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## DESCRIPTION

**[0001]** The invention relates to a coating system for improving adhesion of a RMA crosslinked coating to a substrate. The invention further relates to the use of a primer composition for improving adhesion of RMA crosslinkable top coating compositions, to a method for coating a substrate and to the improved coated substrates obtainable by the invention.

**[0002]** RMA crosslinkable compositions are compositions comprising at least one RMA crosslinkable component comprising 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 RMA 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 CO<sub>2</sub> 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 applications on metal surfaces.

**[0005]** It is known in the coating industry to provide on the metal surface a primer layer or to improve adhesion with known metal pretreatments like silane treatment.

**[0006]** 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.

**[0007]** WO2016/166371 describes a method for improving adhesion of a RMA crosslinked coating comprising the steps of I) providing an RMA crosslinkable composition comprising, 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 RMA crosslinkable component A or B of the RMA crosslinkable composition.

**[0008]** However, it is inconvenient to have to modify existing epoxy primers and more importantly, there is a desire to further improve the adhesion of RMA coating compositions.

**[0009]** According to the invention this problem has been solved by a coating system comprising I. a primer coating composition and II. a RMA crosslinkable coating composition. The primer coating composition comprises a) a binder component PA that contains primary amine functionality blocked with a ketone or aldehyde, preferably a ketone, b) a binder component PB that contains acetoacetate or acetoacetamide, preferably acetoacetate-, functional groups, which components PA and PB form an organic binder network in a cured primer coating. The primary amine functionality blocked with a ketone or aldehyde are ketimine or aldimine functional groups. The RMA crosslinkable coating composition comprises a) a component A with at least two acidic protons C-H in activated methylene or methine groups, b) a component B with at least two activated unsaturated C=C groups, c) a catalyst C for catalyzing the RMA crosslinking reaction between components A and B, d) preferably a reactivity moderator D, which RMA components A and B form an organic binder network in a cured RMA crosslinked coating. The inventors have found a very good adhesion of the cured RMA crosslinked coating to the primer layer and the coating system provides improved adhesion of the cured RMA crosslinked coating on substrates, in particular to polar substrates such as for example metal substrates.

**[0010]** In another aspect, the invention relates to the use of the specified primer coating composition for improving adhesion of a RMA crosslinkable coating composition, in particular to polar substrates such as for example metal substrates.

**[0011]** In yet another aspect, the invention relates to a method for coating a substrate and to coated substrates coated with the coating system of the invention.

**[0012]** Suitable RMA crosslinkable compositions are known in the art. WO11124663, WO11124664 and WO11124665 describe RMA crosslinkable compositions with latent base catalyst comprising carbon dioxide blocked base catalyst which generate a strong base on carbon dioxide deblocking in the coating layer. WO14166880 describes RMA crosslinkable compositions with a catalyst that does not rely on carbon dioxide deblocking, which is particularly suitable for layers where evaporation is hindered, for example for thicker layers. WO13050622, WO13050623, WO13050624 and WO13050574 describe RMA crosslinkable compositions with special pot-life and open time moderators. WO16166361, WO16166381 and WO16166382 describe RMA crosslinkable composition suitable for use in flooring, RMA crosslinkable composition with dual curing properties and RMA crosslinkable composition with easy to clean properties. In particular reference is made to the above identified prior art concerning 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 applicable unless described otherwise herein. Most important features are described below in summary.

**[0013]** In general it is preferred that component A is malonate or acetoacetate, preferably

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

**[0014]** The components A and B are preferably built into a polymer chain or pending or terminal pending on a polymer chain. Preferably, the one or more RMA 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.

**[0015]** The one or more RMA crosslinkable components can be monomeric but preferably at least one RMA crosslinkable component is a polymeric component with a weight average molecular weight  $M_w$  of at least 250 g/mol, preferably a polymer having  $M_w$  between 300 and 5000, more preferably between 400 and 4000 or 500 and 3000 g/mol (as determined by GPC).

**[0016]** The relative amounts of the RMA crosslinkable components in the RMA crosslinkable composition are chosen such that the molar ratio of activated unsaturated reactive group C=C in component B to the activated acidic reactive groups C-H in component A is between 0.5 and 2 and preferably between 0.75 - 1.5 or 0.8 - 1.2. In case a reactive diluent 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 RMA crosslinkable components.

**[0017]** 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 for improving open time and hence working time of application of a coating composition.

**[0018]** The X-H group in component D, preferably an N-H group containing component, has a  $pK_a$  (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  $pK_a$  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.

**[0019]** 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, imidazole or uracil, preferably chosen from the group of succinimides, benzotriazoles and triazoles.

**[0020]** 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 RMA 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.

**[0021]** In principle the RMA crosslinking reaction can be catalysed by any base known in the art. Some of the usual Michael catalysts are alkali metal hydroxides, alkali metal alkoxides, quaternary ammonium hydroxides (such as tetraalkyl ammonium hydroxides), and amine compounds (such as diaza compounds, guanidine compounds, amidines including cyclic amidines, pyridine, imidazoline). Suitable catalysts are for example described in EP1462501.

**[0022]** 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 CO<sub>2</sub> it is preferred for use in coating layers with a thickness up to 500, 400, 300, 200 or 150 micrometer.

**[0023]** A homogeneous base catalyst C, which is more suitable for thicker coating layers, is described in EP0326723 which is a catalyst consisting of the combination of a tertiary amine and an epoxide or in PCT/EP2014/056953 describing a homogeneous catalyst C being a salt of a basic anion X<sup>-</sup> from an acidic X-H group containing compound wherein X is N, P, O, S or C, and wherein anion X<sup>-</sup> is a Michael Addition donor reactable with component B and anion X<sup>-</sup> 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.

**[0024]** 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 essentially free of acidic components.

**[0025]** The RMA composition may comprise one or more organic solvents 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 alkyl acetate (preferably butyl or hexyl acetate), alcohol (preferably C<sub>2</sub> - C<sub>6</sub> alcohol), N alkyl pyrrolidine, glycoether, Dipropylene Glycol Methyl Ether, Dipropylene Glycol Methyl Ether, Propylene Glycol Methyl Ether Acetate, ketones etc. or In a preferred embodiment an alcohol is used as solvent comprising 2 to 12 carbon atoms as this may improve open time.

**[0026]** 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 weight of the RMA crosslinkable components A and B.

**[0027]** 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 diluents which react with RMA crosslinkable components A or B. The one or more reactive diluents 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 group (C=C), most preferably alkyl acetoacetates, dialkyl malonates, 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.

**[0028]** Crosslinking systems based on combinations of ketimine- and acetoacetate functional binder components are known in the art, and descriptions of ketimine and acetoacetate functional components can be found in US5011994 or EP0199087.

**[0029]** US5011994 describes a colorless ketimine or an adduct thereof and the use as a cross-linking agent in a curable coating based on resins containing functional groups such as anhydride, epoxy, isocyanate, acetoacetate and 1,3 ethylenically unsaturated carbonyl, wherein the ketimine is the adduct of a polyamine having a primary and a secondary amino group and containing at least 3 carbon atoms in a linear chain between both amino groups, and a ketone containing not more than 8 carbon atoms and having methylene groups adjacent to the carbonyl group.

**[0030]** EP0199087 describes liquid coating composition based on a polyacetoacetate and a polyamine having primary and/or secondary amino groups and blocked with a ketone or an aldehyde having not more than 18 carbon atoms forming a polyketimine, said composition is characterised in using a specific polyacetoacetate with acetoacetate groups present as ester of hydroxyalkyl acrylate, hydroxyalkyl methacrylate or allyl alcohol structural units.

**[0031]** The coating system according to the invention preferably comprises I. a primer coating composition comprising a) a binder component PA that contains primary amine functionality blocked with a ketone or aldehyde, preferably a ketone, b) a binder component PB that contains acetoacetate or acetoacetamide, preferably acetoacetate-, functional groups, which components PA and PB form an organic binder network in a cured primer coating and II. a RMA crosslinkable coating composition forming an organic binder network in a cured RMA crosslinked coating.

**[0032]** The primer coating composition further may comprise one or more other binder components PC that are co-reactive with component PA or PB, preferably in an amount less than 20 wt%, preferably less than 10 wt% and more preferably less than 5 wt% relative to the total weight of the binder solids in the primer coating composition. Preferably the ketone or aldehyde, preferably the ketone, in component PA is volatile. The boiling point of the ketone or

aldehyde is preferably below 200°C, preferably below 160°C, 140°C, or even below 120°C. A volatile ketone or aldehyde has the advantage that it easily evaporates from the primary coating layer driving the deblocking equilibrium to completion and thus providing a rapid curing of the primer layer. A ketone is preferred because aldehydes tend to be smelly. Ketones are good leaving groups. The primary amine on the binder component PA, formed after deblocking of the ketone, is able to form an enamine bond in combination with the acetoacetate or acetoacetamide functional groups of component PB.

**[0033]** It is preferred that the number average functionality  $F_n$  of ketimine or aldimine groups in component PA is at least 2, preferably 3 and more preferably at least 4.  $F_n$  is preferably below 20, preferably below 10, and more preferably below 6. Further, the ketimine or aldimine equivalent weight of component PA is preferably at least 120 and preferably at least 150 gr/mole and typically below 2000, preferably below 1000 gr/mole. The functionality  $F_n$  is the average number of functional groups per chain and is the number average molecular weight  $M_n$ , as determined by GPC, divided by the equivalent weight EQW, i.e. the average molecular weight per functional groups, determined by titration of the functional groups in the manner known in the art. The functionality  $F_n$  is preferably chosen high in view of crosslinking density but should not be chosen too high in view of having an acceptable potlife because high functionality results in high reactivity decreasing the potlife.

**[0034]** A preferred component PA is the reaction product of a) an amine compound according to formula I:  $H_2N \{-(CH_2)_n-NH\}_m-(CH_2)_n-NH_2$  with  $n$  preferably being 2 or 3, and  $m$  preferably being 1 or 2, most preferably diethylene triamine, b) epoxides, isocyanates or electro-deficient unsaturated C=C double bonds, preferably acrylates, having a reactive functionality of preferably at least 2 towards the secondary amine group -NH in the amine compound of formula I, c) a ketone or aldehyde blocking the primary amine groups of the amine compound. Preferably, the component b) above is a di-epoxy, for example Bisphenol A diglycidyl ether. A suitable commercially available ketimine functional component PA is for example Setalux 10-1440.

**[0035]** In the coating system according to the invention the number average acetoacetate/acetoacetamide functionality  $F_n$  of component PB typically is at least 2, preferably at least 3, more preferably at least 4 and preferably less than 20, more preferably less than 10. The acetoacetate or acetoacetamide equivalent weight EQW of component PB is preferably at least 100, more preferably at least 200, even more preferably at least 300, and preferably at most 2500, more preferably at most 1500, most preferably at most 1200 gr/mol. The functionality  $F_n$  and EQW of component PB is similarly defined as described above for the component PA. Also for the primer component PB, the functionality  $F_n$  is preferably chosen high in view of the crosslinking density but should not be chosen too high in view of having an acceptable potlife because high functionality results in high reactivity decreasing the potlife.

**[0036]** In the coating system according to the invention component PB comprises an acrylic (co-)polymer in which the acetoacetate functional group is introduced a) through (co-)polymerization of an acetoacetate- or acetoacetamide functional (meth-)acrylic

comonomer, for example acetoacetoxyethylmethacrylate, or b) wherein the acetoacetate functional group is introduced by transesterification of an acetoacetate-ester of a low molecular weight alcohol, with a polyfunctional hydroxyl structure of low, medium or high molecular weight typically below 1000, preferably below 500, more preferably below 250 gr/mole.

**[0037]** The low molecular weight alcohols can be diols, triols as for example trimethylol propane, tetraols, or higher functionality materials; higher molecular weight structures can be built by either using prebuild higher molecular weight polyols to be used for acetoacetylation, or components with hydroxyl functionality left after acetoacetylation can be further extended in molecular mass through OH-reactive components. Besides transesterification, reaction of hydroxyl- or amine-functional structures with ketene or diketene can also be used to create acetoacetate or acetoacetamide functional groups, respectively. Setal 26-3701 is an acetoacetate functional material which has a very low molecular weight and a very low viscosity since it is trimethylol propane TMP reacted with t-butyl acetoacetate (t-BAA) comprising, about 1 mole TMP to 3 moles of t-BAA.

**[0038]** Component PB can also be mixtures of different components PB. In a particular embodiment a mixture of high molecular weight acetoacetate functional polymer with a low molecular weight acetoacetate functional polymer can be used; for example an acetoacetate functional acrylic resin combined with TMP-tri-acetoacetate as described in the examples using Setal 26-3705 (an acetoacetate functional polyester) and Setal 26-3701 (tri-methyl propanol (TMP) functionalized with acetoacetate). Component PA can also be mixtures of different components PA.

**[0039]** The primer composition component PB can be a polyacrylic or polyester, preferably polyacrylic, resin comprising acetoacetate functional groups and the component PA preferably is ketimine modified acrylic or epoxy.

**[0040]** In the coating system the total amount of the binder component PA, binder component PB and optional other binder components PC in the primer composition is typically at least 50 wt%, preferably at least 60, 80 or 90 wt% relative to the total dry solids weight of the primer composition not including pigments. The primer formulation optionally also contains organic solvents, (anti-corrosive) pigments, fillers, and further additives typical for coating applications, as generally known to those skilled in the art. Preferably the powder composition comprises a volatile organic solvent or a mixture of solvents, preferably containing a ketone.

**[0041]** The ratio of acetoacetate or acetoacetamide functional groups in component PB to ketimine or aldehyde functional groups in component PA, is between 1:10 and 10:1, preferably between 1:5 and 5:1, more preferably between 1:3 and 3:1, most preferably between 1:2 and 2:1. In view of the stoichiometry of the reactive groups of components PA and PB and making optimal use of the crosslinkable functional groups in the composition it is preferred that the ratio is close to 1. An excess of functional groups PA or PB is however a possibility. In a preferred embodiment an excess of ketimine or aldimine functional groups is used.

**[0042]** The coating system according to the invention is used for preparing a coating on a substrate wherein a layer of the RMA crosslinkable composition is applied onto the primer coating layer. The coating system can be in the form of a kit of parts comprising one or more parts comprising the components PA and PB of the primer coating composition and one or more separate parts comprising the components A, B and C of the RMA crosslinkable composition.

**[0043]** The invention also relates to the use of a primer coating composition comprising a ketimine or aldimine functional binder component PA, an acetoacetate- or acetoacetamide functional binder component PB and optionally an organic solvent T1 as a primer on a substrate for improving adhesion of a RMA crosslinkable coating.

**[0044]** The invention further relates to a method for applying a RMA crosslinked coating on a substrate, comprising the steps of a) applying on a surface of a substrate, preferably a polar substrate and more preferably a metal substrate, a layer of a primer coating composition as described above, b) at least partially curing the layer of the primer coating composition to form a primer layer, preferably at ambient conditions, preferably at temperatures between 10 and 50°C, c) applying over the primer layer, a layer of the RMA crosslinkable coating composition, preferably as a top coating layer, d) curing the RMA crosslinkable coating layer, preferably at ambient conditions, preferably at temperatures between 10 and 50°C.

**[0045]** At least partially curing includes at least partially drying to form a primer layer that still contains reactive functional groups when applying a layer of the RMA crosslinkable coating composition. As a preferred minimum, a minimum flash time is used between the primer application and the application of the RMA crosslinkable layer, typically a 10 minute flash to evaporate fast evaporating solvents from the primer coating film.

**[0046]** In a particular embodiment the primer layer is only partially cured when applying a layer of the RMA crosslinkable coating composition. This not only saves time but also improves the adhesion with the later applied RMA crosslinkable coating layer. In view of coating appearance it may be advantageous to at least have some degree of curing. The degree of curing in partial curing can be established by the skilled person for example by taking less than the normal time needed for full curing and conversion of functional groups can be measured e.g. by spectroscopic techniques.

**[0047]** The curing temperatures both for the primer and for the RMA crosslinkable coating layer can be well above ambient conditions, but the particular advantage of this coating system is that it can be cured at ambient conditions. So the curing temperatures can be between 0 and 100°C, but preferably between 10 and 70°C, more preferably between 10 and 50°C. The primer curing is typically done at ambient conditions and drying/curing overnight, i.e. between 8 and 20 hours. However, faster curing can be achieved by forced drying at elevated temperatures.

**[0048]** The primer can be applied to a variety of substrates, in particular the substrate could be

another coating layer. Coating layers suitable as substrates for the primer include two-component epoxy-amine coatings, cathodic electro-deposition (CED) coatings, two-component polyurethane coatings and other commonly used 1K or 2K coatings systems. Metals are suitable substrates for the primer, especially steel substrates including all types of pretreated steel such as electrocoated, zinc (galvanized), and phosphated steel; aluminium substrates including chrome treated and non-chrome treated aluminum. In view of the low curing temperature, the coating system can be used to coat more heat sensitive substrates. The substrate can be an apolar substrate such as for example plastic substrates. Non-limiting examples are ABS substrates, polycarbonate substrates, ABS/polycarbonate substrates, glass- and carbonfiber reinforced plastics or composites, SMC (sheet molding compound) such as polyester and glass fiber combinations, especially those used in automotive applications, poly(ethylene terephthalate), poly(butylene terephthalate), polyamide-6, polyamide-6.6, (thermoplastic) polyolefins, poly(vinyl chloride), poly(methyl methacrylate) and polystyrene. The primer may also be applied on multisubstrate assemblies composed of metal and/or plastic parts with various different pretreatments and/or coatings including those mentioned above. Most preferably the substrate is metal. The RMA coating layer may not be the topcoat and could also be coated with a further coating layer, but preferably the RMA coating layer is the top coating layer, in particular when using a blocked catalyst such as for example the carbon-dioxide blocked latent base catalyst.

**[0049]** The invention also relates to a coated substrate having improved adhesion and resistance against weathering comprising a primer and a coating layer formed from the coating system according to any of the embodiments described above.

## **EXAMPLES**

**[0050]** The following is a description of certain embodiments of the invention, given by way of example only.

### **Adhesion test:**

**[0051]** 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 35%, but not significantly greater than 65% is affected.

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

**Metal substrate:**

[0052] To test the adhesion of given examples and comparative examples, films were applied onto a metal substrate Bonderite<sup>®</sup> 1000. Bonderite<sup>®</sup> is a trade name of the German producer "Henkel".

**General procedure for preparation of RMA crosslinkable paint**

[0053] A malonate containing polymer (RMA crosslinkable component A) is mixed with TMPTA (Trimethylolpropane triacrylate) (RMA crosslinkable component B) and the thinner n-propanol and optionally with pigments or other coating additives and stirred till a homogenous coating composition was obtained. Prior to application as a coating, all mentioned formulations were activated by adding the stated amount of latent base catalyst which is a tetrabutyl ammoniumhydroxide TBAH solution reactively blocked with di-methylcarbonate or di-ethylcarbonate, with a base concentration of 0.7 to 0.928 meq/g solution (see procedure for preparation of catalyst solutions).

**Preparation of malonated polyester resins MPE1**

[0054] 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 stannic 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. The resins was diluted with butyl acetate to 85% solids, to yield a material with OH value of 16 mg KOH/g, GPC Mn = 1750 g/mole, and a malonate equivalent weight of 350 (active C-H EQW 175).

**Preparation of malonated alkyd MA1**

[0055] MA1 is a malonated alkyd (Acure 510-300, available from Allnex) 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 g/mole and a Mw of 4350 g/mole. The malonate equivalent weight of this material is 360 (active C-H equivalent weight 180).

**Paint preparation: paints A, B and C**

[0056] **Paint A** was prepared by mixing the components as described in Table 1 below. Paint A is based on malonated polyester resin MPE1 and TMPTA.

Table 1: Real Michael Addition Clear Paint

Component	Paint A
<u>MPE1</u>	10.00
TMPTA	3.47
Silmer ACR-D2**	0.03
Methyl propyl ketone	5.00
**Silmer ACR-D2 is reactive silicone comprising multi-functional or linear-difunctional silicone pre-polymers with reactive terminal end groups being acrylates.	

[0057] **Paint B** was prepared by making a mill base using TMPTA (550-100 in Table 2) and then letting it down to make a Real Michael Addition paint with malonated alkyd resin MA1 (510-300 in Table 2), TMP-tri acetoacetate, (510-400 in Table 2) and TMPTA (550-100 in Table 2).

Table 2: Real Michael Addition White Paint B

Mill base	
550-100	1005
Disperbyk 163	63.6
Kronos 2310	2112
Letdown	
510-300	1390
510-400	245
550-100	24
Isopropanol	227
80:20 MAK:IBIB	433
<b>TOTAL Part A</b>	<b>5499.25</b>

MAK:IBIB is methylamylketone:isobutylisobutyrate.  
 Disperbyk 163 is: Wetting and dispersing additive from Byk  
 Kronos2310 is: titanium dioxide pigment

#### **Catalyst preparation examples:**

[0058] Catalyst compositions were prepared by mixing components specified in Table 3.

Table 3: Catalyst compositions

<b>Component</b>	<b>Catalyst 1</b>	<b>Catalyst 2</b>
Aqueous TBAH (40%)	35.8	
Aqueous TBAH (55%)		267.6
Diethylcarbonate	0	121.19
Dimethylcarbonate	21.7	0
n-propanol	0	182.4
2-propanol	1.5	0
DI Water	19.2	29.88

#### **Preparation of acrylic Ketac primer Example 1.**

[0059] A clear primer paint was made by thoroughly mixing 224.75g of an acetoacetate functional acrylic resin, Setalux 17-1450 with 45g of methyl amyl ketone and mixing fifty grams thereof with 9.27g of a ketimine functional compound A, and 5.43g of methyl isobutyl ketone.

[0060] Ketimine functional compound A is a tetrafunctional ketimine compound, which is the reaction product of 2 moles of DETA (diethylenetriamine) on 1 mole of DGEBA (Bisphenol A diglycidyl ether) wherein the primary amine groups are blocked as ketimine by reacting with excess MIBK (Methyl isobutyl ketone).

[0061] The clear primer paint of Example 1 was sprayed onto a Bonderite® 1000 treated steel panel and allowed to dry overnight (16 hours). The next day 58.49g of Paint A was catalyzed with 1.97g of Catalyst 1, thoroughly mixed and then sprayed onto the primed panel and allowed to air-dry overnight (16 hours). The next day adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be very good, ASTM rating 0.

#### **Comparative Example 1: epoxy primer.**

**[0062]** An epoxy primer, Aquapon 97-137 was activated with hardener 97-1200 at the volume ratio suggested by the producer (PPG) and sprayed onto a Bonderite<sup>®</sup>1000 steel panel and allowed to air-dry overnight (16 hours). The next day 58.49g of Paint A was catalyzed with 1.97g of Catalyst 1, thoroughly mixed and then sprayed onto the epoxy primed panel and allowed to air-dry overnight (16 hours). The next day adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be very bad, ASTM rating 5.

### Preparation of polyester Ketac primer Example 2.

**[0063]** A pigmented polyester Ketac primer was made by first making a millbase as shown in Table 4 and then making the letdown also shown in Table 4 and adding and mixing to 84.15g thereof (Part A in Table 4) an amount of 15.85g of a ketimine functional compound A.

**[0064]** A mixture of two different acetoacetate functional polyesters (primer binder component PB) were used: Setal 26-3705 is an acetoacetate functional polyester. Setal 26-3701 is trimethyl propanol (TMP) functionalized with acetoacetate. The ketimine functional component PA used in the examples is always the above described ketimine functional compound A. The ratio of Ketimine to acetoacetate functional groups in all examples was 1.21 to 1.

Table 4: Ketac Pigmented Primer

Millbase	Wt.	Description
Setal 26-3705	123.32	AcetoAcetate functional polyester
Setal 26-3701	38.15	AcetoAcetate functional polyester
Disperbyk 110	26.07	Pigment dispersant
Vansil W40	60.78	extender pigment
Vantalc 4000	60.78	extender pigment
R900	283.63	TiO2
Gamma Sperse 80	243.17	Calcium carbonate
Heucophos ZAPP	162.09	phosphate pigment
Bentone SD1	2.01	anti-settling clay
TOTAL	1000.0	

Paint	Weight
Part A	84.15

Setalux 10-1440	15.85	Ketimine functional resin
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Letdown - Part A		Description
Millbase	857.23	
n-Butyl Acetate	70.96	solvent
Melhy Amyl Ketone	70.96	solvent
Dow Paint Additive #3	0.85	surface active additive
TOTAL	1000.0	

**[0065]** The primer was then sprayed onto a Bonderite<sup>®</sup>1000 steel panel and allowed to air-dry overnight (16 hours). The next day 50g of **Paint B** was mixed with 1.34g of Catalyst 2, thoroughly mixed and then sprayed onto the Ketac primed panel and allowed to air-dry overnight (16 hours). After 3 days, adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be very good, ASTM rating 0. Next the panel was placed onto a QCT test cabinet set at 40°C and exposed to condensing humidity for 135 hours. The adhesion was tested again using the cross-cut adhesion test as described in ASTM D3359 and found to be very good, ASTM rating 0.

### Comparative Example 2: epoxy primer.

[0066] An epoxy paint, Devran 201H was activated with hardener at the volume ratio suggested by the producer (IP) and sprayed onto a Bonderite®1000 steel panel and allowed to air-dry for 48 hours. The epoxy primed panel was then painted with a Real Michael Addition paint by mixing 50g of Paint B with 1.34g of Catalyst 2, thoroughly and then sprayed onto the epoxy primed panel and allowed to air-dry overnight (16 hours). After 3 days, adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be okay, ASTM rating 3. Next the panel was placed onto a QCT test cabinet set at 40°C and exposed to condensing humidity for 135 hours. The adhesion was tested again using the cross-cut adhesion test as described in ASTM D3359 and found to be very bad, ASTM rating 5.

**Example 3 :**

[0067] The primer described in Table 4 was spray-applied to plastic substrates listed in Table 5. The primer was then baked for 30 minutes at 65°C. The primed panels were then painted with a Real Michael Addition paint by mixing 50g of Paint B with 1.34g of Catalyst 2. The panel was then baked for 30 minutes at 65°C. Adhesion was tested using the cross-cut adhesion test as described in ASTM D3359 and found to be good, ASTM rating 0. Next the panels were placed onto a QCT test cabinet set at 40°C and exposed to condensing humidity for 168 hours. The adhesion was tested again using the cross-cut adhesion test as described in ASTM D3359 and found to be good, ASTM rating 0.

Table 5 : plastic substrates

ABS
Polycarbonate
Polycarbonate/ABS blend

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.

## REFERENCES CITED IN THE DESCRIPTION

### Cited references

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## **Patentkrav**

### **1. Coatingsystem omfattende**

I. en primercoatingsammensætning omfattende

- 5 a. en bindemiddelkomponent PA, der indeholder primær aminfunktionalitet blokeret med en keton eller aldehyd, fortrinsvis en keton,  
b. en bindemiddelkomponent PB, der indeholder acetoacetat eller acetoaceta-  
mid, fortrinsvis acetoacetat-, funktionelle grupper,  
hvilke komponenter PA og PB danner et organisk bindemiddelnetværk i en  
10 hærde primercoating og

II. en RMA tværbindelig coatingsammensætning omfattende,

- a) en komponent A med mindst to sure protoner C-H i aktiverede methylen-  
eller methingrupper,  
b) en komponent B med mindst to aktiverede umættede C=C-grupper,  
15 c) en katalysator C til at katalysere RMA-tværbindingsreaktionen mellem kom-  
ponenterne A og B,  
d) fortrinsvis en reaktivitetsmoderator D,  
hvor RMA-komponenterne A og B danner et organisk bindemiddelnetværk i en  
20 hærde RMA-tværbundet coating

**2. Coatingsystem ifølge krav 1, hvor primercoatingsammensætningen yderli-  
gere omfatter en eller flere andre bindemiddelkomponenter PC, der er co-re-  
aktive med komponent PA eller PB, fortrinsvis i en mængde mindre end 20  
vægt%, fortrinsvis mindre end 10 vægt% og mere fortrinsvis mindre end 5  
25 vægt% i forhold til den samlede vægt af bindemiddelfaststofferne i primercoa-  
tingsammensætningen.**

**3. Coatingsystem ifølge krav 1 eller 2, hvor ketonen eller aldehydet, fortrinsvis  
ketonen, i komponent PA er flygtigt, fortrinsvis med et kogepunkt under 200°C,  
30 fortrinsvis under 160°C, 140°C eller endda under 120°C.**

4. Coatingsystem ifølge krav 1-3, hvor den antalsgennemsnitlige funktionalitet  $F_n$  af ketimin- eller aldimingrupper i komponent PA er mindst 2, fortrinsvis 3 og mere fortrinsvis mindst 4, og hvor  $F_n$  fortrinsvis er under 20, fortrinsvis 10, og mere fortrinsvis 6 og hvor fortrinsvis ketimin- eller aldiminækvivalentvægten af komponent PA er mindst 120 og fortrinsvis 150 g/mol og typisk under 2000, fortrinsvis under 1000 g/mol, hvor  $F_n$  er bestemt som defineret i specifikationen.

5. Coatingsystem ifølge krav 1-4, hvor i komponent PA omfatter reaktionsproduktet af

a. en aminforbindelse ifølge formel I:



15 hvor  $n$  fortrinsvis er 2 eller 3, og  $m$  fortrinsvis er 1 eller 2, mest fortrinsvis diethylentriamin

b. epoxider, isocyanater eller elektrodeficiente umættede C=C-dobbeltbindinger, fortrinsvis acrylater, med en reaktiv funktionalitet over for sekundær amingruppe -NH i aminforbindelsen på fortrinsvis mindst 2,

20 c. en keton eller aldehyd, der blokerer de primære amingrupper i aminforbindelsen.

6. Coatingsystem ifølge krav 1-5, hvor den antalsgennemsnitlige acetoacetat-/acetoacetamidfunktionalitet  $F_n$  af komponent PB er mindst 2, fortrinsvis mindst 3, mere fortrinsvis mindst 4 og fortrinsvis mindre end 20, mere fortrinsvis mindre end 10, og acetoacetat- eller acetoacetamidækvivalentvægten af komponent PB er fortrinsvis mindst 100, mere foretrukket mindst 200, endnu mere foretrukket mindst 300 og fortrinsvis højst 2500, mere fortrinsvis højst 1500, mest fortrinsvis højst 1200 gr/mol, hvor  $F_n$  er bestemt som defineret i beskrivelsen.

**7.** Coatingsystem ifølge krav 1 - 6, hvor komponent PB omfatter en acryl(co-)polymer, hvori den funktionelle acetoacetatgruppe er indført

a. gennem (co-)polymerisation af en acetoacetat- eller acetoacetamidfunktionel (meth-)acrylisk comonomer, for eksempel acetoacetoxyethylmethacrylat, eller

b. hvor den funktionelle acetoacetatgruppe indføres ved transesterificering af en acetoacetatester af en alkohol med lav molekylvægt med en polyfunktionel hydroxylstruktur med lav, middel eller høj molekylvægt typisk under 1000, fortrinsvis under 500, mere fortrinsvis under 250 g/mol, hvor molekylvægten måles som defineret i beskrivelsen.

**8.** Coatingsystem ifølge krav 1 - 7, hvor komponenten PB i primersammensætningen er en polyacryl- eller polyester-, fortrinsvis polyacryl-harpiks, der omfatter funktionelle acetoacetatgrupper, og hvor komponenten PA er ketiminmodificeret acryl eller epoxy.

**9.** Coatingsystem ifølge krav 1 - 8, hvor den totale mængde af bindemiddelkomponenten PA, bindemiddelkomponenten PB og eventuelle andre bindemiddelkomponenter PC i primersammensætningen er mindst 50 vægt%, fortrinsvis mindst 60, 80 eller 90 vægt% i forhold til den samlede tørstofvægt af primersammensætningen uden pigmenter.

**10.** Coatingsystem ifølge krav 1 - 9, hvor forholdet mellem funktionelle acetoacetat- eller acetoacetamidgrupper i komponent PB og funktionelle ketimin- eller aldehydgrupper i komponent PA er mellem 1:10 og 10:1, fortrinsvis mellem 1:5 og 5:1 mere fortrinsvis mellem 1:3 og 3:1, mest foretrukket mellem 1:2 og 2:1.

**11.** Coatingsystem ifølge krav 1 - 10, hvor den RMA-tværbindelige coatingsammensætning omfatter en RMA-tværbindelig komponent med komponenter

A, der overvejende er malonat eller et acetoacetat, fortrinsvis malonat, og komponenter B er en acryloyls.

5 **12.** Coatingsystem ifølge krav 1 til 11, i form af et sæt af dele, der omfatter en eller flere dele, der omfatter komponenterne PA og PB i primercoatingsammensætningen og en eller flere separate dele, der omfatter komponenterne A, B og C i den RMA-tværbindelige sammensætning.

10 **13.** Anvendelse af en primercoatingsammensætning omfattende en ketimin- eller aldiminfunktionel bindemiddelkomponent PA, en acetoacetat- eller acetoacetamidfunktionel bindemiddelkomponent PB og eventuelt et organisk opløsningsmiddel T1 som en primer på et substrat til forbedring af adhæsion af en RMA-tværbindelig coating.

15 **14.** Fremgangsmåde til påføring af en RMA-tværbundet coating på et substrat, omfattende trinene med

a) påføring på en overflade af et substrat, fortrinsvis et metalsubstrat, af et lag af en primercoatingsammensætning ifølge et hvilket som helst af kravene 1 til 12,

20 b) i det mindste delvist hærkning af laget af primercoatingsammensætningen til dannelse af et primerlag, fortrinsvis ved omgivende betingelser,

c) påføring over primerlaget af et lag, fortrinsvis et topcoatinglag, af den RMA-tværbindelige coatingsammensætning ifølge et hvilket som helst af kravene 1 til 12,

25 d) hærkning af det RMA-tværbindelige belægningslag, fortrinsvis ved omgivel- sesbetingelser.

30 **15.** Coated substrat omfattende en primer og et coatinglag dannet af coatingsystemet ifølge et hvilket som helst af kravene 1 til 12 eller som kan opnås ved fremgangsmåden ifølge krav 14.