of a commercially available epoxy primer was mixed with 2g of malonated alkyd MA9. Next 6.6g of part B (crosslinker) of the epoxy primer was added and mixed. The primer was spray applied to 2 phosphated steel panels. One panel was cured for 3 hours at room temperature and the second panel was cured at 80°C for 30 minutes. The primed panels were top coated with Paint B, which was catalyzed with CAT4. The panels were allowed to air dry for 7 days and then adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good. The test panels were then exposed in a condensing humidity cabinet set at 40°C for 3 days and again adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good.

Example AMA1.

[0055] 100g of a commercially available epoxy primer was mixed with 10g of Miramer AS1000 (an amine acrylate ex Miwon). Next 6.6g of part B of the epoxy primer was added and mixed. The primer was spray applied to 2 phosphated steel panels. One panel was cured for 3 hours at room temperature and the second panel was cured at 66°C for 30 minutes. The primed panels were top coated with Paint B, which was catalyzed with CAT4. The panels were allowed to air dry for 7 days and then adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good. The test panels were then exposed in a condensing humidity cabinet set at 40°C for 3 days and again adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good.

Example EMA1

[0056] 100g of a commercially available epoxy primer was mixed with 2g of an epoxy functional malonated alkyd EMMR1. Next 6.6g of part B (crosslinker) of the epoxy primer was added and mixed. The primer was spray applied to 2 phosphated steel panels. One panel was cured for 3 hours at room temperature and the second panel was cured at 80°C for 30 minutes. The primed panels were top coated with Paint A, which was catalyzed with CAT4. The panels were allowed to air dry for 7 days and then adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good. The test panels were then exposed in a condensing humidity cabinet set at 40°C for 4 days and again adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good.

Example MPEAA1.

[0057] 93.2g of a commercially available epoxy primer was mixed with 4g of MPE1. Next 6.4g of part B (crosslinker) of the epoxy primer was added and mixed. The primer was spray applied to phosphated steel panels. The primed panels were top coated with Paint B, which was catalyzed with CAT4. The panels were allowed to air dry for 7 days and then adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good. The test panels were then exposed in a condensing humidity cabinet set at 40°C for 3 days and again adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good.

Comparative Example NOA1

[0058] 100g of a commercially available epoxy primer was mixed with 6.6g of part B (crosslinker) of the epoxy primer. The primer was spray applied to 2 phosphated steel panels. One panel was cured for 3 hours at room temperature and the second panel was cured at 80°C for 30 minutes. The primed panels were top coated with Paint A, which was catalyzed with CAT4. The panels were allowed to air dry for 7 days and then adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good. The test panels were then exposed in a condensing humidity cabinet set at 40°C for 4 days and again adhesion was tested using the cross-cut adhesion test as described in ASTM D3359: adhesion was found to be poor.

Preparation of EMMR1

[0059] A four-necked reaction flask equipped with a condenser; agitator; heating mantle; addition funnel; thermocouple attached to a control box; and primed Dean-Stark trap with toluene, was charged with 21.4 parts (by weight) of coconut fatty acid, 29.2 parts of trimethylol propane, 11.6 parts of phthalic anhydride, 0.07 parts of dibutyltin oxide, and heated under 0.5 SCFH (standard cubic feet per hour) (0.014 m3hr-1) nitrogen flow to 165°C. At 165°C, water started to distil azeotropically. The reaction temperature was increased to 230°C and maintained at such temperature until an acid value < 1.0 was attained. The alkyd was cooled to 110°C. To this resin, 30.9 parts of dimethyl malonate was added and the temperature was increased to 180 °C. Minimum amount of toluene was added to distil methanol azeotropically. At 150°C, methanol started to distil out. The reaction temperature was kept at 180°C to collect all the methanol. Once the ethanol stop coming, the reaction was cooled to 110°C. To this resin 20.2 parts of methyl epoxy soyate is added. The temperature increased to 180 °C. Methanol started to distill out due to the transesterification of methyl ester at the chain end. The reaction was held at 180 °C to distill out all methanol. The nitrogen flow was increased to 2 SCFH (0.057 m3hr-1) to remove all the toluene while cooling. The epoxy functional malonated alkyd was filtered and stored. The resulting resin had 98 % non-volatile material (NVM); density 9.40 lb/gallon, Gardener-Holdt viscosity of Z5-Z6, an acid value of 0.42; a number average molecular weight (Mn) of 2500; a weight average molecular weight (Mw) of 8500; and a polydispersity of 3.4.

[0060] Thus, the invention has been described by reference to certain embodiments discussed above. It will be recognized that these embodiments are susceptible to various modifications and alternative forms well known to those of skill in the art.

[0061] Further modifications in addition to those described above may be made to the structures and techniques described herein without departing from the spirit and scope of the invention. Accordingly, although specific embodiments have been described, these are examples only and are not limiting upon the scope of the invention.

WHAT IS CLAIMED IS:

1. A method for applying a RMA crosslinked coating with improved adhesion, comprising the steps of
   I. providing a RMA crosslinkable composition comprising
      f) one or more crosslinkable components comprising a reactive component A with at least two acidic protons C-H in activated methylene or methine groups, preferably predominantly malonate
      g) a reactive component B with at least two activated unsaturated C=C groups, preferably acryloyl and
      h) a catalyst C for catalyzing the RMA crosslinking reaction between components A and B, preferably a carbondioxide blocked strong base,
      i) optional reactivity moderator D and
      j) optional organic solvent T,
   II. applying on the substrate surface a layer of an epoxy primer comprising an epoxy functional polymer binder and a crosslinker, wherein adhesion of the RMA crosslinked coating to the epoxy primer layer is improved by said primer comprising after curing functional groups X reactable with crosslinkable component A or B of the RMA crosslinkable composition or a precursor of functional groups X, preferably a moisture deblockable precursor,
   III. at least partial curing of the primer layer,
   IV. applying, over the at least partially cured primer layer, a coating layer of the RMA crosslinkable composition and
   V. curing the coating layer.

2. The method of claim 1 wherein the primer is an epoxy primer that is formulated with excess amount of amine crosslinking groups relative to epoxy functional groups of the epoxy functional polymer and/or said epoxy primer is modified by addition of a amine component comprising amine functional groups X or a precursor thereof so that said epoxy primer layer after curing has free primary or secondary amine functional groups X or precursors thereof.

3. The method of claims 1 - 2 wherein the RMA crosslinkable composition comprises a crosslinkable component with reactive components A being predominantly malonate or an acetoacetate, preferably malonate, and a crosslinkable component with reactive components B being an acryloyl and the one or more functional groups X are reactable with malonate or acetoacetate and/or with the acryloyl.

4. The method of claims 1 – 3 wherein the primer is modified by addition to the primer of a polyfunctional compound comprising one or more functional groups X reactable with component A or component B of the RMA crosslinkable composition and also one or more groups chemically or physically binding with the epoxy functional binder or its crosslinker before, during or after curing, said one or more functional groups X being a primary or secondary amine, a thiol, isocyanate, epoxy or a RMA reactable component A' or B' or oligomers or polymers of components A' or B' which are same or different from the reactive components A and/or B in the RMA crosslinkable components.

5. The method of claims 1 - 4 wherein the epoxy primer is modified with a polyfunctional moisture deblockable primary or secondary amine, preferably polyfunctional ketimine, aldimine or oxazolidine.

6. The method of claim 5 wherein the epoxy primer composition is modified by addition of polyfunctional compound in an amount not exceeding 20, 15, 10 or preferably 5 wt% relative to the total solids weight of the primer composition.

7. The method of claims 1 - 6 wherein the primer is modified by a polyfunctional RMA crosslinkable component A or B, preferably triacetoacetate and/or a polyfunctional compound comprising a free primary or secondary amine functional group or precursor thereof, preferably moisture deblockable precursors thereof, preferably a polyfunctional ketimine, aldimine or oxazolidine or combinations or reaction products thereof.

8. The method of claims 1 - 7 wherein comprising adding to the primer a RMA crosslinkable component comprising a reactive component A or B preferably having a

molecular weight Mw of at least 400, more preferably at least 700, 1000 or even 2000 dalton.

9. The method of claim 8 wherein the primer comprises RMA crosslinkable component comprising as reactive component A predominantly malonate.

10. The method of claim 8 wherein the primer comprises RMA crosslinkable component comprising as reactive component A two or more acetoacetates.

11. The method of claim 8 wherein the primer comprises RMA crosslinkable component comprising as reactive component B two or more acryloyl groups.

12. The method of claim 1 – 11 wherein the primer comprises an adhesion promotor P having the general structure X-R-Y wherein R is an optional bridging group and Y is a functional group reacts to the epoxy binder or its crosslinker during curing or is physically bonded to the epoxy binder after curing.

13. A primer composition for use in the method according to claims 1 – 12 comprising an epoxy functional binder, a crosslinker and a polyfunctional component as described in claims 1 – 12 as adhesion promotor wherein said polyfunctional component is reacted or reactable with the epoxy binder or its crosslinker in the primer curing conditions or is a separate non reacted component which is physically bonded in the cured primer.

14. A composition for use in an epoxy primer for improving adhesion of a RMA crosslinkable coating on an epoxy primer layer said composition comprising one or more primer adhesion improvers selected from a polyfunctional RMA crosslinkable component A’, in particular tri- or tetra-acetoacetate, or a polyfunctional reactive component B’, in particular a tri- or tetraacrylate, a polyfunctional component comprising a two or more free primary or secondary amine functional group or precursor thereof, preferably moisture deblockable precursors thereof, preferably a polyfunctional ketimine, aldimine or oxazolidine or combinations or reaction products thereof.

15. Use of the composition of claim 14 for improving adhesion of a RMA crosslinkable coating on an epoxy primer layer.


R'O-C(=O)-CH=CH2
R-NH
Primer network
R'O-C(=O)-CH2-CH2
R-N
Primer network

Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/058540

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D167/02 C08J3/24 C09D163/00
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)
C08L C08G C08F C09D C08J C09J

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 A	WO 2013/050623 A1 (NUPLEX RESINS BV [NL]) 11 April 2013 (2013-04-11) page 16, line 20 - page 17, line 8; claims	14 1-13,15
X A	US 2006/078742 A1 (KAUFFMAN THOMAS F [US] ET AL) 13 April 2006 (2006-04-13) claims examples 1,6	14,15 1-13

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☒ 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 11 July 2016	Date of mailing of the international search report 18/07/2016
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 Schlicke, Benedikt

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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