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(54) A CROSSLINKABLE COMPOSITION COMPRISING A LATENT BASE CATALYST AND LATENT BASE CATALYST COMPOSITIONS

KATALYSATOR MIT LATENTER BASIS UND VERNETZBARE ZUSAMMENSETZUNG MIT DEM KATALYSATOR MIT LATENTER BASIS

CATALYSEUR DE BASE LATENTE ET COMPOSITION RÉTICULABLE COMPRENANT LEDIT CATALYSEUR DE BASE LATENTE

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Description

[0001] The present invention relates to a cross-linkable polymer coating composition crosslinkable by Real Michael Addition (RMA) reaction comprising a latent base catalyst composition and to an improved catalyst composition for use in crosslinkable compositions, in particular RMA cross-linkable compositions, which catalyst composition provides improved pot life. The invention further relates to the use of said catalyst composition for curing crosslinkable compositions, in particular cross-linkable coating compositions, at low temperatures, to a process for preparing a coating composition and for preparing a coating and to coatings obtainable by said process.

[0002] A composition crosslinkable by Real Michael Addition (RMA) reaction comprises a component with at least 2 activated unsaturated groups and a component with at least 2 acidic protons C-H in activated methylene or methine groups, that can react and crosslink to each other in the presence of a strong base catalyst. The advantage of RMA crosslinkable compositions in general is that they have a very high curing reaction speed even at room temperature, and can give good film properties, while requiring low VOC levels.

[0003] The crosslinkable composition is a 2-K system, which implies that the crosslinking catalyst is added to and mixed with the crosslinkable components shortly before use. From the moment of mixing, the crosslinking composition is potentially reactive and may start to crosslink. Such crosslinking compositions can be used only relatively shortly before the extent of viscosity build-up is such that the composition can no longer be used well. This effective use time is called the potlife. The potlife is generally considered ended when the viscosity becomes unacceptably high. It depends on the criticality of the application what viscosity is unacceptable. For example spraying is more critical than brushing. A central challenge in developing coating systems, especially those that are cured at low to moderate temperatures, is achieving a good balance between on one hand rapid hardening and crosslinking during application (also referred to as "curing" or "drying") and on the other hand maintaining long pot lives, i.e. the ability to work with the paint without problems for a reasonable amount of time after preparation, at least an hour, but preferably much more.

[0004] For high solids systems containing less solvent to evaporate upon application, this challenge is significantly greater than for low or medium solids systems containing more volatile solvent. High solids systems are preferred or required by law to reduce environmental burden, and/or exposure of the painter to harmful solvent vapours. The preferred solids content is at least 55 wt% (dry weight after crosslinking relative to the total weight of the crosslinking composition), preferably higher.

[0005] Coatings for applications in decorative, vehicle refinish, metal, plastic, marine or protective coatings e.g. require several hours of potlife enabling the applicator to bring the paint composition on a substrate in a well-controlled manner. The viscosity and low solvent content requirements for high solids systems force the resin designer to select resins of lower molecular weight and/or lower glass transition temperatures that will require more reaction with a crosslinker to raise the Tg of the network to levels corresponding to a dry film, in the case of high solids paints. The lower amount of solvent used will create less "physical drying" effects of the film (physical hardening/reduced plastization due to the loss of solvent) than in paints using more volatile solvents, and also, the increase of the reaction rate going from paint to applied coating is less, because the increase of concentration of the reactive groups through the loss of solvent is less helpful. All these phenomena add to the problem that for high solids systems, a combination of fast drying and long pot life is very difficult to achieve, and much more so than in the case of medium or low solids systems.

[0006] A latent base crosslinking catalyst is used to increase this potlife, while allowing fast drying. A latent base catalyst becomes active predominantly only when the composition is applied, for example as a coating.

[0007] CN101879457 and CN 101869844 disclose a solid nanoparticle alkali catalyst comprising a stannic halide and an inorganic alkaline component which can selected from the list including sodiumbicarbonate. The alkali catalyst is used in olefin isomerisation reactions and various other reactions.

[0008] The above described problem has been addressed by Noomen in Progress in Organic Coatings 32 (1997) 137-14 describing the use of latent base catalysed Michael addition as crosslinking reaction for high-solids polymer coating compositions of low VOC. Noomen describes several examples of crosslinking catalysts with the required basicity, for example the amidine types (such as tetra-methylguanidine) 1,5-diazabicyclo (4,3,0) non-5-ene (DBN), 1,8-diazabicyclo (5,4,0) undec-7-ene (DBN), tetra-butylammonium fluoride or in situ formed catalyst from a tertiary amine (like 1,4-diazabicyclo12.2.2]octane: DABCO) with epoxy. Although such prior art catalysts might show quite acceptable curing behaviour in the RMA films, the short potlifes are too limited to get acceptable application times for rolling, brushing and spraying of the coatings, or the drying rate at lower curing temperatures is too low.

[0009] Noomen further describes that, although the film properties (such as durability when using malonate polyesters) looked promising, there were still severe shortcomings with this coating composition, in particular in the field of high solids coatings, because the curing under ambient and forced drying conditions revealed inhibition, speculatively assigned to the interaction of the carbon dioxide from the air with the strong base resulting in a tacky coating surface or inhibition by the interaction with the acidic groups of the substrate resulting in a low degree of cure or a minor adhesion. This was overcome by increasing the amount of catalyst but this resulted in a too short, unacceptable potlife, especially when using high solid formulations and in low temperature applications such as clear coats car refinishing, pigmented topcoats for marine, protective and aircraft, wood coatings, etc. Another problem was often the yellowing of the coating induced especially under stoving conditions.

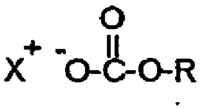
[0010] EP0448154 (also from Noomen) describes to use certain carboxylic acids as a blocking agent for a strong basic catalyst. Although a longer potlife can be achieved, the basic catalyst with carboxylic acids as described in EP448514 provides an insufficient dust- and touch-drying behaviour and a low through-drying especially at ambient conditions. The prior art catalyst does not provide workable potlifes when inhibition problems are to be avoided and does not provide fast free-to-handle coatings, in particular for high solid coatings. Furthermore, deblocking of the catalyst blocked with e.g. carboxylic acids was only applicable at high temperatures.

[0011] Therefore there is still a need for crosslinkable compositions having a high solid content comprising crosslinkable components, preferably RMA crossfinkable polymers, and a latent base crosslinking catalyst that yield a good potlife/drying balance, in particular a workable potlife and a good drying behaviour also at lower temperatures in coating compositions.

[0012] There is also a desire for crosslinkable compositions comprising a catalyst that can be simply cured in ambient conditions as opposed to for example compositions comprising photo-latent amine catalysts, known from T. Jung et al Farbe und Lacke Oct 2003. Such photo-latent amine catalysts that do generate a strong base on UV radiation, are not suitable for coating more complex irregular substrates where parts of the surfaces are not reachable with UV or visible light.

[0013] According to the invention there is provided a crosslinkable polymer coating composition comprising

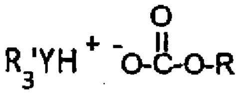
a. 0.1 - 99 wt% of at least one crosslinkable component that is crosslinkable under the action of a base catalyst, (all wt% herein being relative to the crosslinkable composition),
b. a first carbonate salt according to formula 1 as latent base crosslinking catalyst,



$$X^{+}\ {}^{-}O\text{-}\overset{\overset{\displaystyle O}{\parallel}}{C}\text{-}O\text{-}R$$

Formula 1

wherein X^+ represents a non-acidic cation and wherein R is hydrogen, alkyl, or aralkyl group and
c. a second carbonate salt according to Formula 2 as potlife extender:



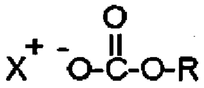
$$R_3'YH^{+}\ {}^{-}O\text{-}\overset{\overset{\displaystyle O}{\parallel}}{C}\text{-}O\text{-}R$$

Formula 2

wherein Y is N or P and wherein each R' can be hydrogen, a substituted or unsubstituted alkyl, aryl or aralkyl group, wherein the second carbonate is present in an amount of at least 5 mole % and preferably at most 500 mole % relative to the molar amount of the first carbonate
d. optionally 0.1 - 70 wt% of solvent, preferably an organic solvent wherein at least 0.5 wt% (relation to total weight of the crosslinkable composition) is a primary alcohol and optionally comprising 0.1 - 10 wt% water
e. optionally 0.1 - 70 wt% of an organic carbonate component according to formula RO-C(=O)O-R wherein R preferably is an alkyl, preferably methyl or ethyl wherein the at least one crosslinkable component comprises 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 and the at least 2 reactive groups of component B are activated unsaturated groups (C=C) and said catalyst composition for starting crosslinking reaction by Real Michael Addition (RMA) upon deblocking of the latent base catalyst b by evaporation of carbon dioxide.

[0014] Further there is provided a catalyst composition for use as a latent base catalyst system in crosslinkable compositions in particular coating composition made from said crosslinkable composition, said catalyst composition being composed of

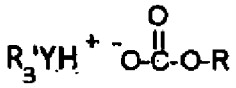
a. a first carbonate salt according to formula 1 as the latent base catalyst



$$X^{+}\ {}^{-}O-\overset{\overset{O}{\|}}{C}-O-R$$

Formula 1

wherein X^+ represents a non-acidic cation and wherein R is hydrogen, alkyl, or aralkyl group and
b. a second carbonate salt according to Formula 2 as a potlife extender :



$$R'_{3}YH^{+}\ {}^{-}O-\overset{\overset{O}{\|}}{C}-O-R$$

Formula 2

wherein Y is N or P, wherein each R' can be hydrogen, a (substituted) alkyl, aryl or aralkyl group, and wherein R can be the same or a different from the R in formula 1.
wherein the second carbonate is present in an amount of at least 5 mole % and preferably at most 500 mole % relative to the molar amount of the first carbonate.
c. optionally a solvent, preferably an organic solvent wherein at least 0.5 wt% (relation to total weight of the crosslinkable composition) is a primary alcohol and which optionally comprises 0.1 - 10 wt% water,
d. optionally an organic carbonate component according to formula RO-C(=O)O-R wherein R preferably is an alkyl, preferably methyl or ethyl.

[0015] The group Y is preferably nitrogen and can be part of a cyclic system including those where a N is linked with a double bond to a neighbouring atom. The R and R' group can be unsubstituted or substituted, but if it is substituted then it should not comprise substituents that substantially interfere with the crosslinking reaction as is known and can be easily established by the skilled person. In particular, acidic substituents, for example carboxylic acids, are preferably present only in insubstantial amounts and are most preferably not included. This similarly applies to substituents on the crosslinkable component and to cation X.

[0016] The first carbonate salt (a) is a latent base catalyst because on drying, the carbonate salt decomposes releasing carbon-dioxide to produce a strong base; either a hydroxide or an alkoxy, or aralkyloxy base. In a pot, in particular in a closed pot, the decomposition takes place only slowly, because the CO_2 cannot escape to shift the reaction equilibria to completion, resulting in a good (long) pot life, whereas during drying of the crosslinkable composition when applied as a coating layer, the base is regenerated quickly resulting in good curing rate upon escape of the CO_2 from the high surface area created.

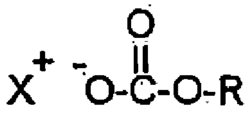
[0017] The second carbonate salts(b) are not initiators for the intended RMA reaction by themselves, since they combine the potential basicity of the anion with an compensating acidic proton on the cationic species, thereby distinguishing from the catalyst carbonate which will generate strongly basic species upon evaporation of CO_2 which can initiate the RMA reaction. The second carbonate in contrast will not act as initiating catalysts but were found to act as pot life extenders. These second carbonate species, upon film formation, lose carbon dioxide and disintegrate in volatile species leaving the film, or remaining without harm. In the crosslinkable composition the cation of the first carbonate salt according to formula 1 preferably has a pKa of at least 11.5, preferably at least 12 and more preferably at least 12.5 and the cation of the second carbonate salt preferably has a pKa of less than 11.5, preferably less than 11. All pKa values herein are defined relative to water irrespective of whether the catalyst composition or the cross-linkable composition have water as solvent or an organic solvent. The pKa values of cations are all well reported or can be tested in the known manner with a "neutral" anion (e.g. chloride).

[0018] The inventors have surprisingly found that crosslinkable compositions comprising substituted carbonate salts as latent crosslinking catalysts in combination with the second carbonate salt as potlife improver provides very good result in providing good balance of longer pot-life even in high solids polymer coating compositions while at the same time having high curing rates during drying and desirably fast drying and hardness build-up behaviour under most if not all curing conditions. Higher amounts of catalysts can be used without significantly affecting the potlife and so the crosslinkable composition can be used in pot-applications of the coating by brushing or rolling or spraying. An extra advantage is the absence of yellowing even under high temperature stoving conditions.

[0019] The use of the second carbonate salt is a significant improvement over an alternative wherein pot life is improved by having an excess of acidic CO_2 as blocking species, because solubility of CO_2 is limited and such an excess would require keeping the composition in pressurized containers which is undesirable in practice. An advantage of the second carbonates is that they will not lead to an increased level of salts and hence will not increase sensitivity to polar components, because the second carbonate decomposes after application in a coating to three neutral species: $R_3NH^+ R^*OCO_2^- \leftrightarrow R_3N + HOR + CO_2$. These neutral species either are volatile and can escape from the coating, or can add to the network, or remain in the film as harmless neutral species. In a preferred embodiment of the second carbonate salt is ammoniumbicarbonate, because it decomposes in entirely neutral species ammonia, water and carbondioxide gas that all can evaporate from the coating (pKa ammonium cation = 9.62). In another preferred embodiment, it is the bicarbonate of a protonated volatile tertiary amine, most preferably triethylamine (pKa = 10.62).

The first carbonate salt

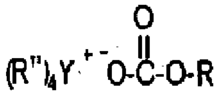
[0020] The latent base catalyst generally is a substituted carbonate salt according to formula 1



$$X^{+}\ {}^{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R$$

Formula 1

wherein X+ represents a nonacidic cation and wherein R is hydrogen, alkyl or aralkyl group. The cation must be nonacidic such that it does not interfere with the base catalyst and can for example be alkali metal, in particular lithium, sodium or potassium, but preferably is a quaternary ammonium or phosphonium carbonate salt according to formula 3,

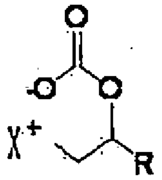


$$(R'')_4Y^{+}\ {}^{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R$$

Formula 3

wherein Y represents N or P (preferably N), and wherein each R" can be a same or different alkyl, aryl or aralkyl group, wherein R and R" can be bridged to form a ring structure or R and/or R" can be a polymer. The R group in the first carbonate of the catalyst a) and/or of the second carbonate preferably is a hydrogen or an alkyl group which preferably is C1 - C4 and most preferably methyl or ethyl. These simple alkyl carbonates can be prepared easily by reaction of corresponding hydroxides with dialkylcarbonates or by the reaction of tertiary amines with dialkylcarbonates in alcohols.

[0021] The catalyst can be a substituted carbonate salt according to formula 4, wherein R can be hydrogen, alkyl-, aryl- or aralkyl group or an oligomer or polymer.



Formula 4

[0022] The catalyst can be incorporated into a polymer. R in formula 4 can be a polymer. Also X can be connected to a polymer, for example X can be a quaternary ammonium or phosphonium wherein one R' group is a polymer, which can for example be obtained by quaternising a polymer, preferably a polyacrylate, comprising a pending tertiary amine, preferably 2-(dimethylamlno)ethylmethacrylate, with a dialkylcarbonate to form a quaternary ammonium carbonate according to formula 1, 3 or 4. Details of the catalysts a) that can be used are described in non-prepublished application PCT/EP2011/055463 and are herewith incorporated by reference.

[0023] In the catalyst composition the catalyst is preferably present in an amount of at least 0.01, preferably at least 0.2, more preferably at least 0.4 meq/gr cat composition.

[0024] The preparation of the quaternary ammonium carbonates is well known in the art. US 6989459and 452635100, describe a process for an in situ method of preparing quaternary ammonium methylcarbonate salts and quaternary ammonium alkylcarbonate salts in high yield from tertiary amines, methanol, and at least one of a cyclic carbonate, an aliphatic polyester, and an ester, and their subsequent conversion to quaternary ammonium bicarbonates, quaternary ammonium carbonates or both in a one-pot reaction.

[0025] Quaternisation of trialkylamine with dialkylcarbonate or cyclic carbonate leads at a high temperature under autogeneous conditions to components of formula 1. Polymers containing tertiary amine groups can also be quaternized with e.g. dimethylcarbonate to a quaternized polymeric ammonium methylcarbonate salt. Using 2-(dimethylamino)ethylmethacrylate (MADAM) as sole monomer or as comonomer in polyacrylates offers a means to get polymers containing tertiary amines suitable for quaternisation with dimethylcarbonate. Many others are possible such as epoxy containing resins modified with secondary amines or isocyanate containing products treated with e.g. 2-dimethylaminoethanol. The described prior art processes and a novel process are herewith incorporated by reference.

[0026] A preferred way to synthesize the catalyst is by reaction of the quaternary ammonium hydroxide with dialkylcarbonate to form a catalyst according to formula 1 or 3 or cyclic carbonate according to formula 4. This is done at room temperature by mixing some molar excess of liquid carbonate with a solution of the ammonium base. The blocking (conversion of hydroxide to alkylcarbonate) can be shown by means of titration with aqueous HCl titration: for the blocked catalyst an equivalence point at a lower pH is found.

The second carbonate salt

[0027] In the catalyst composition the second carbonate b) is present in an amount of at least 5 mole % and preferably at most 500 mole % relative to the molar amount of the first carbonate catalyst (a). Preferably the molar amount of second carbonate b) is at least 10, 20 or 40 mole % and preferably at most 200, 150 and 100 mole % (100% means same molar amount of the first carbonate catalyst a) and potlife extender b).

[0028] In a most preferred embodiment the cation in the second carbonate component is a protonated amine. The protonated amine can be a tertiary amine, a secondary amine, a primary amine, ammonia or a heterocyclic amine. Most preferably the amine is a volatile amine. In a preferred embodiment, it is ammonia; in another preferred embodiment it is a volatile tertiary amine (e.g. triethylamine)

[0029] The anion in the second carbonate preferably is an alkylcarbonate or a bicarbonate, most preferably it is a bicarbonate. In case of alkylcarbonate the alkyl preferably is ethyl or methyl. Most preferably, the second carbonate is ammonium bicarbonate (NH_4HCO_3).

[0030] The catalyst composition may further comprises an organic carbonate component RO-C(=O)O-R wherein R is alkyl, aryl or aralkyl, preferably an alkyl, preferably methyl or ethyl, wherein the molar ratio of the organic carbonate component to the first carbonate catalyst is 0.01 - 50, preferably 0.1 - 20, more preferably 0.15- 10, most preferably 0.25 to 6. It was found that the organic carbonate component acts as a storage shelflife improver for the catalyst composition. It may improve storage stability by counteracting premature loss of carbondioxide during storage, by allowing reformation of the blocked species. This organic carbonate can act as solvent and be part of the solvent of the crosslinkable composition and thus can be present in substantial amount.

[0031] Depending on the choice of the crosslinkable components, in particular components A and B in the RMA system (introduced later), the crosslinkable composition can have a certain amount of an organic solvent or can have no solvent at all. However, the inventors found that particular and unexpected advantage in open time and hardness development can be achieved if in the crosslinkable composition at least part of the solvent is a primary alcohol solvent. The primary alcohol solvent may be included in the catalyst composition which is added to the crosslinkable components before application. The solvent for the crosslinkable components can be a mixture of a non-alcoholic solvent and an alcohol solvent. Preferably, the alcohol is present in an amount of at least 1, preferably 2, more preferably 3, most preferably at least 5, even more preferably at least 10 wt % relative to the total weight of the crosslinkable composition and in view of VOC constraints preferably at most 45, preferably at most 40 wt%.

[0032] The alcohol solvent preferably is one or more primary alcohols, more preferably a mono-alcohol having 1 to 20, preferably 1 - 10, more preferably 1 - 6 carbon atoms, preferably selected from the group of ethanol, n-propanol, n-butanol, n-amyl alcohol and butylglycol. Methanol is less preferred because of the health, environmental and safety risks.

[0033] The catalyst composition may further comprise water in amount between 0.1 - 80 wt%, preferably 1 - 50wt% relative to total weight of the catalyst composition. It was found that, also in case the solvent is organic solvent, a little amount of water in some cases may have a significant improving effect on pot life. It is particularly preferred that the catalyst composition comprise both an organic solvent at least part of which is a primary alcohol and water, preferably from 0.1 - 10 wt% .

[0034] The catalyst composition according to the invention comprises

a. 0.1 - 50 wt% of a first carbonate salt catalyst according to formula 1 (all wt% herein being relative to the catalyst composition), and

b. 0.1 - 50 wt% of a second carbonate salt according to Formula 2 wherein the second carbonate is present in an amount of at least 5 mole % and preferably at most 500 mole % relative to the molar amount of the first carbonate catalyst.
c. optionally 0.1 - 99.8 wt% of solvent, preferably an organic solvent wherein preferably at least part is a primary alcohol,
d. optionally 0.1 - 50 wt% of an organic carbonate component according to formula RO-C(=O)O-R wherein each R is a same or different alkyl, preferably methyl or ethyl,
e. optionally 0.1 - 99.8 wt% water.

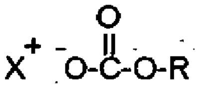
[0035] The catalytic composition can be made simply by mixing the components as described together for later use as a crosslinking catalyst by mixing the catalytic composition with crosslinkable components. It is noted that the water and primary alcohol have an effect on the catalytic activity and the pot-life versus drying rate balance and hence are considered part of the catalytic system and described as part of the catalytic composition, but in practice one or more of the optional components of the catalyst composition can be present in or added separately or in combinations to the crosslinkable components at any suitable time before mixing the crosslinkable components with the crosslinking catalyst and/or the use thereof.

[0036] The invention also relates to the use of the above described catalyst composition according to the invention as a crosslinking catalyst in a low temperature curing coating composition, preferably in a RMA curable coating composition, curable between 0 and 80°C, preferably 5 to 60°C, most preferably between 5 and 30 °C.

<u>The crosslinkable composition</u>

[0037] The invention relates to a crosslinkable polymer coating composition comprising

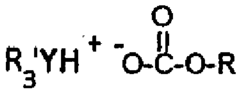
a. 0.1 - 99 wt% of at least one crosslinkable component being an RMA crosslinkable component (all wt% herein being relative to the crosslinkable composition),
b. a first carbonate salt according to formula 1, (meq latent base relative to dry total weight of the crosslinkable composition)



$$X^{+}\;{}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formula 1

wherein X^+ represents a non-acidic cation and wherein R is hydrogen, alkyl, or aralkyl group, preferably in an amount of 0.001 - 0.3 meq/g solids and
c. a second carbonate salt according to Formula 2 as pot life extender:



$$R_3'YH^{+}\;{}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formula 2

wherein Y is N or P and wherein each R' can be hydrogen, a (substituted) alkyl, aryl or aralkyl group, wherein the second carbonate is present in an amount of at least 5 mole % and preferably at most 500 mole % relative to the molar amount of the first carbonate catalyst,
d. optionally 0.1 - 70 wt% of solvent, preferably an organic solvent wherein preferably at least 0.5 wt% (relation to total weight of the crosslinkable composition) is a primary alcohol and optionally comprising 0.1 - 10 wt% water
e. optionally 0.1 - 70 wt% of an organic carbonate component according to formula RO-C(=O)O-R wherein R preferably is an alkyl, preferably methyl or ethyl, wherein the at least one crosslinkable component comprises 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 and the at least 2 reactive groups of component B are activated unsaturated groups (C=C) and said catalyst composition for starting crosslinking reaction by Real Michael Addition (RMA) upon deblocking of the latent base catalyst b by evaporation of carbon dioxide.

[0038] Good results were obtained in crosslinkable compositions having a very high solid content, preferably at least 55, 60, 65 or even more than 70 or more than 75 wt% (dry weight after crosslinking relative to the total weight of the crosslinking composition). It is noted that the solids content relates to the crosslinking composition as described in the claim not including optional particulate fillers or pigments that maybe added at a later stage for example when making a coating composition.

[0039] The at least one crosslinkable components comprise 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 and the at least 2 reactive groups of component B are activated unsaturated groups (C=C) and said catalyst composition for starting crosslinking reaction by Real Michael Addition (RMA) upon deblocking of the latent base catalyst by evaporation of carbon dioxide.

[0040] Reactive components A and B can be separate molecules and each independently in the form of polymers, oligomers, dimers or monomers. Reactive components A, B and/or the catalyst can be combined in one or more molecules. The activated C-H group in component A is preferably a malonate, acetoacetate or acetylacetone or mixtures thereof, more preferably dominantly malonate. In the crosslinkable composition preferably at least 50%, preferably at least 70%, more preferably at least 80% and even more preferably at least 90% of the acidic protons (C-H) in activated methylene or methine groups in crosslinkable component A come from malonate.

[0041] The concentrations and stoichiometry of the reactive groups in the cross-linkable components is chosen in a way to create good network properties in an efficient way. Typically, the ratio of reactive C-H groups (A) over C=C groups (B) is between 0.1 and 10, preferably between 0.5 and 3, more preferably between 0.7 and 2, most preferably between 0.8 and 1.5.

[0042] Preferably the component B comprises an unsaturated acryloyl or maleate functional group, preferably acryloyl. The crosslinkable composition preferably comprises as component A a polymer, preferably a polyester, polyurethane, acrylic or polycarbonate or a mixture/hybrid of these and as component B an unsaturated acryloyl functional component. The latent crosslinking catalyst is utilized in an amount ranging between 0.001 and 0.3 meq/g solids mole, preferably between 0.01 and 0.2 meq/g solids, more preferably between 0.02 and 0.1 meq/g solids (meq/g solids defined as moles latent base relative to the total dry weight of the crosslinkable composition).

[0043] In the crosslinkable composition the reactive component A preferably is a malonate or a acetoacetate or a acetylacetone, or mixtures thereof preferably comprising at least 50 mole% malonate and wherein the component B comprises an unsaturated acryloyl or maleate functional group, preferably acryloyl. In a particularly preferred embodiment, component A comprises malonate and the cross-linkable composition comprises 0.1 - 10 wt% preferably 0.1-5, more preferably 0.2-3 and most preferably 0.5-1.5 wt% water (relative to total weight of the crosslinkable composition). Details of the preferred RMA systems that can be used are described in application PCT/EP2011/055463 and are herewith incorporated by reference.

[0044] The solvent in the cross-linkable composition can either be water or an organic solvent which may optionally comprise water. The crosslinkable composition preferably comprises an organic solvent wherein at least part of the solvent is a primary alcohol solvent and optional water. Good results are already obtained when the alcohol is present in the crosslinkable composition in an amount of at least at least 0.5 wt%. Sometimes the optimum amount may be more than 1, 2, 5, 7 or 10%. Generally the amount is at most 45, preferably at most 40 and more preferably less than 30 wt%, most preferably less than 20wt% (relative to the total weight of the crosslinkable composition).

[0045] The crosslinkable composition -preferably comprises a primary alcohol, preferably a mono-alcohol having 1 to 20, preferably 1 - 10, more preferably 1 - 6 carbon atoms, preferably selected from the group of methanol, ethanol, n-propanol, n-butanol, n-amyl alcohol and butylglycol.

The coating composition

[0046] The invention further relates to a coating composition comprising the above described crosslinkable polymer coating composition according to the invention and optional and preferably non-acidic additional binders, coating additives or fillers.

[0047] The coating composition preferably has a solids content between 55 and 100 and 0 to 45 wt% volatile organic components, and preferentially has a tack-free time at room temperature between 5 to 120 min, preferably 5 to 60 min, most preferably 10-45 min, and a time to double viscosity at least 30 minutes, preferably at least 1 hr most preferable at least 2 hours, more preferably 4 hours, even more preferably at least 8 hr, most preferably more than 16 hrs at room temperature. The coating composition has low VOC and excellent properties, in particular good potlife / drying balance as described above.

[0048] Depending upon the field of application, the coating compositions in accordance with the present invention may optionally contain one or more pigments, dyes and usual intermediary agents, additives and/or solvents. Examples of suitable inert organic solvents include esters, ketones, ethers, alcohols, aromatic and aliphatic hydrocarbons. Examples of suitable reactive organic solvents include dimethyl malonate, diethyl malonate, ethyl acetoacetate and 2-ethylhexyl acrylate (mono-acrylates should be counted as compound B in terms of total functionality and because they are chain stoppers should not be present in too high amounts).

[0049] As examples of preferred additives may be mentioned minor amounts of a co-binder not containing activated unsaturated or CH acidic groups, for example, cellulose acetate butyrate, acrylic, epoxy and polyester resins. As is known to one skilled in the art, these cobinders are commonly utilized in the coatings industry to modify certain properties such as drying speed and adhesion to substrates.

[0050] As mentioned earlier, the coating compositions in accordance with the present invention are suitable for a variety of coatings uses, for example, as paint, impregnating, sealing and bonding compositions. A preferred application is as a primer, pigmented topcoat, or clearcoat ; the coating compositions may be applied to a substrate in any convenient manner such as, for example, by brushing, spraying or dipping. Suitable substrates include metals, wood, board, plastics and leather.

[0051] The curing of the above-described coating composition is preferably carried out at elevated temperatures above about 0°C generally between about 5°C and about 150°C. Preferred coating compositions based on RMA crosslinkable composition comprising components A, B and C as described are preferably cured at curing temperature is between 0 and 80°C, preferably 5 to 60°C, most preferably between 5 and 30°C.

[0052] The cross-linkable composition typically is a 2K system, comprising one part containing the cross-linkable components and another part containing a cross-linking catalyst composition which are mixed together shortly before use. The invention hence also relates to a process for preparing a base cross-linkable coating composition, which process comprises mixing of base crosslinkable components, preferably RMA crosslinkable components A and B as described above and optional coating additives, with the catalyst composition according to the invention.

[0053] The invention further relates to a process for preparing a cross-linked coating comprising applying a layer of the crosslinkable coating composition according to the invention on a substrate and curing the coating composition by evaporation of carbon dioxide from the layer. As described, the catalyst this suitable for low temperature curing of the coating composition, preferably between 0 and 80°C, preferably 5 to 60°C, most preferably between 5 and 30°C. The coating has a good hardness properties and short dry to touch time. The invention hence also relates to the coating and the coated substrate obtainable by the process according to the invention.

Examples

[0054] The foregoing more general discussion of the present invention will be further illustrated by the following specific examples, which are exemplary only.

[0055] The gel time is the time at which the sample is gelled and has lost all fluidity which was determined by making a mixture of the components and the latent base catalyst, placing 10 ml sample of the mixture in a 20 ml closed glass container (50% headspace) and keeping the sample at room temperature (23 °C) until gelation occurs. The container was tilted at regular time intervals and visually inspected to check whether or not the sample still flowed. The gel time is the time at which the container could be held upside down without flow of the sample.

[0056] Dust-dry and tack-free times were measured according to the so-called TNO method with a wad of cotton-wool. Dust-dry time means the time needed for the coating after dropping the wad on the surface of the coating and after leaving it there for 10 second, to get no residue of the wool-cotton sticking onto the surface after blowing away the wad. For tack-free time the same holds but now a weight load of 1 kg is applied on the wad for 10 seconds.

[0057] Persoz pendulum hardness was measured in a climatized room at 23°C, and 55+/-5% relative humidity.

[0058] Viscosities were measured with a TA Instruments AR2000 Rheometer, using a cone and plate setup (cone 4cm 1°) at 1 Pa stress. Tube and ball viscometry for determining pot life: A glass test tube (length 12 cm, diameter 13 mm) was filled with a stainless steel ball of 12 mm diameter, and the formulation to be studied to leave a very limited head space, and closed. Time was recorded for the ball to fall and pass a distance of 5 cm when the tube was tilted vertically. An average was taken over 2 measurements, Relative viscosities are determined relative to the starting condition by dividing the time found, by the time found for the first measurement after mixing.

[0059] Reported molecular weights were measured by GPC in THF, and expressed in polystyrene equivalent weights.

[0060] The following abbreviations were used for chemicals used in the experiments: DITMPTA is di-(trimethylolpropane)tetraacrylate (obtained from Aldrich (MW = 466 g/mole)), IPA is isopropanol, MeAcac is methylacetoacetate, DEC is diethylcarbonate, MEK is methyl ethyl ketone (2-butanone), BuAc is butylacetate, TBAH is tetrabutylammonium hydroxide, AbC is ammonium bicarbonate from Acros (98% pure).

Preparation of malonate polyester A

[0061] Into a reactor provided with a distilling column filed with Raschig rings were brought 17.31 mol of neopentyl glycol, 8.03 mol of hexahydrophthalic anhydride and 0.0047 mol of butyl stannoic acid. The mixture was polymerised at 240°C under nitrogen atmosphere to an acid value of 0.2mg KOH/g, cooled down to 130°C. Subsequently, 10.44 mol of diethylmalonate was added, and the reaction mixture was heated to 170 °C, to remove ethanol, in the later stages under reduced pressure. The material was cooled down and diluted with 420g of butyl acetate to a nominal 90% solid content. The final resin had an acid value of 0.3mg KOH/g solids, an OH value of 20 mg KOH/g solids, and a weight average molecular weight of 3400 Da.

Syntheses of the blocked catalysts

C1:

[0062] 147.1 g of a 40% TBAH solution in water was mixed with 34.0 g diethyl carbonate (DEC) and 43.6 g ethanol, and 15.8 grams of water. The reaction mixture was stirred overnight to yield a clear solution. Titration in 2-propanol with aqueous HCl revealed complete blocking into the carbonated species, with a concentration of 0.80 meq catalyst per g solution.

[0063] C2: 178.1 g of a 40% TBAH solution in water was mixed with 40.5 g DEC and 38.2 g isopropanol. The reaction mixture was stirred overnight to yield a clear solution. Titration in 2-propanol with aqueous HCl indicated complete blocking, and a concentration of active species of 0.87 meq catalyst per g solution.

Catalyst solutions S1-S6, comparative catalyst solutions CS1 and CS2

[0064] Catalyst solutions were prepared by formulating catalyst preparation C1 and C2 with various levels of ammonium bicarbonate, and (co)solvents, as tabulated below (amounts in gram).

code	CS1	S1	S2	S3
Catalyst C1	29.7	22.7	22.5	33.4
ammonium bicarbonate	0.00	0.36	0.71	2.11
H_2O	12.9	9.8	9.7	14.5

Code	CS2	S4	S5	S6
Catalyst C2	49.95	49.96	49.93	49.93
ammonium bicarbonate	0.00	0.86	1.72	3.43
H_2O	7.8	7.8	7.8	7.8

Preparation of triethylamine bicarbonate T1

[0065] A flask was charged with 20 grams of triethylamine, 15.6 gram ammonium bicarbonate and 75 gram water. This mixture was stirred for 5 days at RT and was daily purged with nitrogen. Finally the last ammonia formed was removed by applying vacuum (25 mbar) at ambient temperature during 4 hours. During the preparation, the smell of ammonia was clearly present and two equivalence points were detected. After the vacuum treatment, titration with hydrochloric acid revealed only one equivalence point. The load of triethylamine bicarbonate ($Et_3NH^+ HCO_3^-$) was 1.48 mmol/ gram solution.

Comparative formulation example 1.

[0066] A lacquer was formulated with 15.0 g of malonate polyester A, 6.6 g of DiTMPTA, 1.5g of catalyst solution CS1, and thinned down with 2.3 g of a MEK/BuAc mixture (1:1 by volume), to end up with a formulation of 750 mPas viscosity at a solids content of 79%. This formulation contained an estimated water level of 3.1 wt%, an estimated ethanol level of 1.1 wt%; the catalyst level was 50 μeq/gram of reactive components expected as solid end product.

Formulation examples 1-2.

[0067] Lacquers were formulated with 15.0 grams of malonate polyester A, 6.6 g of DITMPTA, 1.5g of catalyst solution S1 or S2, and thinned down with 2.3 g of MEK/BuAc mixture (1:1 by volume), to end up with a formulation of 750 mPas viscosity at a solids content of 79%. This formulation contained an estimated water level of 3.1 wt%, an estimated ethanol level of 1.1wt%, and an amount of ammonium bicarbonate of 25 mole% (1) or 50mole% (2) relative to the equivalents of base catalyst added catalyst added (50 μeq /g solids).

[0068] Formulations 1 and 2, and comparative formulation 1 were tested for their behavior in the pot by measuring gel time, and upon application by drawdown of these formulations onto glass to obtain a dry film thickness of 45-55 μm. Drying was followed as dust-dry and tack-free limits (TNO cotton ball testing), as was hardness development (Persoz hardness) upon cure at RT as well as that following an initial flash-off period of 10 minutes followed by a forced dry step of 45 minutes at 60°C, and subsequent RT storage. Results can be found in table A.

[0069] It can be seen that the addition of ammonium bicarbonate at the levels indicated results in a significant increase in gel time, while maintaining the drying times at the very fast level also found in the comparative example. Moreover, a faster buildup of Persoz hardness is observed (>5<20 means more than 5, less than 20 hours).

Table A. Gel time and cure behaviour

	Comp 1	Ex 1	Ex2
mole % AbC (on base catalyst)	0	25	50
gel time (h)	>5<20	>24	>24
TNO-drying (min)			
dust-dry	10’	10’	10’
tack-free	15’	15’	15’
Persoz hardness (sec)			
RT cure			
1 day	47	88	82
7 days	70	120	119
14 days	85	125	136
3 weeks	115	131	139
45’ 60°C - RT cure			
1 hour	37	155	113
1 day	47	146	115
1 week	70	155	127
2 weeks	87	168	158
3 weeks	98	175	197

[0070] Further experiments zoom in on the advantages that can be created through the use of ammonium bicarbonate.

[0071] Formulation examples 3-5 were prepared by mixing malonate polyester A (15 g), dITMPTA (6.6 g), 6.8 g of a MEK/BuAc mixture (1:1 by volume), and amounts of catalyst solutions S1-S3 with increasing levels of ammonium bicarbonate (relative to TBA catalyst species), and compared with a similar comparative formulation 2 (formulated with catalyst solution CS1, not containing ammonium bicarbonate) according to the table B. These formulations all contained about 50 μeq/g solids active base, a water level of approximately 2.7 wt%, and 0.9wt% ethanol, and ad a viscosity around 80 mPas.

Table B

Code	**Comp 2**	**Ex3**	**Ex4**	**Ex5**
catalyst solution	1.54 g CS1	1.54 g S1	1.57 g S2	1.62g S3
AbC mole % relative to TBA catalyst	0	25	50	100

[0072] The pot life was measured with the tube and ball method, and the viscosities, normalized relative to the starting viscosity as 1, are expressed in table C:

Table C:

code	comp2	ex 3	ex 4	ex 5
time (h)	0% abc	25%abc	50%abc	100%abc
0	1.0	1.0	1.0	1.0
1	1.0	1.0	1.0	1.2
2	1.0	0.8	1.2	1.2
3	1.2	1.0	1.2	1.2
4	1.3	1.2	1.3	1.3
5	1.7	1.2	1.3	1.3
6	2.0	1.2	1.3	1.3
8	2.7	1.3	1.3	1.3
10	3.3	1.3	1.3	1.3
12	6.0	1.5	1.5	1.3
20		2.0	1.5	1.3
30			2.2	1.3

[0073] It can be seen that the time to doubling viscosity, being around 6 hours in the case of comparative example 2, is extended to significantly higher values: with 25% AbC, it is already 20 hours, higher levels increasing potlife significantly beyond that level.

[0074] Initial pot life without AbC in these systems is a variable affected by levels of water and primary alcohols (maintained constant in the previous comparison), but also the level of acetoacetate components as secondary donor group type next to malonates: acetoacetates are more critical in pot life.

[0075] Example formulations 6-10 were prepared along the same lines as described above (malonate polyester A, diTMPTA, varying levels of methylacetoacetate and thinning solvent mixture MEK/BuAc to obtain a viscosity of around 80 mPas, and with a level of AbC at 25% relative relative to TBA using catalyst solution S1 (catalyst concentrations at 50 μeq/g intended solids). Compositions are given in table D.

Table D

Code	Ex6	Ex7	Ex8	Ex9	Ex10
malonate polyester A / g	15.0	15.0	15.0	15.0	15.0
di-TMPTA / g	6.6	7.3	8.2	9.4	11.0
MeAcAc / g	0.0	0.48	1.03	1.90	2.89
MEK:BuAc (1:1 (vol)) / g	6.7	6.7	6.5	4.0	3.60
catalyst solution S1 / g	1.52	1.61	1.72	1.87	2.07
wt% water (on total)	3.5%	3.5%	3.6%	4.0%	4.1%
wt% EtOH (on total)	0.8%	0.8%	0.8%	0.9%	1.0%

[0076] Comparative example formulations 3-7 were prepared along the same lines as described above (malonate polyester A, diTMPTA, varying levels of methylacetoacetate and thinning solvent mixture MEK/BuAc to obtain a viscosity of around 80 mPas, using comparative catalyst solution CS1, no AbC added (catalyst concentrations at 50 μeq/g intended solids). Compositions are given in table E.

Table E:

code	Comp3	Comp4	Comp5	Comp6	Comp7
malonate polyester A/g	15.0	15.0	15.0	15.0	15.0
di-TMPTA / g	6.60	7.30	8.20	9.40	11.00
MeAcAc / g	0.00	0.47	1.06	1.81	2.82
MEK:BuAc (1:1 (vol)) /g	6.70	6.70	6.50	4.00	3.60

(continued)

code	Comp3	Comp4	Comp5	Comp6	Comp7
catalyst CS1 / g	1.52	1.61	1.72	1.87	2.07
wt% water (on total)	3.5%	3.5%	3.6%	4.0%	3.8%
wt% EtOH (on total)	0.8%	0.8%	0.8%	0.9%	0.9%

[0077] The pot life of examples formulations 6-10, and comparative example formulations 3-7, was measured with the tube and ball method, and the viscosities, normalized relative to the starting viscosity as 1, are expressed in table F:

Table F:

Code	Comp3	Ex6	Comp4	Ex7	Comp5	Ex8	Comp6	Ex9	Comp7	Ex10
mole% AbC on TBA base	0	25	0	25	0	25	0	25	0	25
mole% acetoacetate on total donor CH2 groups	0	0	10	10	20	20	30	30	40	40
time (h)										
0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
1	1.0	1.0	1.0	1.0	1.0	1.0	1.5	1.0	2.0	1.3
2	1.0	1.0	1.0	1.0	1.0	1.0	2.5	1.0	3.0	2.0
3	1.0	1.0	1.0	1.0	1.3	1.0	4.0	1.0	6.0	4.0
4	1.0	1.0	1.3	1.6	1.5	1.6	5.0	2.0	10	4.8
5	1.3	1.3	1.3	1.6	2.5	2.0	6.0	2.8	14	5.0
6	1.3	1.3	1.3	1.6	3.0	2.0	9.0	2.8	25	5.3
8	2.0	1.3	2.0	1.6	4.0	2.0	17	3.0		7.0
9	2.0	1.3	2.0	1.6	4.3	2.4	21	3.0		7.5
12	2.2	1.5	3.0	1.6	5.0	2.6		4.0		10
22	3.0	1.5	4.0	1.6	9.0	2.6		6.0		17
28	3.3	1.5	4.3	2.4	12	3.2		8.0		

[0078] It can be observed in the comparative examples that the pot life (to viscosity doubling) decreases with increasing levels of acetoacetates to values in the order of one hours when using 40% acetoacetates; it can also be observed that the use of AbC levels of only 25% on catalyst leads to a doubling or more of this pot life, also in the formulations containing acetoacetates besides malonates.

[0079] The next examples illustrate the impact of varying levels of AbC on pot life in formulations quite critical in their pot life.

[0080] Example formulations 11-13, and comparative example formulation 8, were prepared as described above, and formulated with catalyst solutions S4-6, or CS2. Compositions are given in table G. All compositions contained 20mole% acetoacetate groups on total CH2 donor groups, and 50 μeq/g solids of catalyst. Water levels were 2.3%, IPA levels 0.6%

Table G:

Code	Comp 8	Exp11	Exp12	Exp13
malonate polyester A / g	15.0	15.0	15.0	15.0
di-TMPTA / g	8.30	8.30	8.30	8.30
MeAcAc / g	1.00	1.00	1.00	1.00

(continued)

Code	Comp 8	Exp11	Exp12	Exp13
MEK:BuAc (1:1) (vol) / g	6.30	6.30	6.30	6.30
catalyst solution / g	CS2 / 1.49	S4 / 1.54	S5 / 1.58	S6 / 1.67
mole% AbC on base cat	0	25	50	100

[0081] The pot life of examples formulations 11-13, and comparative example formulation 8, was measured with the tube and ball method, and the viscosities, normalized relative to the starting viscosity as 1, are expressed in table H:

Table H:

Time (h)	Comp 9 0% abc	Ex 11 25% abc	Ex 12 50% abc	Ex 13 100% abc
0	1	1	1	1
1	1.6	1.2	1	1
1.5	2.4	1.6	1	1
2	7.2	4	1	1
2.5	29.6	8.8	1.2	1
3		12	1.4	1
3.5			1.6	1
4			1.6	1
5			1.8	1
6			1.8	1
7			1.8	1.2
10			3.2	1.6
11			4	2.4
12			4.8	3.2
13			5.6	3.2
24			9.6	3.2
48			12.8	4.8

[0082] Time to viscosity doubling is extended from about an hour in comparative example 9, to about 8 hours at 50% AbC added, and being extended even further at 100% AbC relative to catalyst.

Comparative example 10 :

[0083] A formulation was made, blending 15.05 g of malonate polyester A, 6.61 g of DiTMPTA, 4.4. g of a 1:1 by mass mixture of MEK and BuAc, and 0.68 g of a 7.9 wt% aqueous solution of ammonium bicarbonate (corresponding to 0.034 mmole/g solids). When applied as a film, the coating remains tacky, and does not appear to exhibit a curing reaction. This proves that the role of AbC is clearly different from that of the cure initiating quaternary ammonium blocked base catalysts.

[0084] Formulation example 14 was formulated to allow a comparison with comparative example formulation 2, by mixing 15 g malonate polyester A, 6.6 g DiTMPTA, 7.1 g MEK/BuAc 1:1 by mass, 1.2 g of catalyst solution C2,, 0.17 g of triethylamine bicarbonate solution T1, 0.24 g water and 0.22 g ethanol, to have water and ethanol levels in this formulation of 2.8 and 0.9 wt% respectively. Pot life was determined by following viscosity using the tune and ball method; results are indicated in table I below, alongside of the results of comparative example formulation 2. The amount of triethylamine bicarbonate is estimated to be 25 mole% relative to the amount of activating blocked TBA catalyst (50 μeq/g solids). It can be seen that the use of the triethylamine bicarbonate extends time to doubling of viscosity from about 6, to more than 48 hours.

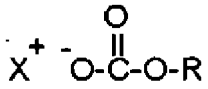
Table I relative viscosity development:

code	comp2	ex 14
time (h)		
0	1.0	1.0
1	1.0	1.0
2	1.0	1.0
3	1.2	1.0
4	1.3	1.0
5	1.7	1.0
6	2.0	1.0
8	2.7	1.0
10	3.3	1.0
12	6.0	1.0
20		1.2
30		
48		1.4

Claims

1. A crosslinkable polymer coating composition comprising

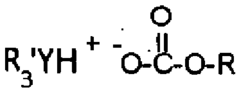
a. 0.1 - 99 wt% of at least one crosslinkable component that is crosslinkable under the action of a base catalyst, (all wt% herein being relative to the crosslinkable composition),
b. a first carbonate salt according to formula 1 as latent base crosslinking catalyst,



$$X^{+}\;{}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formula 1

wherein X^+ represents a non-acidic cation and wherein R is hydrogen, alkyl, or aralkyl group, and
c. a second carbonate salt according to Formula 2 as potlife extender:



$$R_3'YH^{+}\;{}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formula 2

wherein Y is N or P and wherein each R' can be hydrogen, a substituted or unsubstituted alkyl, aryl or aralkyl group, wherein the second carbonate is present in an amount of at least 5 mole % and preferably at most 500 mole % relative to the molar amount of the first carbonate,
d. optionally 0.1 - 70 wt% of solvent, preferably an organic solvent wherein at least. 0.5 wt% (relation to total weight of the crosslinkable composition) is a primary alcohol and optionally comprising 0.1 - 10 wt% water
e. optionally 0.1 - 70 wt% of an organic carbonate component according to formula RO-C(=O)O-R wherein R preferably is an alkyl, preferably methyl or ethyl,

wherein the at least one crosslinkable component comprises 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 and the at least 2 reactive groups of component B are activated unsaturated groups (C=C) and said catalyst composition for starting crosslinking reaction by Real Michael Addition (RMA) upon deblocking of the latent base catalyst b by evaporation of carbon dioxide.

2. The crosslinkable composition according to claim 1, wherein the first carbonate salt is present in an amount of 0.001 - 0.3 meq/g solids (meq latent base relative to dry total weight of the crosslinkable composition).

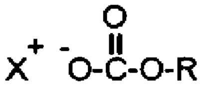
3. The crosslinkable composition according to claim 1 or 2, wherein the cation of the first carbonate salt according to formula 1 has a pKa of at least 11.5, preferably at least 12 and more preferably at least 12.5 and wherein the cation of the second carbonate salt has a pKa of less than 11.5 (pKa relative to water).

4. The crosslinkable composition according to claims 1 to 3, wherein the reactive component A is a malonate or an acetoacetate or an acetylacetone, or mixtures thereof preferably comprising at least 50 mole% malonate and wherein the component B comprises an unsaturated acryloyl or maleate functional group, preferably acryloyl.

5. A coating composition comprising the crosslinkable composition according to claims 1 - 4 and optional additional binders, coating additives or fillers.

6. A catalyst composition for use as a latent base catalyst system in crosslinkable compositions according to claims 1 - 4 or coating composition of claim 5, composed of

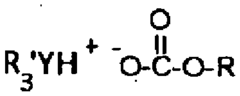
    a. a first carbonate salt according to formula 1 as the latent base catalyst



$$X^{+}\ {}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formula 1

    wherein X+ represents a non-acidic cation and wherein R is hydrogen, alkyl, or aralkyl group and
    b. a second carbonate salt according to Formula 2:



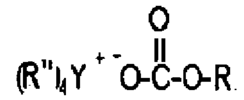
$$R'_{3}YH^{+}\ {}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formula 2

    wherein Y is N or P, wherein each R' can be hydrogen, a substituted or unsubstituted alkyl, aryl or aralkyl group, and wherein R can be the same or a different from the R in formula 1, wherein the second carbonate is present in an amount of at least 5 mole % and preferably at most 500 mole % relative to the molar amount of the first carbonate,
    c. optionally a solvent, preferably an organic solvent wherein at least 0.5 wt% (relation to total weight of the crosslinkable composition) is a primary alcohol and which optionally comprises 0.1 - 10 wt% water
    d. optionally an organic carbonate component according to formula RO-C(=O)O-R wherein R preferably is an alkyl, preferably methyl or ethyl.

7. The catalyst composition according to claim 6, wherein the cation of the first carbonate salt according to formula 1 has a pKa of at least 11.5, preferably at least 12 and more preferably at least 12.5 and wherein the cation of the second carbonate salt has a pKa of at most 11.5 (pKa relative to water).

8. The catalyst composition according to claim 6 or 7, wherein the cation X+ is a quaternary ammonium or phosphonium carbonate salt according to formula 3,



$$(R'')_4Y^{+}\ {}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formula 3

wherein Y represents N or P, and wherein each R" can be a same or different alkyl, aryl or aralkyl group, wherein R and R" can be bridged to form a ring structure or R and/or R" can be a polymer and wherein the carbonate anion preferably is bicarbonate or methocarbonate or ethocarbonate.

9. The catalyst composition according to claims 6 -8, wherein the cation in the second carbonate salt is a protonated amine, preferably ammonia, or a preferably volatile tertiary amine and wherein the anion in the second carbonate is a bicarbonate or an alkylcarbonate wherein alkyl preferably is ethyl or methyl.

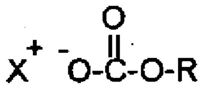
10. The catalyst composition according to claims 6 - 9, wherein the second carbonate salt is ammonium bicarbonate (NH_4HCO_3) or a bicarbonate of a protonated volatile tertiary amine, preferably triethylamine.

11. The catalyst composition according to claims 6 - 10, further comprising as a catalyst storage stability improver an organic carbonate component according to formula ROC(=O)O-R wherein R preferably is an alkyl, preferably methyl or ethyl, wherein the molar ratio of this organic carbonate component to the first carbonate catalyst is 0.01 - 50.

12. The catalyst composition according to claims 6 - 11, further comprising an organic solvent at least part of which is a primary alcohol, and optionally water in amount between 0.1 - 80 wt%, preferably 1 - 50wt% relative to total weight of the catalyst composition.

13. The catalyst composition according to claims 6-12 comprising

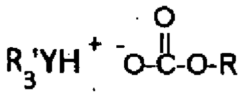
a. 0.1 - 50 wt% of a first substituted carbonate salt catalyst according to formula 1 (all wt% herein being relative to the catalyst composition),



$$X^{+}\ {}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formula 1

wherein X^+ represents a non-acidic cation and wherein R is hydrogen, alkyl, aryl or aralkyl group and
b. 0.1 - 50 wt% of a second carbonate salt according to Formula 2:



$$R_3'YH^{+}\ {}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formula 2

wherein Y is N or P and wherein each R' can be hydrogen, a (substituted) alkyl, aryl or aralkyl group, wherein the second carbonate is present in an amount of at least 5 mole % and preferably at most 500 mole % relative to the molar amount of the first carbonate catalyst.
c. optionally 0.1 - 99.8 wt% of solvent, preferably an organic solvent wherein at least part is a primary alcohol (preferably at least 5wt%) and
d. Optionally 0.1 - 50 wt% of an organic carbonate component according to formula RO-C(=O)O-R wherein each R is a same or different alkyl, preferably methyl or ethyl
e. optionally 0.1 - 99.8 wt% water.

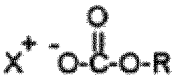
14. Process for preparing a cross-linked coating comprising applying a layer of the crosslinkable coating composition according to claim 5 on a substrate and curing the coating composition by evaporation of carbon dioxide from the layer.

15. Use of a catalyst composition according to claims 6 - 13 as a crosslinking catalyst in a low temperature curing coating composition, preferably a RMA curable coating composition, preferably curable between 0 and 80°C, preferably 5 to 60°C, most preferably between 5 and 30 °C.

Patentansprüche

1. Vernetzbare Polymerbeschichtungszusammensetzung umfassend:

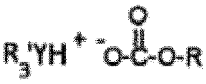
a. 0,7 bis 99 Gew.-% wenigstens einer vernetzbaren Komponente, die unter der Wirkung eines basischen Katalysators vernetzbar ist (wobei sich hier alle Gew.-% auf die vernetzbare Zusammensetzung beziehen);
b. ein erstes Carbonatsalz gemäß Formel 1 als Latente-Base-Vernetzungskatalysator:



$$X^{+}\ {}^{-}O-\overset{\overset{O}{\|}}{C}-O-R$$

Formel 1

wobei X^+ für ein nichtsaures Kation steht und wobei R Wasserstoff, eine Alkyl- oder Aralkylgruppe ist; und
c. ein zweites Carbonatsalz gemäß Formel 2 als Topfzeitverlängerer:



$$R'_3YH^{+}\ {}^{-}O-\overset{\overset{O}{\|}}{C}-O-R$$

Formel 2

wobei Y N oder P ist und wobei R' jeweils Wasserstoff, eine substituierte oder unsubstituierte Alkyl-, Aryl- oder Aralkylgruppe sein kann, wobei das zweite Carbonat in einer Menge von wenigstens 5 Mol-% und vorzugsweise höchstens 500 Mol-% vorhanden ist, bezogen auf die Stoffmenge des ersten Carbonats;
d. gegebenenfalls 0,1 bis 70 Gew.-% Lösungsmittel, vorzugsweise ein organisches Lösungsmittel, bei dem wenigstens 0,5 Gew.-% (bezogen auf das Gesamtgewicht der vernetzbaren Zusammensetzung) ein primärer Alkohol ist und das gegebenenfalls 0,1 bis 10 Gew.-% Wasser umfasst;
e. gegebenenfalls 0,1 bis 70 Gew.-% einer organischen Carbonatkomponente gemäß Formel RO-C(=O)O-R, wobei R vorzugsweise Alkyl, vorzugsweise Methyl oder Ethyl, ist.

wobei die wenigstens eine vernetzbare Komponente reaktive Komponenten A und B umfasst, die jeweils wenigstens 2 reaktive Gruppen umfassen, wobei die wenigstens 2 reaktiven Gruppen der Komponente A saure Protonen (C-H) in aktivierten Methylen- oder Methingruppen sind und die wenigstens 2 reaktiven Gruppen der Komponente B aktivierte ungesättigte Gruppen (C=C) sind und der Katalysator eine Zusammensetzung zum Starten einer Vernetzungsreaktion durch reale Michael-Addition (RMA) nach Deblockieren des Latente-Base-Katalysators b durch Verdampfen von Kohlendioxid ist.

2. Vernetzbare Zusammensetzung gemäß Anspruch 1, wobei das erste Carbonatsalz in einer Menge von 0,001 bis 0,3 mäq/g Feststoffe (mäq latente Base pro Trockengesamtgewicht der vernetzbaren Zusammensetzung) vorhanden ist.

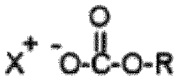
3. Vernetzbare Zusammensetzung gemäß Anspruch 1 oder 2, wobei das Kation des ersten Carbonatsalzes gemäß Formel 1 ein pKa von wenigstens 11,5, vorzugsweise wenigstens 12 und besonders bevorzugt wenigstens 12,5 aufweist und wobei das Kation des zweiten Carbonatsalzes ein pka von weniger als 11,5 (pka relativ zu Wasser) aufweist.

4. Vernetzbare Zusammensetzung gemäß Anspruch 1 bis 3, wobei es sich bei der reaktiven Komponente A um ein Malonat oder ein Acetoacetat oder ein Acetylaceton oder Gemische davon handelt und sie vorzugsweise wenigstens 50 Mol-% Malonat umfasst und wobei Komponente B eine funktionelle ungesättigte Acryloyl- oder Maleatgruppe, vorzugsweise Acryloyl, umfasst.

5. Beschichtungszusammensetzung, umfassend die vernetzbare Zusammensetzung gemäß Anspruch 1 bis 4 und gegebenenfalls zusätzliche Bindemittel, Beschichtungsadditive oder Füllstoffe.

6. Katalysatorzusammensetzung zur Verwendung als Latente-Base-Katalysatorsystem in vernetzbaren Zusammensetzungen gemäß Anspruch 1 bis 4 oder einer Beschichtungszusammensetzung gemäß Anspruch 5, zusammengesetzt aus:

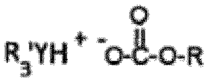
a. einem ersten Carbonatsalz gemäß Formel 1 als Latente-Base-Katalysator:



$$X^{+}\ {}^{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R$$

Formel 1

wobei X^+ für ein nichtsaures Kation steht und wobei R Wasserstoff, eine Alkyl- oder Aralkylgruppe ist; und
b. ein zweites Carbonatsalz gemäß Formel 2:



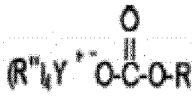
$$R'_3YH^{+}\ {}^{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R$$

Formel 2

wobei Y N oder P ist und wobei R' jeweils Wasserstoff, eine substituierte oder unsubstituierte Alkyl-, Aryl- oder Aralkylgruppe sein kann und wobei R gleich dem R in Formel 1 oder davon verschieden sein kann; wobei das zweite Carbonat in einer Menge von wenigstens 5 Mol-% und vorzugsweise höchstens 500 Mol-% vorhanden ist, bezogen auf die Stoffmenge des ersten Carbonats;
c. gegebenenfalls ein Lösungsmittel, vorzugsweise ein organisches Lösungsmittel, bei dem wenigstens 0,5 Gew.-% (bezogen auf das Gesamtgewicht der vernetzbaren Zusammensetzung) ein primärer Alkohol ist und das gegebenenfalls 0,1 bis 10 Gew.-% Wasser umfasst;
d. gegebenenfalls eine organische Carbonatkomponente gemäß Formel RO-C(=O)O-R, wobei R vorzugsweise Alkyl, vorzugsweise Methyl oder Ethyl, ist.

7. Katalysatorzusammensetzung gemäß Anspruch 6, wobei das Kation des ersten Carbonatsalzes gemäß Formel 1 ein pKa von wenigstens 11,5, vorzugsweise wenigstens 12 und besonders bevorzugt wenigstens 12,5 aufweist und wobei das Kation des zweiten Carbonatsalzes ein pka von höchstens 11,5 (pka relativ zu Wasser) aufweist.

8. Katalysatorzusammensetzung gemäß Anspruch 6 oder 7, wobei das Kation X^+ ein quartäres Ammonium- oder Phosphoniumcarbonatsalz gemäß Formel 3 ist:



$$(R'')_4Y^{+}\ {}^{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R$$

Formel 3

wobei Y für N oder P steht und wobei R" jeweils eine gleiche oder unterschiedliche Alkyl-, Aryl- oder Aralkylgruppe sein kann, wobei R und R" unter Bildung einer Ringstruktur verbrückt sein können oder R und/oder R" ein Polymer sein können und wobei das Carbonatanion vorzugsweise Hydrogencarbonat oder Methocarbonat oder Ethocarbonat ist.

9. Katalysatorzusammensetzung gemäß Anspruch 6 bis 8, wobei das Kation im zweiten Carbonatsalz ein protoniertes Amin, vorzugsweise Ammoniak, oder ein vorzugsweise flüchtiges tertiäres Amin ist und wobei das Anion im zweiten Carbonat ein Hydrogencarbonat oder ein Alkylcarbonat, wobei Alkyl vorzugsweise Ethyl oder Methyl ist, ist.

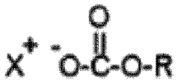
10. Katalysatorzusammensetzung gemäß Anspruch 6 bis 9, wobei das zweite Carbonatsalz Ammoniumhydrogencarbonat (NH_4HCO_3) oder ein Hydrogencarbonat eines protonierten flüchtigen tertiären Amins, vorzugsweise Triethylam in, ist.

11. Katalysatorzusammensetzung gemäß Anspruch 6 bis 10, weiterhin umfassend als Katalysatorlagerstabilitätsverbesserer eine organische Carbonatkomponente gemäß der Formel RO-C(=O)O-R, wobei R vorzugsweise Alkyl, vorzugsweise Methyl oder Ethyl, ist, wobei das Stoffmengenverhältnis dieser organischen Carbonatkomponente zu dem ersten Carbonatkatalysator 0,01 bis 50 beträgt.

12. Katalysatorzusammensetzung gemäß Anspruch 6 bis 11, weiterhin umfassend ein organisches Lösungsmittel, bei dem wenigstens ein Teil ein primärer Alkohol und gegebenenfalls Wasser in einer Menge von 0,1 bis 80 Gew.-%, vorzugsweise 1 bis 50 Gew.-%, bezogen auf das Gesamtgewicht der Katalysatorzusammensetzung, ist.

13. Katalysatorzusammensetzung gemäß Anspruch 6 bis 12, umfassend

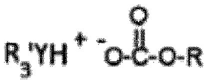
a. 0,1 bis 50 Gew.-% eines ersten substituierten Carbonatsalzkatalysators gemäß Formel 1 (wobei sich hier alle Gew.-% auf die Katalysatorzusammensetzung beziehen);



$$X^{+}\ {}^{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R$$

Formel 1

wobei X^+ für ein nichtsaures Kation steht und wobei R Wasserstoff, eine Alkyl-, Aryl- oder Aralkylgruppe ist; und
b. 0,1 bis 50 Gew.-% eines zweiten Carbonatsalzes gemäß Formel 2:



$$R'_{3}YH^{+}\ {}^{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R$$

Formel 2

wobei Y N oder P ist und wobei R' jeweils Wasserstoff, eine (substituierte) Alkyl-, Aryl- oder Aralkylgruppe sein kann, wobei das zweite Carbonat in einer Menge von wenigstens 5 Mol-% und vorzugsweise höchstens 500 Mol-% vorhanden ist, bezogen auf die Stoffmenge des ersten Carbonatkatalysators;
c. gegebenenfalls 0,1 bis 99,8 Gew.-% Lösungsmittel, vorzugsweise ein organisches Lösungsmittel, bei dem wenigstens ein Teil ein primärer Alkohol ist (vorzugsweise wenigstens 5 Gew.-%) und;
d. gegebenenfalls 0,1 bis 50 Gew.-% einer organischen Carbonatkomponente gemäß Formel RO-C(=O)O-R, wobei R jeweils gleiches oder unterschiedliches Alkyl, ist;
e. gegebenenfalls 0,1 bis 99,8 Gew.-% Wasser.

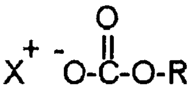
14. Verfahren zur Herstellung einer vernetzten Beschichtung, umfassend das Auftragen einer Schicht der vernetzbaren Beschichtungszusammensetzung gemäß Anspruch 5 auf ein Substrat und Aushärtenlassen der Beschichtungszusammensetzung durch Verdampfung von Kohlendioxid aus der Schicht.

15. Verwendung einer Katalysatorzusammensetzung gemäß Anspruch 6 bis 13 als Vernetzungskatalysator in einer bei tiefer Temperatur härtenden Beschichtungszusammensetzung, vorzugsweise einer RMA-härtbaren Beschichtungszusammensetzung, die vorzugsweise zwischen 0 und 80 °C, vorzugsweise 5 und 60 °C, am meisten bevorzugt zwischen 5 und 30 °C, härtbar ist.

Revendications

1. Composition de revêtement polymère réticulable comprenant

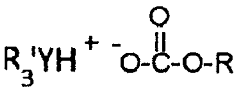
a. de 0,1 à 99 % en poids d'au moins un composant réticulable qui est réticulable sous l'action d'un catalyseur de base (tous les % en poids ici se rapportant à la composition réticulable),
b. un premier sel de carbonate selon la formule 1 à titre de catalyseur de réticulation de base latent,



$$X^{+}\ {}^{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R$$

Formule 1

dans laquelle X⁺ représente un cation non acide et R est un atome d'hydrogène, un groupe alkyle, ou aralkyle, et
c. un second sel de carbonate selon la Formule 2 à titre d'allongeur de durée de vie en pot :



$$R'_{3}YH^{+}\ {}^{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R$$

Formule 2

dans laquelle Y est N ou P et dans laquelle chaque R' peut être un atome d'hydrogène, un groupe alkyle, aryle ou aralkyle substitué ou non, le second carbonate étant présent en une quantité d'au moins 5 % en moles et de préférence d'au plus 500 % en moles par rapport à la quantité molaire du premier carbonate,
d. éventuellement de 0,1 à 70 % en poids de solvant, de préférence un solvant organique dont au moins 0,5 % en poids (par rapport au poids total de la composition réticulable) est un alcool primaire et comprenant éventuellement de 0,1 à 10 % en poids d'eau
e. éventuellement de 0,1 à 70 % en poids d'un composant carbonate organique répondant à la formule RO-C(=O)O-R dans laquelle R est de préférence un groupe alkyle, de préférence méthyle ou éthyle,

dans laquelle ledit au moins composant réticulable comprend des composants A et B réactifs, contenant chacun au moins 2 groupes réactifs, les 2 groupes réactifs au moins du composant A étant des protons acides (C-H) dans du méthylène activé ou des groupes méthine et les 2 groupes réactifs au moins du composant B étant des groupes insaturés activés (C=C), ladite composition de catalyseur servant à démarrer la réaction de réticulation par addition de Michael réelle (RMA) après déblocage du catalyseur de base latent b par évaporation du dioxyde de carbone.

2. Composition réticulable selon la revendication 1, dans laquelle le premier sel de carbonate est présent en une quantité de 0,001 à 0,3 méq/g de fractions solides (méq de base latente par rapport au poids sec total de la composition réticulable).

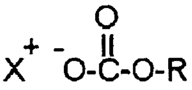
3. Composition réticulable selon la revendication 1 ou 2, dans laquelle le cation du premier sel de carbonate selon la formule 1 a une valeur pKa d'au moins 11,5, de préférence d'au moins 12 et de préférence encore d'au moins 12,5 et dans laquelle le cation du second sel de carbonate a une valeur pKa inférieure à 11,5 (pKa par rapport à l'eau).

4. Composition réticulable selon les revendications 1 à 3, dans laquelle le composant réactif A est un malonate ou un acétoacétate ou une acétylacétone, ou des mélanges de ceux-ci comprenant de préférence au moins 50 % en moles de malonate et dans laquelle le composant B comprend un groupe fonctionnel acryloyle insaturé ou maléate, de préférence un acryloyle.

5. Composition de revêtement comprenant la composition réticulable selon les revendications 1 à 4 et des liants, des additifs ou des charges pour revêtement facultatifs supplémentaires.

6. Composition de catalyseur pour son utilisation à titre de système de catalyseur de base latent dans des compositions réticulables selon les revendications 1 à 4 ou la composition de revêtement selon la revendication 5, comprenant

a. un premier sel de carbonate selon la Formule 1 à titre de catalyseur de base latent

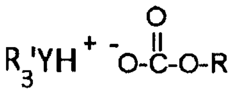


$$X^{+}\ {}^{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R$$

Formule 1

dans laquelle X⁺ représente un cation non acide et dans laquelle R est un atome d'hydrogène, un groupe alkyle, ou aralkyle et

b. un second sel de carbonate selon la Formule 2 :



$$R_3'YH^{+}\ {}^{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R$$

Formule 2

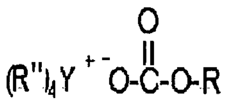
dans laquelle Y est N ou P, chaque R' peut être un atome d'hydrogène, un groupe alkyle, aryle ou aralkyle substitué ou non, et dans laquelle R peut être identique ou différent du R dans la formule 1, le second carbonate étant présent en une quantité d'au moins 5 % en moles et de préférence d'au plus 500 % en moles par rapport à la quantité molaire du premier carbonate,

c. éventuellement un solvant, de préférence un solvant organique dont au moins 0,5 % en poids (par rapport au poids total de la composition réticulable) est un alcool primaire et qui comprend éventuellement de 0,1 à 10 % en poids d'eau

d. éventuellement un composant carbonate organique répondant à la formule RO-C(=O)O-R dans laquelle R est de préférence un groupe alkyle, de préférence méthyle ou éthyle.

7. Composition de catalyseur selon la revendication 6, dans laquelle le cation du premier sel de carbonate selon la formule 1 a une valeur pKa d'au moins 11,5, de préférence d'au moins 12 et de préférence encore d'au moins 12,5 et dans laquelle le cation du second sel de carbonate a une valeur pKa d'au plus 11,5 (pKa par rapport à l'eau).

8. Composition de catalyseur selon la revendication 6 ou 7, dans laquelle le cation X^+ est un sel d'ammonium quaternaire ou de carbonate de phosphonium selon la formule 3,



$$(R'')_4Y^{+}\ {}^{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R$$

Formule 3

dans laquelle Y est N ou P, chaque R" peut être un groupe alkyle, aryle ou aralkyle identique ou différent, R et R" peuvent être liés par un pont pour former une structure de cycle ou R et/ou R" peuvent être un polymère, l'anion carbonate étant de préférence bicarbonate ou méthocarbonate ou éthocarbonate.

9. Composition de catalyseur selon les revendications 6 à 8, dans laquelle le cation dans le second sel de carbonate est une amine protonée, de préférence l'ammoniac, ou une amine tertiaire de préférence volatile et dans laquelle l'anion dans le second carbonate est bicarbonate ou alkylcarbonate, l'alkyle étant de préférence un éthyle ou méthyle.

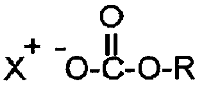
10. Composition de catalyseur selon les revendications 6 à 9, dans laquelle le second sel de carbonate est un bicarbonate d'ammonium (NH_4HCO_3) ou un bicarbonate d'une amine tertiaire volatile protonée, de préférence une triéthylamine.

11. Composition de catalyseur selon les revendications 6 à 10, comprenant en outre à titre d'agent améliorant la stabilité au stockage du catalyseur un composant carbonate organique répondant à la formule RO-C(=O)O-R dans laquelle R est de préférence un alkyle, de préférence un méthyle ou éthyle, le rapport molaire de ce composant carbonate organique au premier catalyseur de carbonate étant de 0,01 à 50.

12. Composition de catalyseur selon les revendications 6 à 11, comprenant en outre un solvant organique dont une partie au moins est un alcool primaire et éventuellement de l'eau en une quantité entre 0,1 et 80 % en poids, de préférence 1 à 50 % en poids par rapport au point total de la composition de catalyseur.

13. Composition de catalyseur selon les revendications 6 à 12 comprenant

a. de 0,1 à 50 % en poids d'un premier catalyseur de sel de carbonate substitué selon la formule 1 (tous les % en poids ici se rapportant à la composition de catalyseur),

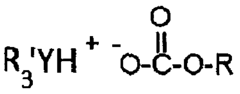


$$X^{+}\ {}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formule 1

dans laquelle X⁺ représente un cation non acide et dans laquelle R est un atome d'hydrogène, un groupe alkyle, ou aralkyle et

b. de 0,1 à 50 % en poids d'un second sel de carbonate selon la Formule 2 :



$$R'_{3}YH^{+}\ {}^{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R$$

Formule 2

dans laquelle Y est N ou P, chaque R' peut être un atome d'hydrogène, un groupe alkyle (substitué), aryle ou aralkyle, le second carbonate étant présent en une quantité d'au moins 5 % en moles et de préférence d'au plus 500 % en moles par rapport à la quantité molaire du premier catalyseur de carbonate,

c. éventuellement de 0,1 à 99,8 % en poids de solvant, de préférence un solvant organique dont une partie au moins est un alcool primaire (de préférence au moins 5 % en poids) et

d. éventuellement de 0,1 à 50 % en poids d'un composant carbonate organique répondant à la formule RO-C(=O)O-R dans laquelle chaque R est un groupe alkyle identique ou différent, de préférence un méthyle ou un éthyle

e. éventuellement de 0,1 à 99,8 % en poids d'eau.

14. Procédé de préparation d'un revêtement réticulé comprenant l'application d'une couche de la composition de revêtement réticulable selon la revendication 5 sur un substrat et le durcissement de la composition de revêtement par évaporation du dioxyde de carbone contenu dans la couche.

15. Utilisation d'une composition de catalyseur selon les revendications 6 à 13 à titre de catalyseur de réticulation dans une composition de revêtement à durcissement à basse température, de préférence une composition de revêtement durcissable par RMA, de préférence durcissable entre 0 et 80 °C, de préférence entre 5 et 60 °C, et de manière préférée entre toutes entre 5 et 30 °C.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

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- *Noomen in Progress in Organic Coatings,* 1997, vol. 32, 137-14 **[0008]**