

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization

International Bureau

(43) International Publication Date
14 April 2022 (14.04.2022)



(10) International Publication Number
WO 2022/073986 A1

(51) International Patent Classification:

C09D 5/00 (2006.01) G01N 33/00 (2006.01)
G01N 33/44 (2006.01)

(21) International Application Number:

PCT/EP2021/077416

(22) International Filing Date:

05 October 2021 (05.10.2021)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

20200104.6 05 October 2020 (05.10.2020) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: SCREENING METHOD USING CURED COATING FILM PROPERTIES

(57) Abstract: The present invention relates to a method of screening coating material compositions for development of new coating formulations in the automotive field, said method comprising at least steps (1) to (8) and (10) to (13) and optionally a step (9) as defined hereinafter, said method making use of measuring, selecting and improving at least one property of the cured coating films obtained by the inventive method, and to a use of said method for investigating the influence of certain constituents of coating material compositions on the properties of the resulting cured coating films obtained from applying and curing said coating material compositions onto optionally pre-coated surfaces of substrates.



WO 2022/073986 A1

Screening method using cured coating film properties

The present invention relates to a method of screening coating material compositions for development of new coating formulations in the automotive field, said method comprising at least steps (1) to (8) and (10) to (13) and optionally a step (9) as defined hereinafter, said method making use of measuring, selecting and improving at least one property of the cured coating films obtained by the inventive method, and to a use of said method for investigating the influence of certain constituents of coating material compositions on the properties of the resulting cured coating films obtained from applying and curing said coating material compositions onto optionally pre-coated surfaces of substrates.

Background of the invention

In typical automotive coating processes, usually at least four layers are applied to the surface of a suitable substrate such as a metallic substrate in form of a multilayer coating system: an electrodeposition coat (e-coat), at least one of a primer and a sealer, at least one basecoat, and a topcoat, in particular a clearcoat.

There are quite a number of requirements necessary, which have to be fulfilled and/or met by the coatings used in the automotive industry due to regulations, but also due to quality standards set by the automotive industry as such. Thus, the coatings obtained from using coating formulations in the automotive field have to exhibit or display a number of desired characteristics to at least a sufficient extent in order to meet these requirements. For example, an avoidance of optical defects and/or surface defects such as pinholes, mottling etc. is desired. In addition, the coatings are e.g. ought to have a good scratch resistance and a good stone chip resistance. Coatings intended to provide good stone chip resistance are, e.g., disclosed in WO 2017/097642 A1. However, as outlined above in a conventional automotive multilayer coating system there are at least four kinds of different coating layers present and each layer is used for a different reason and to accomplish different desired characteristics of the overall coating. In addition, the coating formulations used for preparing each of the coating layers are usually rather complex, i.e., contain a comparably high number of different constituents. In addition, some of

the coating formulations are predominantly provided in form of solventborne formulations such as clearcoats, whereas other coating formulations are provided to a high extent in the form of aqueous formulations such as basecoats. Thus, when constituents such as film-forming binders and crosslinking agents have been optimized for an incorporation into a solventborne system, these constituents are usually not optimized or even not applicable for a use in an aqueous system, and vice versa.

In practice, when developing new coating formulations, which are of rather complex nature as outlined above, in particular in research facilities of automotive manufacturers, it is therefore usually not only necessary to provide/produce the new complex coating formulations per se including testing if all constituents used or intended to be used have the desired compatibility, but it is usually also necessary to apply each of these complex coating formulations to a substrate, to cure the resulting films and to perform a testing or a series of testings with respect to the desired characteristics to be achieved based on these complex systems.

Thus, there is a need to provide a method of screening coating material compositions for development of new coating formulations in the automotive field in order to be able to provide coatings resulting therefrom with improved characteristics, which method allows a development based on non-complex standard coating material compositions, but with a sufficient number of degrees of freedom in order to allow a screening of as many coating compositions as possible, in particular as far as the constituents such as film-forming polymers and/or crosslinking agents present therein are concerned. At the same time said method should be able to be performed rather fast, cost-efficient and sustainable manner and in a manner saving resources (use of less amounts of materials and less waste production). In particular, there is a need to provide such a method, which allows an investigation of the influence of different constituents such as film-forming polymers and/or crosslinking agents used in such standard coating material compositions on the desired characteristics of the coatings prepared therefrom in order to provide tailor made new coating formulations in a target-oriented manner, which in turn lead to coatings obtainable therefrom with improved properties.

Problem

It has been therefore an object underlying the present invention to provide a method of screening coating material compositions for development of new coating formulations in the automotive field in order to be able to provide coatings resulting therefrom with improved characteristics, which method allows a development based on non-complex standard coating material compositions, but with a sufficient number of degrees of freedom in order to allow a screening of as many coating compositions as possible in a defined time frame, in particular as far as the constituents such as film-forming polymers and/or crosslinking agents present therein are concerned. At the same time said method is ought to be able to be performed in a fast, cost-efficient and sustainable manner and in a manner saving resources (use of less amounts of materials and less waste production). In particular, it has been therefore an object underlying the present invention to provide such a method, which allows an investigation of the influence of different constituents such as film-forming polymers and/or crosslinking agents used in such standard coating material compositions on the desired characteristics of the coatings obtainable therefrom in order to provide tailor made new coating formulations in a target-oriented manner, which in turn lead to coatings obtainable therefrom with improved properties.

Solution

This object has been solved by the subject-matter of the claims of the present application as well as by the preferred embodiments thereof disclosed in this specification, i.e. by the subject matter described herein.

A first subject-matter of the present invention is a method of screening coating material compositions for development of new coating formulations in the automotive field, said method comprising at least steps (1) to (8) and (10) to (13) and optionally a step (9), namely

(1) providing a first coating material composition F1,

the first coating material composition F1 comprising

- (i) at least one film-forming polymer P1, said polymer P1 having crosslinkable functional groups,
- (ii) at least one crosslinking agent CA1 having functional groups, which are reactive at least towards the crosslinkable functional groups of polymer P1,
- (iii) water and/or at least one organic solvent,
- (iv) optionally at least one phase compatibilizing polymer PMP,
- (v) optionally at least one additive A, and
- (vi) optionally at least one pigment P11 and/or filler F11,
- wherein the constituents (i), (ii), (iii) and (iv) as well as (v) and (vi) are each different from one another,

(2) applying the first coating material composition F1 onto at least one optionally pre-coated surface of a substrate to form a coating film on said surface of the substrate,

(3) curing the coating film obtained after step (2) to form a cured coating film on the surface of the substrate,

(4) measuring at least one property of the cured coating film obtained after step (3),

(5) providing at least one further coating material composition being different from the first coating material composition F1 in precisely one or at most two, preferably precisely one, parameter(s),

wherein said parameter(s) is/are selected from the group consisting of (a) partial or full exchange of polymer P1 with a further polymer being different from polymer P1 and having crosslinkable functional groups being reactive at least towards the functional groups of crosslinking agent CA1, (b) partial or full exchange of crosslinking agent CA1 with a further crosslinking agent being different from crosslinking agent CA1 and having functional groups being reactive at least towards the crosslinkable functional groups of polymer P1, (c) lowering or increasing

the amount of polymer P1 and/or of the polymer being different from polymer P1, which has been used for partial or full exchange of polymer P1 as defined in (a) in the further coating material composition, (d) lowering or increasing the amount of crosslinking agent CA1 and/or of the crosslinking agent being different from CA1, which has been used for partial or full exchange of CA1 as defined in (b) in the further coating material composition, (e) partial or full exchange of additive A if present with a further additive being different from additive A, (f) lowering or increasing the amount of additive A if present and/or of the additive being different from additive A if present, which has been used for partial or full exchange of additive A as defined in (e) in the further coating material composition, (g) partial or full exchange of pigment PI1 and/or filler FI1 if present with a further pigment and/or filler being different from pigment PI1 and/or filler FI1, and (h) lowering or increasing the amount of pigment PI1 and/or filler FI1 if present and/or of the pigment and/or filler being different from pigment PI1 and/or filler FI1 if present, which has been used for partial or full exchange of pigment PI1 and/or filler FI1 as defined in (g) in the further coating material composition,

- (6) applying the further coating material composition onto at least one optionally pre-coated surface of a substrate to form a coating film on said surface of the substrate,
- (7) curing the coating film obtained after step (6) to form a cured coating film on the surface of the substrate,
- (8) measuring at least one property of the cured coating film obtained after step (7), said at least one property being the same property as measured in step (4),
- (9) optionally repeating steps (5) to (8) at least once, wherein each of the further coating compositions provided is different from one another and different from coating material composition F1,

- (10) incorporating the results of the properties measured in steps (4) and (8) and optionally of the results of the properties measured in case of an at least one-fold repetition as defined in step (9) into a preferably electronic database,
- 5 (11) selecting at least one of the measured properties present in the preferably electronic database due to incorporation step (10),
- (12) evaluating and comparing the results of the at least one selected property of
10 the cured coating films measured according to steps (4) and (8) and optionally after an at least one-fold repetition as defined in step (9) with each other, and
- (13) using the information obtained from evaluation and comparison step (12) for formulating and providing at least one new coating formulation being different
15 from the first coating material composition F1 and from each of the further coating material compositions obtained after step (5) and from any coating material composition obtained optionally after an at least one-fold repetition as defined in step (9), wherein the at least one new coating formulation, when applied and cured as defined in steps (2) and (3), leads to a cured coating film
20 showing an improvement of the at least one property selected in step (11), when measured as defined in step (4) and/or (8).

Preferably, the parameter(s) selected in step (5) and, optionally, during an at least one-fold repetition as defined in step (9), is/are associated with partial or full
25 exchange and/or lowering or increasing of the amount of at least one constituent that contributes to the total solid content of each of the coating material compositions, such as constituents (i) and (ii) and if present constituent (v) and/or (vi) in case of coating material composition F1, more preferably of at least one constituent that contributes to the total binder solid content of each of the coating material
30 compositions, such as constituents (i) and (ii) and if present constituent (v) in case of coating material composition F1.

A further subject-matter of the present invention is a use of the inventive method for developing and providing new coating formulations in the automotive field, said new

coating formulations preferably being basecoat compositions, in particular aqueous basecoat compositions.

A further subject-matter of the present invention is a use of the inventive method for
5 investigating the influence of film-forming polymers (i), said polymers having crosslinkable functional groups, and/or of crosslinking agents (ii) having functional groups, which are reactive at least towards the crosslinkable functional groups of the polymers, and/or of additives (v) and/or of pigments and/or fillers (vi) on properties of cured coating films obtained from applying and curing coating material compositions
10 containing (i) and (ii) and optionally (v) and/or (vi) onto optionally pre-coated surfaces of substrates. The inventive use preferably aims at improvement of these properties.

It has been surprisingly found that by the inventive method a screening of coating material compositions for development of new coating formulations in the automotive
15 field with improved characteristics is available, which can be performed fast and in a cost-efficient manner. This is in particular the case as the method makes use of screening rather non-complex standard coating material compositions, preferably with only a limited number of constituents. Thus, the screening does not have to be performed by making use of rather complex coating formulations with a high number
20 of different constituents, but can be based on said non-complex standard system. Therefore, the inventive method cannot only be practiced in a cost-efficient manner as only a limited number of constituents has to be used, but additionally resources can be saved as less amounts of constituent materials have to be used and less waste is produced. In addition, the inventive method has, therefore, advantages from
25 an ecological point of view.

It has been further surprisingly found that the inventive method can be performed in a cost-efficient and sustainable manner as all results of the properties measured are incorporated into a preferably electronic database, which can be accessed at any
30 time and which can be updated during the process of performing the inventive method. The more data are present in the database, the more efficient, promising and exact can steps (12) and (13) be performed.

It has been further surprisingly found that the inventive method allows a screening of a higher number of coating compositions in the same time interval as conventional screening methods.

5 In particular, it has been surprisingly found that the inventive method allows an investigation of the influence of constituents such as film-forming polymers and/or crosslinking agents present in the standard coating material compositions used on the desired characteristics of the coatings obtained therefrom and that in this manner tailor made new coating formulations can be provided in a target-oriented manner,
10 which in turn lead to coatings obtainable therefrom with improved properties. This in particular applies to the investigation of hydroxyl- (OH-) and optionally also acid-functional polymers as film-forming polymers and/or melamine aldehyde resins as crosslinking agents and their influence on desired characteristics of the coatings obtained such as stone chip robustness. It has been found in this context that new
15 tailor made coating formulations containing OH- and optionally also acid-functional polymers as film-forming polymers and melamine aldehyde resins as crosslinking agents can be provided in a target-oriented manner by the inventive method, which lead to cured coatings having an improved property such as lowered glass transition temperature that in turn leads to an improvement of at least one characteristics of the
20 cured coating films such as stone chip robustness.

Detailed description of the invention

Inventive method

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Step (1)

In step (1) of the inventive method a first coating material composition F1 is provided. The first coating material composition F1 comprises at least constituents (i), (ii) and (iii) and optionally (iv) and/or (v) and/or (vi). The constituents (i), (ii), (iii) and (iv) as
30 well as (v) and (vi) are different from one another.

The term “comprising” in the sense of the present invention, in connection for example with any of the inventively used coating material compositions such as F1 or any of the new coating formulations preferably has the meaning of “consisting of”. In

this case it is possible – in addition to all mandatory constituents present therein – for one or more of the further constituents identified hereinafter to be also optionally included therein. All constituents may in each case be present in their preferred embodiments as identified hereinafter.

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The proportions and amounts in wt.-% (% by weight) of any of the constituents given hereinafter, which are present in any of the coating material compositions add up to 100 wt.-%, based in each case on the total weight of each composition.

10 *Coating material composition F1 and further coating material compositions*

Preferably, constituents (i) to (iii) and optionally (iv) and/or optionally (v) and/or (vi) are the only constituents of the first coating material composition F1. Thus, preferably, the first coating material composition F1 consists of constituents (i) to (iii) and optionally (iv) and/or (v) and/or (vi). Preferably, constituent (iv) is present in the first coating material composition F1. The same preferably applies to each of the further coating material compositions different from F1.

Preferably, the first coating material composition F1 and any of the further coating material compositions provided in step (5) and, optionally, obtained after an at least one-fold repetition as defined in step (9), are one-component (1K) or two-component (2K) coating material compositions, preferably are each one-component (1K) coating material compositions, more preferably for use as basecoat material compositions. The basecoat material compositions can be aqueous (waterborne) or organic solvent-based (solventborne, non-aqueous) and can be used both as OEM coating material compositions and for refinish applications. The same preferably applies to each of the further coating material compositions different from F1.

The term “basecoat” is known in the art and, for example, defined in Römpp Lexikon, paints and printing inks, Georg Thieme Verlag, 1998, 10th edition, page 57. A basecoat is therefore in particular used in automotive painting and general industrial paint coloring in order to give a coloring and/or an optical effect by using the basecoat as an intermediate coating composition. This is generally applied to a metal or plastic substrate, optionally pretreated with a primer and/or filler and/or sealer,

sometimes in the case of plastic substrates also directly on the plastic substrate, and in the case of metal substrates on an electrodeposition coating layer coated onto the metal substrate, wherein the metal substrate may already bear a phosphate layer such as a zinc phosphate layer, or on the metal substrate already bearing a primer and/or filler and/or sealer and/or electrodeposition coating, or to already existing coatings in case of refinish applications, which can also serve as substrates. In order to protect a basecoat film in particular against environmental influences, at least one additional topcoat film, on particular clearcoat film is applied to it.

10 Preferably, the coating material composition F1 has a total solid content (non-volatile content) in the range of from 10 to 85 wt.-%, more preferably of from 15 to 80 wt.-%, even more preferably of from 20 to 65 wt.-%. The same preferably applies to each of the further coating material compositions different from F1. The total solid content is determined according to the method described in the 'Methods' section. Preferably, 15 the total solid content in each case exceeds 40 wt.-%, more preferably exceeds 50 wt.-%.

Film-forming polymers and crosslinking agents

20 The first coating material composition F1 comprises at least one film-forming polymer P1, said polymer P1 having crosslinkable functional groups, as constituent (i). The first coating material composition F1 further comprises at least one crosslinking agent CA1 having functional groups, which are reactive at least towards the crosslinkable functional groups of polymer P1, as constituent (ii). A crosslinking reaction preferably 25 taking place between the crosslinkable functional groups of polymer P1 and the functional groups of crosslinking agent CA1 can but does not necessarily have to be catalyzed by at least one crosslinking catalyst. If such a catalysis is desired the first coating material composition F1 additionally comprises at least one crosslinking catalyst. Preferably, however, it does not contain such a catalyst. The same 30 preferably applies to each of the further coating material compositions different from F1.

Film-forming polymers

The film-forming polymer P1 represents a binder. For the purposes of the present invention, the term "binder" is understood in accordance with DIN EN ISO 4618 (German version, date: March 2007) to be the non-volatile (solid) constituent of a coating material composition, which is responsible for the film formation. The term includes crosslinking agents (crosslinkers) and additives such as catalysts if these represent non-volatile constituents. Pigments and/or fillers are not subsumed under the term "binder" as these are not responsible for film formation. Preferably, however, no pigments and/or fillers are present. Preferably, each of constituents (i), (ii), (iv) and (v) contributes to the total binder solids content of the coating material composition F1. The same preferably applies to each of the further coating material compositions different from F1.

Preferably, the at least one polymer P1 is the main binder of the coating material composition. As the main binder in the sense of the present invention, a binder constituent is preferably referred to, when there is no other binder constituent in the coating material composition, which is present in a higher proportion based on the total weight of the coating material composition.

The term "polymer" is known to the person skilled in the art and, for the purposes of the present invention, encompasses polyadducts and polymerizates as well as polycondensates. The term "polymer" includes both homopolymers and copolymers.

Suitable polymers which can be used as film-forming polymers are, for example, known from EP 0 228 003 A1, DE 44 38 504 A1, EP 0 593 454 B1, DE 199 48 004 A1, EP 0 787 159 B1, DE 40 09 858 A1, WO 92/15405 A1, WO 2005/021168 A1, WO 2017/097642 A1 and WO 2017/121683 A1.

Preferably, the at least one polymer P1 present as constituent (i) in the first coating material composition F1 and any further at least one film-forming polymer being present in any of the further coating material compositions provided in step (5) and, optionally, obtained after an at least one-fold repetition as defined in step (9), is selected from the group consisting of physically drying polymers, chemically crosslinking polymers, radiation curing polymers, and mixtures thereof, more

preferably is selected from the group consisting of physically drying polymers, chemically self-crosslinking polymers, chemically non-self-crosslinking polymers (i.e. externally crosslinking polymers), radiation curing polymers, and mixtures thereof, even more preferably is selected from the group consisting of chemically non-self-crosslinking polymers.

Radiation curing polymers are curable via inducing radiation. Preferably, such polymers contain functional groups comprising carbon-carbon double bonds, e.g. vinyl and/or (meth)acryl groups. Physically drying polymers are primarily curable, preferably are curable, via physical drying. The presence of crosslinkable functional groups such as acid groups within these polymers is not in contradiction to the fact that they are (primarily) cured by physical drying. Even in case of (primarily) a physical drying, these polymers can additionally undergo at least partially a crosslinking reaction with the at least one crosslinking agent. Chemically crosslinking polymers are in particular chemically self-crosslinking polymers and chemically non-self-crosslinking polymers (i.e. externally crosslinking polymers). Even in case of (primarily) a self-crosslinking reaction, these polymers can additionally at least partially undergo a crosslinking reaction with the at least one crosslinking agent. Particularly preferred are, however, chemically non-self-crosslinking polymers.

The polymer P1 has crosslinkable functional groups, which preferably enable a crosslinking reaction with the functional groups of crosslinking agent CA1. Any common suitable crosslinkable reactive functional group known to those skilled in the art can be present. Preferably, the polymer P1 has at least one kind of functional reactive groups selected from the group consisting of hydroxyl groups (also referred to herein as OH-groups), amino groups such as primary and/or secondary amino groups, thiol groups, epoxide groups, keto groups including diketo groups, acid groups such as carboxyl groups, and carbamate groups, siloxane groups, as well as functional groups comprising carbon-carbon double bonds, e.g. vinyl and/or (meth)acryl groups. Preferably, the polymer P1 has functional hydroxyl groups and/or acid groups, in particular hydroxyl and/or carboxylic acid groups, most preferably hydroxyl groups. Preferably, the same applies to any polymers used for partial or full exchange of polymer P1 as defined in step (5) of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9).

Preferably, the polymer P1 is hydroxyl-functional and more preferably has an OH number in the range of 5 to 400 mg KOH/g, more preferably from 7.5 to 350 mg KOH/g, more preferably of from 10 to 300 mg KOH/g. Preferably, the polymer P1 is additionally or alternatively acid-functional and more preferably has an acid number in the range of 0 to 200 mg KOH/g, more preferably from 1 to 150 mg KOH/g, even more preferably of from 1 to 100 mg KOH/g. Preferably, the same applies to any polymers used for partial or full exchange of polymer P1 as defined in step (5) of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9).

Preferably, the at least one polymer P1 present as constituent (i) in the first coating material composition F1 and any further at least one polymer being present in any of the further coating material compositions provided in step (5) and, optionally, obtained after an at least one-fold repetition as defined in step (9), are selected from the groups consisting of polyesters, poly(meth)acrylates, polyurethanes, polyureas, polyamides and polyethers, preferably are selected from the groups consisting of polyesters, poly(meth)acrylates, polyurethanes and polyethers. This includes copolymers containing structural units of said homopolymers such as polyurethane-poly(meth)acrylates. The same preferably applies to each of the film-forming polymers present in any of the further coating material compositions different from F1.

Most preferred are polyesters, poly(meth)acrylates, polyurethanes, and polyethers, each having at least OH-groups as crosslinkable functional groups, and optionally additionally having acid groups.

The term "(meth) acryl" or "(meth) acrylate" or "(meth)acrylic" in the context of the present invention in each case comprises the meanings "methacryl" and/or "acryl" "methacrylic" and/or "acrylic" or "methacrylate" and/or "acrylate". Therefore, a "(meth)acrylic copolymer" in general may be formed from only "acrylic monomers", only "methacrylic monomers" or "acrylic and methacrylic monomers". However, polymerizable monomers other than acrylic and/or methacrylic monomers as e.g. styrene and the like may also be contained in a "(meth)acrylic copolymer". In other

words, a (meth)acrylic polymer may consist of only acrylic and/or methacrylic monomer units but does not have to. The notation “(meth)acrylate polymer or copolymer” or “(meth)acrylic polymer or copolymer” is intended to mean that the polymer/copolymer (polymer skeleton/backbone) is formed predominantly, i.e. preferably more than 50 mol-% or more than 75 mol-% of the monomer units used, from monomers having a (meth)acrylate group. In the preparation of a (meth)acrylic copolymer, preferably more than 50 mol-% or 75 mol-% of the monomers thus have a (meth)acrylate group. However, the use of further monomers as comonomers such as copolymerizable vinyl monomers, e.g. styrene, for its preparation is not excluded.

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Preferred polyurethanes are described, for example, in German patent application DE 199 48 004 A1, page 4, line 19 to page 11, line 29 (polyurethane prepolymer B1), in European patent application EP 0 228 003 A1, page 3, line 24 to page 5, Line 40, European Patent Application EP 0 634 431 A1, page 3, line 38 to page 8, line 9, and international patent application WO 92/15405, page 2, line 35 to page 10, line 32.

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Preferred polyesters are described, for example, in DE 4009858 A1 in column 6, line 53 to column 7, line 61 and column 10, line 24 to column 13, line 3 or WO 2014/033135 A2, page 2, line 24 to page 7, line 10 and page 28, line 13 to page 29, line 13 described. Likewise, preferred polyesters are polyesters having a dendritic structure or star-shaped structure, as described, for example, in WO 2008/148555 A1.

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Preferred polyethers are, e.g., described in WO 2017/097642 A1 and WO 2017/121683 A1.

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Preferred polyurethane-poly(meth)acrylate copolymers (e.g., (meth)acrylated polyurethanes)) and their preparation are described, for example, in WO 91/15528 A1, page 3, line 21 to page 20, line 33.

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Particularly preferred are (meth)acrylic copolymers, in particular when they are OH-functional. Hydroxyl-containing monomers include hydroxy alkyl esters of acrylic or methacrylic acid, which can be used for preparing the copolymer. Non-limiting examples of hydroxyl-functional monomers include hydroxyethyl(meth)acrylate,

hydroxypropyl(meth)acrylates, hydroxybutyl-(meth)acrylates, hydroxyhexyl(meth)-acrylates, propylene glycol mono(meth)acrylate, 2,3-dihydroxypropyl(meth)acrylate, pentaerythritol mono(meth)acrylate, polypropylene glycol mono(meth)acrylates, polyethylene glycol mono(meth)acrylates, reaction products of these with epsilon-caprolactone, and other hydroxyalkyl-(meth)acrylates having branched or linear alkyl groups of up to about 10 carbons, and mixtures of these. Hydroxyl groups on a vinyl polymer such as an (meth)acrylic polymer can be generated by other means, such as, for example, the ring opening of a glycidyl group, for example from copolymerized glycidyl methacrylate, by an organic acid or an amine. Hydroxyl functionality may also be introduced through thio-alcohol compounds, including, without limitation, 3-mercapto-1-propanol, 3-mercapto-2-butanol, 11-mercapto-1-undecanol, 1-mercapto-2-propanol, 2-mercaptoethanol, 6-mercapto-1-hexanol, 2-mercaptobenzyl alcohol, 3-mercapto-1,2-propanediol, 4-mercapto-1-butanol, and combinations of these. Any of these methods may be used to prepare a useful hydroxyl-functional (meth)acrylic polymer. Examples of suitable comonomers that may be used include, without limitation, α,β -ethylenically unsaturated monocarboxylic acids containing 3 to 5 carbon atoms such as acrylic, methacrylic, and crotonic acids and the alkyl and cycloalkyl esters, nitriles, and amides of acrylic acid, methacrylic acid, and crotonic acid; α,β -ethylenically unsaturated dicarboxylic acids containing 4 to 6 carbon atoms and the anhydrides, monoesters, and diesters of those acids; vinyl esters, vinyl ethers, vinyl ketones, and aromatic or heterocyclic aliphatic vinyl compounds. Representative examples of suitable esters of acrylic, methacrylic, and crotonic acids include, without limitation, those esters from reaction with saturated aliphatic alcohols containing 1 to 20 carbon atoms, such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, hexyl, 2-ethylhexyl, dodecyl, 3,3,5-trimethylhexyl, stearyl, lauryl, cyclohexyl, alkyl-substituted cyclohexyl, alkanol-substituted cyclohexyl, such as 2-tert-butyl and 4-tert-butyl cyclohexyl, 4-cyclohexyl-1-butyl, 2-tert-butyl cyclohexyl, 4-tert-butyl cyclohexyl, 3,3,5,5-tetramethyl cyclohexyl, tetrahydrofurfuryl, and isobornyl acrylates, methacrylates, and crotonates; unsaturated dialkanoic acids and anhydrides such as fumaric, maleic, itaconic acids and anhydrides and their mono- and diesters with alcohols such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, and tert-butanol, like maleic anhydride, maleic acid dimethyl ester and maleic acid monohexyl ester; vinyl acetate, vinyl propionate, vinyl ethyl ether, and vinyl ethyl ketone; styrene, a-methyl styrene, vinyl toluene, 2-vinyl pyrrolidone, and p-

tert-butylstyrene. The (meth)acrylic copolymer may be prepared using conventional techniques, such as by heating the monomers in the presence of a polymerization initiating agent and optionally a chain transfer agent.

5 Suitable poly(meth)acrylates are also those which can be prepared by multistage free-radical emulsion polymerization of olefinically unsaturated monomers in water and/or organic solvents. Examples of seed-core-shell polymers (SCS polymers) obtained in this manner are disclosed in WO 2016/116299 A1.

10 Preferably, the at least one polymer P1 is present in the coating material composition F1 in an amount in a range of from 10.0 to 90 wt.-%, more preferably of from 15.0 to 85 wt.-%, even more preferably of from 17.5 to 65 wt.-%, still more preferably of from 20.0 to 60 wt.-%, in each case based on the total binder solids content of the coating material composition. Preferably, the same applies to any polymers used for partial or
15 full exchange of polymer P1 as defined in step (5) of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9), with respect to any of the further coating material compositions different from F1 and from one another.

20 Preferably, the at least one polymer P1 is present in the coating material composition F1 in an amount in a range of from 50.0 to 90 wt.-%, more preferably of from 55.0 to 85 wt.-%, even more preferably of from 57.5 to 80 wt.-%, in each case based on the total solids content of the coating material composition. Preferably, the same applies to any polymers used for partial or full exchange of polymer P1 as defined in step (5)
25 of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9), with respect to any of the further coating material compositions different from F1 and from one another.

Crosslinking agents

30 All conventional crosslinking agents can be used. This includes melamine resins, preferably melamine aldehyde resins, more preferably melamine formaldehyde resins, blocked polyisocyanates, polyisocyanates having free (unblocked) isocyanate groups, crosslinking agents having amino groups such as secondary and/or primary amino groups, and crosslinking agents having epoxide groups and/or hydrazide

groups, as well as crosslinking agents having carbodiimide groups, as long as the functional groups of the particular crosslinking agent are suitable to be reacted with the crosslinkable functional groups of the film-forming polymers used as binders in a crosslinking reaction. For example, a crosslinking agent having blocked or free isocyanate groups can be reacted with a film-forming polymer having crosslinkable OH-groups and/or amino groups at elevated temperatures in case of 1K formulations and at ambient temperature in case of 2K formulations. Further possible combinations are epoxide groups, for example of a film-forming polymer, which can be reacted with acid and/or amino groups of a crosslinking agent, or vice versa. Further possible combinations are keto groups, for example of a film-forming polymer, which can be reacted with hydrazide groups of a crosslinking agent, or vice versa, or carbodiimide groups, for example of a crosslinking agent, which can be reacted with acid groups of a film-forming polymer or vice versa.

Preferably, the at least one crosslinking agent CA1 present as constituent (ii) in the first coating material composition F1 and any further at least one crosslinking agent being present in any of the further coating material compositions provided in step (5) and, optionally, obtained after an at least one-fold repetition as defined in step (9), are melamine aldehyde resins, preferably melamine formaldehyde resins. This in particular applies in case of 1K coating material compositions. As outlined hereinbefore crosslinking agents are to be included among the film-forming non-volatile components of a material coating composition, and therefore fall within the general definition of the "binder" as mentioned hereinbefore.

Preferably, the melamine aldehyde resins, preferably the melamine formaldehyde resins, in each case bear at least one of imino groups, alkylol groups and etherified alkylol groups as functional groups, which are reactive towards the functional groups of polymer P1. Examples of alkylol groups are methylol groups.

At least some of the alkylol groups present in the melamine aldehyde resins may be alkylated through further reaction with at least one alcohol to produce nitrogen-bonded alkoxyalkyl groups (etherified alkylol groups). In particular, the hydroxyl groups in the nitrogen-bonded alkylol groups may be reacted with the alcohol through an etherification reaction to produce nitrogen-bonded alkoxyalkyl groups. The

alkoxyalkyl groups are available for a crosslinking reaction with, for example, suitable crosslinkable functional groups of polymer P1 such as OH- and/or acid groups. The remaining imino groups present after the aldehyde/melamine reaction are unreactive with the alcohol used for alkylation.

5

As outlined above the alkylol groups of the melamine aldehyde resins may be partially alkylated. By "partially alkylated", it is meant that a sufficiently low amount of alcohol is reacted with the melamine aldehyde resins to leave some of the alkylol groups in the melamine aldehyde resins, under reaction conditions that should result in incomplete alkylation of the alkylol groups. When the melamine aldehyde resins are partially alkylated, they are typically alkylated with alcohol in amounts sufficient to leave alkylol groups present in the aminoplast in an amount of at least about 2%, more preferably of from about 10% to about 50%, even more preferably of from about 15% to about 40%, in each case based on the total number of reactive sites present in the melamine prior to reaction. Typically, the melamine aldehyde resin is partially alkylated to obtain from about 40 to about 98% of alkoxyalkyl groups, more preferably of from about 50% to about 90%, even more preferably of from about 60% to about 75%, in each case based on the total number of reactive sites present in the melamine prior to reaction.

20

Preferably, at least a portion, more preferably only a portion, of the alkylol groups such as methylol groups of the melamine aldehyde resin is etherified by reaction with at least one alcohol. Any monohydric alcohol can be employed for this purpose, including methanol, ethanol, n-propanol, iso-propanol, n-butanol, sec-butanol, t-butanol, pentanol, hexanol, heptanol, as well as benzyl alcohol and other aromatic alcohols, cyclic alcohols such as cyclohexanol, monoethers of glycols, and halogen-substituted or other substituted alcohols such as 3-chloropropanol and butoxyethanol. In particular, at least a part of the alkylol groups of the melamine aldehyde resins are partially modified with methanol and/or n-butanol and/or iso-butanol.

30

Preferably, constituent (ii) is present in the first coating material composition F1 in an amount in a range of from 7.5 to 45 wt.-%, more preferably of from 10.0 to 40 wt.-%, even more preferably of from 12.5 to 35 wt.-%, in particular of from 15 to 40 wt.-%, in

each case based on the total binder solids of the coating material composition. Preferably, the same applies to any crosslinking agents used for partial or full exchange of crosslinking agent CA1 as defined in step (5) of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9),
5 with respect to any of the further coating material compositions different from F1 and from one another.

Preferably, the at least one crosslinking agent CA1 is present in the coating material composition F1 in an amount in a range of from 10.0 to 50 wt.-%, more preferably of
10 from 15.0 to 45 wt.-%, even more preferably of from 20.5 to 42.5 wt.-%, in each case based on the total solids content of the coating material composition. Preferably, the same applies to any crosslinking agents used for partial or full exchange of crosslinking agent CA1 as defined in step (5) of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9), with respect to
15 any of the further coating material compositions different from F1 and from one another.

Preferably, the at least one film-forming polymer P1 and the at least one crosslinking agent CA1 are present in the coating material composition in a relative weight ratio,
20 based on their solids, in a range of from 9.0:1 to 1.2:1, in particular of from 8.5:1.5 to 1.5:1. Preferably, the same applies to any crosslinking agents used for partial or full exchange of crosslinking agent CA1 as defined in step (5) of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9), with respect to any of the further coating material compositions different from F1 and
25 from one another.

Constituent (iii)

The first coating material composition F1 comprises water and/or at least one organic solvent as constituent (iii).

30 All conventional organic solvents known to those skilled in the art can be used as organic solvents. The term "organic solvent" is known to those skilled in the art, in particular from Council Directive 1999/13 / EC of 11 March 1999. Examples of such organic solvents would include heterocyclic, aliphatic, or aromatic hydrocarbons,

mono- or polyhydric alcohols, especially methanol and/or ethanol, ethers, esters, ketones, and amides, such as, for example, N-methylpyrrolidone, N-ethylpyrrolidone, dimethylformamide, toluene, xylene, butanol, ethyl glycol and butyl glycol and also their acetates, butyl diglycol, diethylene glycol dimethyl ether, cyclohexanone, methyl ethyl ketone, methyl isobutyl ketone, acetone, isophorone, or mixtures thereof. Preferably, however, no mono- or polyhydric alcohols are used.

Depending on the content and amount of water and/or organic solvent(s) the coating material composition can be "solventborne" ("non-aqueous") or "waterborne" ("aqueous"). The term "solventborne" or "non-aqueous" is understood preferably for the purposes of the present invention to mean that organic solvent(s), used as solvent and/or as diluent, is/are present as the main constituent of all solvents and/or diluents present in the coating material composition. If the coating material composition is solventborne, constituent (iii) preferably is at least one organic solvent and does not represent water or comprises an amount of water being less than the amount of organic solvent(s). The coating composition when solventborne preferably is free or essentially free of water. The term "waterborne" or "aqueous" is understood preferably for the purposes of the present invention to mean that water is present as the main constituent of all solvents and/or diluents present in the inventive coating material composition. If it is waterborne, constituent (iii) comprises water at least as main solvent/diluent. Organic solvent(s) may be additionally present, but in a lower amount than water.

Preferably, the same applies to any of the further coating material compositions different from F1 and from one another provided according to step (5) of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9).

Constituent (iv)

The first coating material composition F1 optionally and preferably comprises at least one phase compatibilizing polymer PMP as constituent (iv). Phase compatibilizing polymer PMP is used as phase mediator and/or phase promoter in particular in case both water and at least one organic solvent are present in the first coating material

composition. Preferably, constituent (iv) is present in the first coating material composition F1 when constituent (iii) represents at least partially water.

Constituent (iv) preferably exhibits phase compatibilizing properties, i.e. has tenside characteristics. Constituent (iv) is, however, only an optional constituent as the
5 desired compatibilizing properties may alternatively be introduced into the coating material composition via constituent (i). Thus, polymer P1 may not only function as film-forming polymer, but additionally also as phase mediator/phase promoter, in which case the presence of optional constituent (iv) is not necessary. Furthermore,
10 the presence of constituent (iv) may in particular be not necessary when the crosslinking agent present such as CA1 is a water-dilutable crosslinking agent such as a water-dilutable melamine formaldehyde resin.

Preferably, constituent (iv) is a polymer having a non-polar as well as a polar moiety.
15 Preferably, these two moieties are sterically separated from each other within the backbone of the polymer. The polar moiety has a hydrophilic character, whereas the non-polar moiety has a hydrophobic character. Constituent (iv) has phase compatibilizing properties as it is able to function as phase mediator/phase promoter between hydrophilic constituents or parts/groups of constituents present in the
20 coating material composition - via its hydrophilic moiety - and hydrophobic constituents or parts/groups of constituents present in the coating material composition - via its hydrophobic moiety. For example, polymer PMP can be at least one polymer selected from the group of polyurethanes, polyesters, (meth)acrylic (co)polymers and polymers composed of at least two of the structural units of these
25 polymers, wherein each of these polymers used as polymer PMP preferably has at least one aforementioned polar moiety and at least one aforementioned non-polar moiety. Preferably, polymer PMP is obtainable by copolymerization of at least two different kinds of monomers in subsequent polymerization steps, each monomer having at least one ethylenically unsaturated carbon-carbon double bond, the first
30 step involving a polymerization of at least one monomer being a non-polar monomer, for example a monomer having a low solubility (g/l) in water at 20°C such as styrene, the second subsequent step involving a polymerization of at least one monomer being a polar monomer, for example a monomer having a high solubility (g/l) in water at 20°C such as acrylic acid. The polymerization may be performed in presence of a

polyurethane, which may or may not have, preferably does not have, ethylenically unsaturated carbon-carbon double bonds. Suitable polymers which can be used as constituents (iv) are, for example, known from DE 4437535 A1. In particular, constituent (iv) is a polyurethane poly(meth)acrylate.

5

Preferably, constituent (iv) is present in the first coating material composition F1 in an amount in a range of from 1.5 to 20 wt.-%, more preferably of from 2.5 to 18 wt.-%, even more preferably of from 3.5 to 15 wt.-%, in each case based on the total binder solids of the coating material composition. Preferably, the same applies to any of the further coating material compositions different from F1 and from one another provided in step (5) of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9).

10

Constituent (v)

The first coating material composition F1 optionally comprises at least one additive A as constituent (v). Likewise, each of the further coating material compositions provided in the inventive method may optionally comprise additive A and/or at least one additive being different from additive A.

15

The concept of an "additive" is known to the skilled person, from Römpp Lexikon "Lacke und Druckfarben", Thieme Verlag, 1998, page 13, for example.

20

Examples of additives are reactive diluents, light stabilizers, crosslinking catalysts, antioxidants, deaerators, emulsifiers, surface-active agents such as surfactants, wetting agents and dispersants, and also thickeners, thixotropic agents, plasticizers, lubricity and antiblocking additives, slip additives, polymerization inhibitors, initiators for free-radical polymerizations, adhesion promoters, flow control agents, film-forming auxiliaries, sag control agents (SCAs), flame retardants, corrosion inhibitors, siccatives, thickeners, biocides and/or matting agents.

25

30

Preferably, if constituent (v) is present, it is a constituent that contributes to the total solids content of the respective coating material composition such as coating material composition F1, more preferably that contributes to the total binder solids content of the respective coating material composition such as coating material composition F1.

A preferred constituent (v) is at least one rheology additive and/or at least one crosslinking catalyst. The term "rheology additive" as well is known to the skilled person, from Römpp Lexikon "Lacke und Druckfarben", Thieme Verlag, 1998, page 497, for example. The terms "rheology additive", "rheological additive" and "rheology assistant" are interchangeable here. The additive optionally present as constituent (v) is preferably selected from the group consisting of flow control agents, surface-active agents such as surfactants, wetting agents and dispersants, and also thickeners, thixotropic agents, plasticizers, lubricity and antiblocking additives, and mixtures thereof. These terms are likewise known to the skilled person, from Römpp Lexikon, "Lacke und Druckfarben", Thieme Verlag, 1998, for example. Flow control agents are components which by lowering the viscosity and/or surface tensions help coating composition materials to form films which flow out evenly. Wetting agents and dispersants are components which lower the surface tension or, generally, the interfacial tension. Lubricity and antiblocking additives are components which reduce mutual sticking (blocking).

If, e.g. crosslinking catalysts are used as additives (v) it is possible that these may exhibit further functions besides their catalytic activity. For example, in case blocked or unblocked sulfonic acids are used as crosslinking catalysts, these may also function as surfactants and thus also have an influence on the surface tension as a further example of a to be a measured property. This principle applies to all additives used as constituent (v).

In addition, or alternatively, as outlined above, each of the first and the further coating material compositions may comprise a crosslinking catalyst as constituent (v). Preferably, at least one sulfonic acid such as an unblocked sulfonic acid or a blocked sulfonic acid, more preferably a blocked sulfonic acid, is used as catalyst. Examples of sulfonic acids are para-toluenesulfonic acid (pTSA), methanesulfonic acid (MSA), dodecylbenzene sulfonic acid (DDBSA), dinonylnaphthalene disulfonic acid (DNNDSA), and mixtures thereof. Blocking can be performed by making use of ammonium salts and/or organic amines. Alternatively, blocking may also be performed by making use of epoxides that form β -OH-sulfonates when reversibly reacted with sulfonic acids.

As it is desired to use a rather non-complex standard coating material composition as composition F1, coating material composition F1 preferably does not contain any other constituents besides (i), (ii), (iii) and optionally (iv) and/or (v) and/or (vi).
5 Preferably, the same applies to any of the further coating material compositions different from F1 and from one another provided in step (5) of the inventive method, and similarly in case of an at least one-fold repetition as defined in optional step (9).

The optionally present constituent (v) can be used in the known and customary
10 proportions. Preferably, their content, based on the total weight of the coating material composition is 0.01 to 20.0 wt.-%, more preferably 0.05 to 15.0 wt.-%, particularly preferably 0.1 to 10.0 % by weight, most preferably from 0.1 to 7.5% by weight, especially from 0.1 to 5.0% by weight and most preferably from 0.1 to 2.5% by weight.

15
Constituent (vi)

The first coating material composition F1 optionally comprises at least one pigment PI1 and/or at least one filler FI1 as constituent (vi). Likewise, each of the further coating material compositions provided in the inventive method may optionally
20 comprise pigment PI1 and/or filler FI1 and/or at least one pigment being different from pigment PI1 and/or at least filler being different from filler FI1. Preferably, however, the first coating material composition F1 does not comprise any pigments and/or fillers.

25 The term "pigment" is known to the skilled person, for example from DIN 55943 (date: October 2001). A "pigment" in the sense of the present invention refers preferably to a component in powder or flake form which is substantially, preferably entirely, insoluble in the medium surrounding them, such as in any of the coating material compositions. Pigments are preferably colorants and/or substances which can be
30 used as pigment on account of their magnetic, electrical and/or electromagnetic properties. Pigments differ from "fillers" preferably in their refractive index, which for pigments is ≥ 1.7 . The term "filler" is known to the skilled person, from DIN 55943 (date: October 2001), for example. For fillers their refractive index is < 1.7 .

The term "pigment" includes color pigments and effect pigments and color and effect pigments. Effect pigments are preferably pigments which have an optical effect or a color and optical effect. Examples of effect pigments are platelet-shaped metallic effect pigments such as platelet-shaped aluminum pigments, gold bronzes, fire-colored bronzes and/or iron oxide-aluminum pigments, perglaze pigments and/or metal oxide-mica pigments (mica). A person skilled in the art is familiar with the concept of color pigments. The terms "coloring pigment" and "color pigment" are interchangeable. As a color pigment inorganic and/or organic pigments can be used. Preferably, the color pigment is an organic color pigment. Particularly preferred color pigments used are white pigments, colored pigments and/or black pigments. Examples of suitable fillers are kaolin, dolomite, calcite, chalk, calcium sulfate, barium sulfate, talc, silicic acids, in particular pyrogenic silicic acids, hydroxides such as aluminum hydroxide or magnesium hydroxide or organic fillers such as textile fibers, cellulose fibers and/or polyolefine fibers; in addition, reference is made to Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, 1998, pages 250 ff., "Fillers".

Preferably, the at least one optional filler F11 is present in the coating material composition F1 in an amount in the range of from 1.0 to 40 wt.-%, more preferably of from 2.0 to 35 wt.-%, still more preferably of from 5.0 to 30 wt.-%, in each case based on the total weight of the coating composition. Preferably, the at least one pigment PI1 is present in the coating material composition F11 in an amount in the range of from 1.0 to 40 wt.-%, more preferably of from 2.0 to 35 wt.-%, still more preferably of from 5.0 to 30 wt.-%, in each case based on the total weight of the coating composition. The same preferably applies to any pigments and/or fillers being present in any of the further coating material compositions different from F1.

Step (2)

In step (2) the first coating material composition F1 is applied onto at least one optionally pre-coated surface of a substrate to form a coating film on said surface of the substrate.

The method of the invention is particularly suitable for the coating of automotive vehicle bodies or parts thereof including respective metallic substrates, but also

plastic substrates. Consequently, the preferred substrates are automotive vehicle bodies or parts thereof.

Suitability as metallic substrates used in accordance with the invention are all
5 substrates used customarily and known to the skilled person. The substrates used in
accordance with the invention are preferably metallic substrates, more preferably
selected from the group consisting of steel, preferably steel selected from the group
consisting of bare steel, cold rolled steel (CRS), hot rolled steel, galvanized steel
such as hot dip galvanized steel (HDG), alloy galvanized steel (such as, for example,
10 Galvalume, Galvannealed or Galfan) and aluminized steel, aluminum and
magnesium, and also Zn/Mg alloys and Zn/Ni alloys, or are alternatively preferably
plastic substrates such as polyolefin substrates, e.g. Stamyln® products.
Particularly suitable substrates are parts of vehicle bodies or complete bodies of
automobiles for production.

15 The metallic substrate used in accordance with the invention is preferably a substrate
pretreated with at least one metal phosphate such as zinc phosphate. A pretreatment
of this kind by means of phosphating, which takes place normally after the substrate
has been cleaned and before the substrate is electrodeposition-coated, is in
20 particular a pretreatment step that is customary in the automobile industry.

As outlined above the substrate used may be a pre-coated substrate, i.e. a substrate
bearing at least one cured coating film. The substrate used in step (1) can be pre-
coated with a cured electrodeposition coating layer and/or a cured primer or filler
25 layer.

Applying according to step (2) can be performed by conventional means such as
dipping, brushing, doctor blading or preferably spraying.

Optional step (2a)

Preferably, the inventive method further comprises a step (2a), which is carried out after step (2) and before step (3). In said step (2a) the coating film obtained after step (2) is flashed-off before performing curing step (3), preferably for a period of 1 to 30 minutes, more preferably for a period of 1.5 to 25 minutes, in particular for a period of 2 to 20 minutes, most preferably for a period of 3 to 15 minutes. Preferably, step (2a) is performed at a temperature not exceeding 100°C, more preferably at a temperature in the range of from 18 to 80°C.

The term “flashing off” or “flash-off” in the sense of the present invention means a drying, wherein at least some of the solvents and/or water are evaporated from the coating film before curing is carried out. No intended and in particular no complete curing is performed by the flashing-off.

Step (3)

In step (3) the coating film obtained after step (2) or (2a) is cured to form a cured coating film on the surface of the substrate. Curing is preferably performed at elevated temperatures in an oven, preferably at a temperature in the range of from 75 to 180 °C, more preferably of from 80 to 160 °C. The cured coating film represents a coating layer.

Step (4)

In step (4) at least one property of the cured coating film obtained after step (3) is measured.

Preferably, the at least one property measured in step (4), and optionally measured after an at least one-fold repetition as defined in step (9), is at least one property selected from the group consisting of crosslinking density, glass transition temperature, shrinkage, spread, and surface tension of the cured coating films, in particular is at least one property selected from the group consisting of crosslinking density and glass transition temperature of the cured coating films.

Crosslinking density and glass transition temperature of the cured coating films are measured properties associated with the elasticity of the cured coating films and can

be determined by the DMA V Echo measurements described hereinafter in the “Methods” section. Improvements of these properties are in particular a lowering of the glass transition temperature and/or of the crosslinking density of the cured coating films as the resulting cured coating films are more flexible, which leads to an improvement of the stone chip robustness as an example of a characteristic of the cured coating film, as these measured properties are in correlation to this characteristic. Shrinkage means the changes in volume that occur during baking of a wet or partially dried coating film in order to obtain a cured coating film. Shrinkage can be measured as disclosed in paragraphs [0055] to [0061] of EP 3 099 423 B1. Surface tension is determined according to ISO 19403-2:2017-06. Determination of the surface tension may include determination of the contact angle and of the electrical dipole moment, in particular in association with the polarity and the surface energy of the cured coating films. Spread is determined according to ISO 19403-2:2017-06 and DIN EN ISO 19403-5:2020-04.

Preferably, the at least one property measured in step (4), and optionally measured after an at least one-fold repetition as defined in step (9), correlates to at least one characteristic of the cured coating films, preferably correlates to at least one of the characteristics selected from the group consisting of stone chip robustness (determined according to DIN EN ISO 20567-1:2017-07), hardness, preferably surface hardness (determined according to DIN 55662:2009-12; pressure water resistance test), pencil hardness (determined according to DIN EN ISO 15184:2019-10) and/or micro hardness (determined according to DIN 55676:1996-02; test according to Vickers), scratch resistance (determined according to DIN EN ISO 1518-1:2019-10), impact resistance (determined according to DIN EN ISO 6272-1:2011-11), resistance to UV light exposure (determined according to DIN EN ISO 2810:2004-10), resistance to heat (determined according to DIN EN ISO 2812-5:2018-12 and DIN EN ISO 3248:2016-12), resistance to moisture (determined according to DIN EN ISO 2812-5:2018-12 and DIN EN ISO 6270-1:2018-04), cohesion (determined according to DIN EN ISO 2409:2019-09; cross-cut test), adhesion (determined according to DIN EN ISO 4624:2016-08), appearance (determined according to DIN EN ISO 13803:2015-02), color stability and flop, in particular after storage, (determined according to DIN EN ISO/CIE 11664-1:2020-03, DIN EN ISO/CIE 11664-2:2020-03, DIN EN ISO/CIE 11664-3:2020-03, DIN EN

ISO/CIE 11664-4:2020-03 and DIN EN ISO 11664-5:2011-07), levelling (determined according to DIN EN ISO 13803:2015-02; haze test) and wettability (determined according to ISO 19403-2:2017-06), in particular correlates to at least one of the characteristics selected from the group consisting of stone chip robustness, hardness, preferably surface hardness, pencil hardness and/or micro hardness, scratch resistance, impact resistance, resistance to UV light exposure, resistance to heat, resistance to moisture, cohesion, adhesion, and appearance.

For example, crosslinking density correlates to stone chip robustness, hardness, preferably surface hardness, pencil hardness and/or micro hardness, scratch resistance, impact resistance, resistance to UV light exposure, resistance to heat, resistance to moisture, and appearance. For example, glass transition temperature correlates to stone chip robustness, hardness, preferably surface hardness, pencil hardness and/or micro hardness, impact resistance, and appearance. For example, shrinkage correlates to appearance, flop, and levelling. For example, surface tension correlates to wettability, cohesion and adhesion as well as appearance (in particular stability against overspray). For example, spread correlates to appearance (stability against overspray).

Step (5)

In step (5) at least one, preferably precisely one, further coating material composition being different from the first coating material composition F1 in precisely one or at most two parameters is provided. Said parameters are selected from the group consisting of (a) partial or full exchange of polymer P1 with a further polymer being different from polymer P1 and having crosslinkable functional groups being reactive at least towards the functional groups of crosslinking agent CA1, (b) partial or full exchange of crosslinking agent CA1 with a further crosslinking agent being different from crosslinking agent CA1 and having functional groups being reactive at least towards the crosslinkable functional groups of polymer P1, (c) lowering or increasing the amount of polymer P1 and/or of the polymer being different from polymer P1, which has been used for partial or full exchange of polymer P1 as defined in (a) in the further coating material composition, (d) lowering or increasing the amount of crosslinking agent CA1 and/or of the crosslinking agent being different from CA1, which has been used for partial or full exchange of CA1 as defined in (b) in the

further coating material composition, (e) partial or full exchange of additive A if present with a further additive being different from additive A, (f) lowering or increasing the amount of additive A if present and/or of the additive being different from additive A if present, which has been used for partial or full exchange of additive
5 A as defined in (e) in the further coating material composition, (g) partial or full exchange of pigment P11 and/or filler F11 if present with a further pigment and/or filler being different from pigment P11 and/or filler F11, and (h) lowering or increasing the amount of pigment P11 and/or filler F11 if present and/or of the pigment and/or filler being different from pigment P11 and/or filler F11 if present, which has been used for
10 partial or full exchange of pigment P11 and/or filler F11 as defined in (g) in the further coating material composition. Preferably, as additives A and as any further additives different from additive A, crosslinking catalysts are used.

Preferably, the parameter(s) selected in step (5) and, optionally, during an at least
15 one-fold repetition as defined in step (9), is/are associated with partial or full exchange and/or lowering or increasing of the amount of at least one constituent that contributes to the total solid content of the coating material composition, such as constituents (i) and (ii) and if present constituent (v) and/or (vi) in the coating material composition F1, preferably that contributes to the total binder solid content of the
20 coating material composition, such as constituents (i) and (ii) and if present constituent (v) in the coating material composition F1.

If for example, polymer P1 present in coating material composition F1 is fully exchanged with another polymer being different from P1, this exchange is considered
25 to be a one parameter change. However, in practice it is sometimes necessary to perform two modification steps: If, for example, polymer P1 has been used in a first water-based dispersion having a solid content of 50 wt.-% P1 and the other polymer being different from P1 is provided in a second water-based dispersion having a solids content of 75 wt.-% a less amount of the second dispersion needs to be used
30 compared to the amount of the first dispersion that has been used for preparing F1. Thus, additional water has to be added so that - in total - both coating material compositions contain the same constituents in the same total amounts with the exception of the exchange of polymer P1 with the other polymer. However, in total

only one parameter has been changed (namely the exchange of polymer P1 with another polymer).

Preferably, the at least one further coating material composition provided in step (5) and, optionally, provided after an at least one-fold repetition as defined in step (9), is different from the first coating material composition F1 in precisely one or at most two parameters, preferably in precisely one parameter, wherein said parameters are selected from the group consisting of (a) partial or full exchange of polymer P1 with a further polymer being different from polymer P1 and having crosslinkable functional groups being reactive at least towards the functional groups of crosslinking agent CA1, (b) partial or full exchange of crosslinking agent CA1 with a further crosslinking agent being different from crosslinking agent CA1 and having functional groups being reactive at least towards the crosslinkable functional groups of polymer P1, (c) lowering or increasing the amount of polymer P1 and/or of the polymer being different from polymer P1, which has been used for partial or full exchange of polymer P1 as defined in (a) in the further coating material composition, (d) lowering or increasing the amount of crosslinking agent CA1 and/or of the crosslinking agent being different from CA1, which has been used for partial or full exchange of CA1 as defined in (b) in the further coating material composition.

In particular, the at least one further coating material composition provided in step (5) and, optionally, provided after an at least one-fold repetition as defined in step (9), is different from the first coating material composition F1 in precisely one or at most two parameters, preferably in precisely one parameter, wherein said parameters are selected from the group consisting of (a) partial or full exchange of polymer P1 with a further externally crosslinking polymer being different from polymer P1 and having crosslinkable functional groups being reactive at least towards the functional groups of crosslinking agent CA1, (b) partial or full exchange of crosslinking agent CA1 with a further crosslinking agent being different from crosslinking agent CA1 and having functional groups being reactive at least towards the crosslinkable functional groups of polymer P1.

Preferably,

the crosslinkable functional groups of polymer P1 being present as constituent (i) in the first coating material composition F1 and the crosslinkable functional groups of each polymer being different from polymer P1 and being present in any of the further coating material compositions provided in step (5) and, optionally, after an at least one-fold repetition as defined in step (9), are identical, preferably are in each case selected from hydroxyl and/or acid groups, more preferably represent in each case at least partially hydroxyl groups, and

the functional groups of crosslinking agent CA1 being present as constituent (ii) in the first coating material composition F1 and the functional groups of each crosslinking agent being different from crosslinking agent CA1 and being present in any of the further coating material compositions provided in step (5) and, optionally, after an at least one-fold repetition as defined in step (9), are identical, preferably are in each case selected from imino groups, alkylol groups, etherified alkylol groups and optionally blocked isocyanate groups, more preferably represent in each case at least partially etherified alkylol groups.

Step (6)

In step (6) the further coating material composition provided in step (5) is applied onto at least one optionally pre-coated surface of a substrate to form a coating film on said surface of the substrate. The same substrates named hereinbefore can also be used in step (6) by the same conventional application means mentioned above.

Optional step (6a)

Preferably, the inventive method further comprises a step (6a), which is carried out after step (6) and before step (7). In said step (6a) the coating film obtained after step (6) is flashed-off before performing curing step (7), preferably for a period of 1 to 30 minutes, more preferably for a period of 1.5 to 25 minutes, in particular for a period of 2 to 20 minutes, most preferably for a period of 3 to 15 minutes. Preferably, step (6a) is performed at a temperature not exceeding 100 °C, more preferably at a temperature in the range of from 18 to 80 °C.

Step (7)

In step (7) the coating film obtained after step (6) is cured to form a cured coating film on the surface of the substrate. Curing is preferably performed at elevated temperatures in an oven, preferably at a temperature in the range of from 75 to 180 °C, more preferably of from 80 to 160 °C. The cured coating film represents a coating layer.

Step (8)

In step (8) at least one property of the cured coating film obtained after step (7) is measured, said at least one property being the same property as measured in step (4).

Preferably, the at least one property measured in step (8), and optionally measured after an at least one-fold repetition as defined in step (9), is at least one property selected from the group consisting of crosslinking density, glass transition temperature, shrinkage, spread, and surface tension of the cured coating films, in particular is at least one property selected from the group consisting of crosslinking density and glass transition temperature of the cured coating films.

Crosslinking density and glass transition temperature of the cured coating films are measured properties associated with the elasticity of the cured coating films and can be determined by the DMA V Echo measurements described hereinafter in the "Methods" section. Improvements of these properties are in particular a lowering of the glass transition temperature and/or of the crosslinking density of the cured coating films as the resulting cured coating films are more flexible, which leads to an improvement of the stone chip robustness as an example of a characteristic of the cured coating film, as these measured properties are in correlation to this characteristic. Shrinkage means the changes in volume that occur during baking of a wet or partially dried coating film in order to obtain a cured coating film. Shrinkage can be measured as disclosed in paragraphs [0055] to [0061] of EP 3 099 423 B1. Surface tension is determined according to ISO 19403-2:2017-06. Determination of the surface tension includes determination of the contact angle and of the electrical dipole moment, in particular in association with the polarity and the surface energy.

Spread is determined according to ISO 19403-2:2017-06 and DIN EN ISO 19403-5:2020-04.

Preferably, the at least one property measured in step (8), and optionally measured
5 after an at least one-fold repetition as defined in step (9), correlates to at least one
characteristic of the cured coating films, preferably correlates to at least one of the
characteristics selected from the group consisting of stone chip robustness
(determined according to DIN EN ISO 20567-1:2017-07), hardness, preferably
surface hardness (determined according to DIN 55662:2009-12; pressure water
10 resistance test), pencil hardness (determined according to DIN EN ISO 15184:2019-
10) and/or micro hardness (determined according to DIN 55676:1996-02; test
according to Vickers), scratch resistance (determined according to DIN EN ISO 1518-
1:2019-10), impact resistance (determined according to DIN EN ISO 6272-1:2011-
11), resistance to UV light exposure (determined according to DIN EN ISO
15 2810:2004-10), resistance to heat (determined according to DIN EN ISO 2812-
5:2018-12 and DIN EN ISO 3248:2016-12), resistance to moisture (determined
according to DIN EN ISO 2812-5:2018-12 and DIN EN ISO 6270-1:2018-04),
cohesion (determined according to DIN EN ISO 2409:2019-09; cross-cut test),
adhesion (determined according to DIN EN ISO 4624:2016-08), appearance
20 (determined according to DIN EN ISO 13803:2015-02), color stability and flop, in
particular after storage, (determined according to DIN EN ISO/CIE 11664-1:2020-03,
DIN EN ISO/CIE 11664-2:2020-03, DIN EN ISO/CIE 11664-3:2020-03, DIN EN
ISO/CIE 11664-4:2020-03 and DIN EN ISO 11664-5:2011-07), levelling (determined
according to DIN EN ISO 13803:2015-02; haze test) and wettability (determined
25 according to ISO 19403-2:2017-06), in particular correlates to at least one of the
characteristics selected from the group consisting of stone chip robustness,
hardness, preferably surface hardness, pencil hardness and/or micro hardness,
scratch resistance, impact resistance, resistance to UV light exposure, resistance to
heat, resistance to moisture, cohesion, adhesion, and appearance.

30

For example, crosslinking density correlates to stone chip robustness, hardness,
preferably surface hardness, pencil hardness and/or micro hardness, scratch
resistance, impact resistance, resistance to UV light exposure, resistance to heat,
resistance to moisture, and appearance. For example, glass transition temperature

correlates to stone chip robustness, hardness, preferably surface hardness, pencil hardness and/or micro hardness, impact resistance, and appearance. For example, shrinkage correlates to appearance, flop, and levelling. For example, surface tension correlates to wettability, cohesion and adhesion as well as appearance (in particular stability against overspray). For example, spread correlates to appearance (stability against overspray).

Optional step (9)

In optional step (9) steps (5) to (8) are repeated optionally at least once, wherein each of the further coating compositions provided in this manner is different from one another and different from coating material composition F1. The number of repetitions is not limited and can be, for example, in a range of from 1 to 1000 or of from 1 to 100 repetitions.

Step (10)

In step (10) the results of the properties measured in steps (4) and (8) and optionally of the results of the properties measured in case of an at least one-fold repetition as defined in step (9) are incorporated into a preferably electronic database. Preferably, step (10) is performed with support of at least one software. The database can be updated constantly while performing the inventive method.

Step (11)

In step (11) at least one of the measured properties present in the preferably electronic database due to incorporation step (10) is selected.

Preferably, the at least one property selected in step (11) is at least one property selected from the group consisting of crosslinking density, glass transition temperature, shrinkage, spread, and surface tension, of the cured coating films, in particular is at least one property selected from the group consisting of crosslinking density and glass transition temperature of the cured coating films.

Crosslinking density and glass transition temperature of the cured coating films are measured properties associated with the elasticity of the cured coating films and can be determined by the DMA V Echo measurements described hereinafter in the

“Methods” section. Improvements of these properties are in particular a lowering of the glass transition temperature and/or of the crosslinking density of the cured coating films as the resulting cured coating films are more flexible, which leads to an improvement of the stone chip robustness as an example of a characteristic of the cured coating film, as these measured properties are in correlation to this characteristic. Shrinkage means the changes in volume that occur during baking of a wet or partially dried coating film in order to obtain a cured coating film. Shrinkage can be measured as disclosed in paragraphs [0055] to [0061] of EP 3 099 423 B1. Surface tension is determined according to ISO 19403-2:2017-06. Determination of the surface tension includes determination of the contact angle and of the electrical dipole moment, in particular in association with the polarity and the surface energy. Spread is determined according to ISO 19403-2:2017-06 and DIN EN ISO 19403-5:2020-04.

Preferably, the at least one property selected in step (11) correlates to at least one characteristic of the cured coating films, preferably correlates to at least one of the characteristics selected from the group consisting of stone chip robustness (determined according to DIN EN ISO 20567-1:2017-07), hardness, preferably surface hardness (determined according to DIN 55662:2009-12; pressure water resistance test), pencil hardness (determined according to DIN EN ISO 15184:2019-10) and/or micro hardness (determined according to DIN 55676:1996-02; test according to Vickers), scratch resistance (determined according to DIN EN ISO 1518-1:2019-10), impact resistance (determined according to DIN EN ISO 6272-1:2011-11), resistance to UV light exposure (determined according to DIN EN ISO 2810:2004-10), resistance to heat (determined according to DIN EN ISO 2812-5:2018-12 and DIN EN ISO 3248:2016-12), resistance to moisture (determined according to DIN EN ISO 2812-5:2018-12 and DIN EN ISO 6270-1:2018-04), cohesion (determined according to DIN EN ISO 2409:2019-09; cross-cut test), adhesion (determined according to DIN EN ISO 4624:2016-08), appearance (determined according to DIN EN ISO 13803:2015-02), color stability and flop, in particular after storage, (determined according to DIN EN ISO/CIE 11664-1:2020-03, DIN EN ISO/CIE 11664-2:2020-03, DIN EN ISO/CIE 11664-3:2020-03, DIN EN ISO/CIE 11664-4:2020-03 and DIN EN ISO 11664-5:2011-07), levelling (determined according to DIN EN ISO 13803:2015-02; haze test) and wettability (determined

according to ISO 19403-2:2017-06), in particular correlates to at least one of the characteristics selected from the group consisting of stone chip robustness, hardness, preferably surface hardness, pencil hardness and/or micro hardness, scratch resistance, impact resistance, resistance to UV light exposure, resistance to heat, resistance to moisture, cohesion, adhesion, and appearance.

For example, crosslinking density correlates to stone chip robustness, hardness, preferably surface hardness, pencil hardness and/or micro hardness, scratch resistance, impact resistance, resistance to UV light exposure, resistance to heat, resistance to moisture, and appearance. For example, glass transition temperature correlates to stone chip robustness, hardness, preferably surface hardness, pencil hardness and/or micro hardness, impact resistance, and appearance. For example, shrinkage correlates to appearance, flop, and levelling. For example, surface tension correlates to wettability, cohesion and adhesion as well as appearance (in particular stability against overspray). For example, spread correlates to appearance (stability against overspray).

Step (12)

In step (12) the results of the at least one selected property of the cured coating films measured according to steps (4) and (8) and optionally after an at least one-fold repetition as defined in step (9) are evaluated and compared with each other. Preferably, this is performed by means of at least one software.

Preferably, evaluation and comparison step (12) as well as step (13) make use of all results of the at least one property selected in step (11), which are present in the electronic database.

Step (13)

In step (13) the information obtained from evaluation and comparison step (12) are used for formulating and providing at least one new coating formulation being different from the first coating material composition F1 and from each of the further coating material compositions obtained after step (5) and from any additional coating material composition obtained optionally after an at least one-fold repetition as defined in step (9), wherein the at least one new coating formulation, when applied

and cured as defined in steps (2) and (3), leads to a cured coating film showing an improvement of the at least one property selected in step (11), when measured as defined in step (4) and/or step (8).

5 Preferably, the at least one new coating formulation provided in step (13) is different from the first coating material composition F1 and from any of the further coating material compositions obtained after step (5) and from any coating material composition obtained optionally after an at least one-fold repetition as defined in step (9), in at least one of the parameters as defined within step (5).

10

Preferably, the at least one new coating formulation provided in step (13) when applied and cured as defined in steps (2) and (3), not only leads to a cured coating film showing an improvement of the at least one property selected in step (11), preferably of at least one property as defined hereinbefore when measured as
15 defined in step (4) and/or (8), but also leads to a cured coating film showing an improvement of at least one characteristic of the cured coating film, said characteristic preferably being a characteristic as defined hereinbefore, and being in correlation to said at least one property.

20 *Inventive uses*

A further subject-matter of the present invention is a use of the inventive method for developing and providing new coating formulations in the automotive field, said new coating formulations preferably being basecoat compositions, in particular aqueous
25 basecoat compositions.

All preferred embodiments described hereinbefore in connection with the inventive method are also preferred embodiments with regard to the aforementioned inventive use.

30

A further subject-matter of the present invention is a use of the inventive method for investigating the influence of film-forming polymers (i), said polymers having crosslinkable functional groups, and/or of crosslinking agents (ii) having functional groups, which are reactive at least towards the crosslinkable functional groups of the

polymers, and/or of additives (v) and/or of pigments and/or fillers (vi) on properties of cured coating films obtained from applying and curing coating material compositions containing (i) and (ii) and optionally (v) and/or (vi) onto optionally pre-coated surfaces of substrates. The inventive use preferably aims at improvement of these properties.

5 All preferred embodiments described hereinbefore in connection with the inventive method as well as the above defined inventive use are also preferred embodiments with regard to the inventive use of the inventive method for investigating the influence of film-forming polymers (i), said polymers having crosslinkable functional groups, and/or of crosslinking agents (ii) having functional groups, which are reactive at least
10 towards the crosslinkable functional groups of the polymers, and/or on additives (v) and/or on pigments and/or fillers (vi) on properties of cured coating films obtained from applying and curing coating material compositions containing (i) and (ii) and optionally (v) and/or (vi) onto optionally pre-coated surfaces of substrates.

METHODS

1. Determining the non-volatile fraction

The amount of solid content (non-volatile matter, solid fraction) including the total
5 solid content is determined via DIN EN ISO 3251:2019-09 at 110 °C for 60 min.

2. DMA V Echo measurements

DMA (dynamic mechanical analysis) V Echo measurements of cured coating films
were used in order to determine E''_{\max} (maximum loss modulus, corresponding to
10 glass transition temperature, [°C]) and E'_{\min} (minimum storage modulus,
corresponding to crosslinking density, [Pa]) values of the films. The measurements
were performed at a frequency of 1 Hz (amplitude: 0.2%) and in a range of from -80
°C to 200 °C (2 °C/min). The following parameters were determined: temperature
position of the loss factor $\tan \delta$ at a level of 0.1 [°C], temperature position of the
15 maximum loss modulus E''_{\max} [°C], temperature position of the maximum loss factor
 $\tan \delta_{\max}$ [°C] and minimum storage modulus E'_{\min} in the rubber-elastic range
[Pa]. The measurements were performed according to ISO 6721-4:2019.

EXAMPLES

The following examples further illustrate the invention, but are not to be construed as limiting its scope. 'Pbw' means parts by weight. If not defined otherwise, 'parts' means 'parts by weight'.

1. Preparation of coating material compositions

1.1 A number of coating compositions (I1, I2 and I3) have been prepared. The constituents listed in Table 1 have been mixed under stirring in a dissolver in the sequence given in said Table to prepare the coating compositions.

Table 1: Coating compositions I1 to I3

<i>Constituent</i>	<i>Amount [pbw]</i>			<i>Amount binder solids with respect to total binder solids [wt.-%]</i>			
	I1	I2	I3	I1	I2	I3	
Binder 1	7.41			50			
Binder 2		5.55			50		
Binder 3			4.44			50	
Crosslinker	8.03	8.03	8.03	36	36	36	
Additional binder	5.00	5.00	5.00	14	14	14	
Butyl glycol	0.77	1.14	2.25				

Binder 1 is an aqueous polyester dispersion prepared as disclosed in example D of DE 4009858 A1 except that butyl glycol has been used instead of butanol and having a solid content of 60 wt.-%. Binder 2 is a polyether dispersion prepared as disclosed in example ER1 of WO 2017/097642 A1 and having a solid content of 80 wt.-%. Binder 3 is a polyether dispersion prepared as disclosed in example ER1 of WO 2017/121683 A1 and having a solid content of 99.9 wt.-%. Luwipal® 052 is a commercially available melamine formaldehyde resin crosslinker (BASF SE) and has a solid content of 77 wt.-%. A polyurethane poly(meth)acrylate dispersion has been used as additional binder. This dispersion was prepared as disclosed in example D of

DE 4437535 A1 and has a solid content of 40 wt.-%. Butyl glycol was merely added to ensure that each of I1 to I3 has the same binder solids content and the same solvent composition as the binders 1 to 3 used for preparing I1 to I3 each have different solids contents and contain different amounts of butyl glycol.

5

1.2 A number of further coating compositions (I4, I5 and I6) have been prepared. The constituents listed in Table 1b have been mixed under stirring in a dissolver in the sequence given in said Table to prepare the coating compositions.

10 Table 1b: Coating compositions I4 to I6

<i>Constituent</i>	<i>Amount [pbw]</i>				<i>Amount binder solids with respect to total binder solids [wt.-%]</i>			
	I4	I5	I6		I4	I5	I6	
Binder 1	7.41	7.41	7.41		50	50	50	
Crosslinker	8.03	8.03	8.03		36	36	36	
Additional binder	5.00	5.00	5.00		14	14	14	
Butyl glycol	0.77	1.14	2.25					
Catalyst 1	-	0.77	-					
Catalyst 2	-	-	1.33					
Iso-propanol	0.23	-	0.23					
n-propanol	0.10	-	0.10					
Deionized water	1.15	1.08	-					

Binder 1, crosslinker and additional binder have already been identified hereinbefore in item 1.1. Catalyst 1 is a mixture of 30.3 wt.-% iso-propanol, 10 wt.-% deionized water, 13.6 wt.-% n-propanol, 30.3 wt.-% para-toluene sulfonic acid and 15.8 wt.-% of a solution of 2-amino-2-methyl-1-propanol in deionized water (90 wt. %). Catalyst 2 is a mixture of 17.2 pbw para-toluene sulfonic acid, 71.47 pbw water and 10.95 pbw of a solution of ammonia in deionized water (15 wt.-%). Iso-propanol, n-propanol and/or deionized water were added to ensure that each of I4 to I6 has the same solvent composition.

20

2. Preparation of cured coating films obtained from the coating material compositions

Each of the coating compositions I1 to I6 was applied to a plastic substrate (Stamylan®) in a wet layer thickness of 100 µm and then flashed-off at a temperature of 80 °C for 10 minutes. Afterwards curing/baking was performed for 20 minutes at 140 °C in an oven. The cured coating films were then separated from the substrates and obtained as free films.

3. Investigation of properties of the cured coating films

3.1 *Influence of binders on glass transition temperature and crosslinking density*

The influence of the binders used for preparation of the coating films on the glass transition temperature and crosslinking density of the coating films has been investigated by DMA V Echo measurements according to the method identified hereinbefore in the 'Methods' section. The results are summarized in Table 2:

Table 2.1: DMA V Echo results

	E''max	E'min [Pa]
Cured coating film obtained from	Glass transition temperature [°C]	Crosslinking density
I1	10	$13.7 \cdot 10^7$
I2	-74	$10.8 \cdot 10^7$
I3	-71	$18.3 \cdot 10^7$

These results show that significant differences in glass transition temperatures and crosslinking densities of the coating films resulting from coating compositions I1 to I3 are obtained. The differences in the measured parameters can be directly related to the different polymers used as binders in I1 to I3 as the coating compositions used otherwise contain the same constituents.

These results can be used for optimization of coating film properties, i.e. for the tailor-made provision of new coating material formulations, which are much more complex than the systems I1 to I3.

5 For example, both binder 1 and binder 2 can be used for preparing aqueous basecoat compositions as it is, e.g., disclosed in WO 2017/097642 A1 (basecoat example 1 containing polyester binder 1 vs. basecoat example E1 containing polyether binder 2 disclosed therein). The exchange of binder 1 with binder 2 leads to an improvement of the stone chip properties of multilayer coatings as illustrated in
10 Table 1 of WO 2017/097642 A1. This improvement in stone chip robustness can be correlated to the lower glass transition temperature (E''_{max}) as measured by DMA V echo measurements for I2 vs. I1.

Similar observations apply in case of binder 1 vs. binder 3. Both binder 1 and binder
15 3 can be used for preparing aqueous basecoat compositions as it is, e.g., disclosed in WO 2017/121683 A1 (basecoat example V1 containing polyester binder 1 vs. basecoat example E1 containing polyether binder 3 disclosed therein). The exchange of binder 1 with binder 3 leads to an improvement of the stone chip properties of multilayer coatings as illustrated in Table 1 of WO 2017/121683 A1. This
20 improvement in stone chip robustness can be correlated to the lower glass transition temperature (E''_{max}) as measured by DMA V echo measurements for I3 vs. I1.

3.2 Influence of catalysts on glass transition temperature and crosslinking density

25 The influence of catalysts used for preparation of the coating films on the glass transition temperature and crosslinking density of the coating films has been investigated by DMA V Echo measurements according to the method identified hereinbefore in the 'Methods' section. The results are summarized in Table 2.2:

Table 2.2: DMA V Echo results

	E''max	E'min [Pa]
Cured coating film obtained from	Glass transition temperature [°C]	Crosslinking density
I4	10	$13.7 \cdot 10^7$
I5	14	$27.4 \cdot 10^7$
I6	14	$27.8 \cdot 10^7$

5 These results show that differences in glass transition temperatures and, in particular, crosslinking densities of the coating films resulting from coating compositions I4 to I6 are observed. The differences in the measured parameters can be directly related to the presence/non-presence of different catalysts used in I4 to I6 as the coating compositions used otherwise substantially contain the same constituents.

CLAIMS

1. A method of screening coating material compositions for development of new coating formulations in the automotive field, said method comprising at least steps (1) to (8) and (10) to (13) and optionally a step (9), namely
- (1) providing a first coating material composition F1,
- the first coating material composition F1 comprising
- (i) at least one film-forming polymer P1, said polymer P1 having crosslinkable functional groups,
 - (ii) at least one crosslinking agent CA1 having functional groups, which are reactive at least towards the crosslinkable functional groups of polymer P1,
 - (iii) water and/or at least one organic solvent,
 - (iv) optionally at least one phase compatibilizing polymer PMP,
 - (v) optionally at least one additive A, and
 - (vi) optionally at least one pigment PI1 and/or at least one filler FI1,
- wherein the constituents (i), (ii), (iii) and (iv) as well as (v) and (vi) each are different from one another,
- (2) applying the first coating material composition F1 onto at least one optionally pre-coated surface of a substrate to form a coating film on said surface of the substrate,
- (3) curing the coating film obtained after step (2) to form a cured coating film on the surface of the substrate,
- (4) measuring at least one property of the cured coating film obtained after step (3),

- (5) providing at least one further coating material composition being different from the first coating material composition F1 in precisely one or at most two parameter(s),

5 wherein said parameter(s) are selected from the group consisting
of (a) partial or full exchange of polymer P1 with a further
polymer being different from polymer P1 and having
crosslinkable functional groups being reactive at least towards
the functional groups of crosslinking agent CA1, (b) partial or full
10 exchange of crosslinking agent CA1 with a further crosslinking
agent being different from crosslinking agent CA1 and having
functional groups being reactive at least towards the
crosslinkable functional groups of polymer P1, (c) lowering or
increasing the amount of polymer P1 and/or of the polymer being
15 different from polymer P1, which has been used for partial or full
exchange of polymer P1 as defined in (a) in the further coating
material composition, (d) lowering or increasing the amount of
crosslinking agent CA1 and/or of the crosslinking agent being
different from CA1, which has been used for partial or full
20 exchange of CA1 as defined in (b) in the further coating material
composition, (e) partial or full exchange of additive A if present
with a further additive being different from additive A, and (f)
lowering or increasing the amount of additive A if present and/or
of the additive being different from additive A if present, which
25 has been used for partial or full exchange of additive A as
defined in (e) in the further coating material composition, (g)
partial or full exchange of pigment P11 and/or filler F11 if present
with a further pigment and/or filler being different from pigment
P11 and/or filler F11, and (h) lowering or increasing the amount of
30 pigment P11 and/or filler F11 if present and/or of the pigment
and/or filler being different from pigment P11 and/or filler F11 if
present, which has been used for partial or full exchange of
pigment P11 and/or filler F11 as defined in (g) in the further
coating material composition,

- 5
- (6) applying the further coating material composition onto at least one optionally pre-coated surface of a substrate to form a coating film on said surface of the substrate,
- (7) curing the coating film obtained after step (6) to form a cured coating film on the surface of the substrate,
- 10 (8) measuring at least one property of the cured coating film obtained after step (7), said at least one property being the same property as measured in step (4),
- (9) optionally repeating steps (5) to (8) at least once, wherein each of the further coating compositions provided is different from one another and different from coating material composition F1,
- 15 (10) incorporating the results of the properties measured in steps (4) and (8) and optionally of the results of the properties measured in case of an at least one-fold repetition as defined in step (9) into a database,
- 20 (11) selecting at least one of the measured properties present in the database due to incorporation step (10),
- (12) evaluating and comparing the results of the at least one selected property of the cured coating films measured according to steps (4) and (8) and optionally after an at least one-fold repetition as defined in step (9) with each other, and
- 25 (13) using the information obtained from evaluation and comparison step (12) for formulating and providing at least one new coating formulation being different from the first coating material composition F1 and from each of the further coating material compositions obtained after step (5) and from any coating material composition obtained optionally after an at least one-fold repetition as defined in step (9), wherein the at least
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one new coating formulation, when applied and cured as defined in steps (2) and (3), leads to a cured coating film showing an improvement of the at least one property selected in step (11), when measured as defined in step (4) and/or (8).

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2. The method according to claim 1, characterized in that

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the crosslinkable functional groups of polymer P1 being present as constituent (i) in the first coating material composition F1 and the crosslinkable functional groups of each polymer being different from polymer P1 and being present in any of the further coating material compositions provided in step (5) and, optionally, after an at least one-fold repetition as defined in step (9), are identical, preferably are in each case selected from hydroxyl and/or acid groups, more preferably represent in each case at least partially hydroxyl groups, and

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the functional groups of crosslinking agent CA1 being present as constituent (ii) in the first coating material composition F1 and the functional groups of each crosslinking agent being different from crosslinking agent CA1 and being present in any of the further coating material compositions provided in step (5) and, optionally, after an at least one-fold repetition as defined in step (9), are identical, preferably are in each case selected from imino groups, alkylol groups, etherified alkylol groups and optionally blocked isocyanate groups, more preferably represent in each case at least partially imino groups, alkylol groups, and/or etherified alkylol groups.

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3. The method according to claim 1 or 2, characterized in that the first coating material composition F1 and any of the further coating material compositions provided in step (5) and, optionally, obtained after an at least one-fold repetition as defined in step (9), are one-component (1K) or two-component (2K) coating material compositions, preferably are each one-component (1K) coating material compositions, more preferably for use as basecoat material compositions.

4. The method according to any of the preceding claims, characterized in that the at least one crosslinking agent CA1 present as constituent (ii) in the first coating material composition F1 and any further at least one crosslinking agent being present in any of the further coating material compositions provided in step (5) and, optionally, obtained after an at least one-fold repetition as defined in step (9), are melamine aldehyde resins, preferably melamine formaldehyde resins.
5. The method according to any of the preceding claims, characterized in that the at least one polymer P1 present as constituent (i) in the first coating material composition F1 and any further at least one film-forming polymer being present in any of the further coating material compositions provided in step (5) and, optionally, obtained after an at least one-fold repetition as defined in step (9), is selected from the group consisting of physically drying polymers, chemically crosslinking polymers, radiation curing polymers, and mixtures thereof, preferably is selected from the group consisting of physically drying polymers, chemically self-crosslinking polymers, chemically non-self-crosslinking polymers, radiation curing polymers, and mixtures thereof, more preferably is selected from the group consisting of chemically non-self-crosslinking polymers.
6. The method according to any of the preceding claims, characterized in that the at least one polymer P1 present as constituent (i) in the first coating material composition F1 and any further at least one film-forming polymer being present in any of the further coating material compositions provided in step (5) and, optionally, obtained after an at least one-fold repetition as defined in step (9), are selected from the groups consisting of polyesters, poly(meth)acrylates, polyurethanes, polyureas, polyamides and polyethers, preferably are selected from the groups consisting of polyesters, poly(meth)acrylates, polyurethanes and polyethers.
7. The method according to any of the preceding claims, characterized in that the constituents (i) to (iii) and optionally (iv) and/or (v) and/or (vi) are the only constituents of the first coating material composition F1.

8. The method according to any of the preceding claims, characterized in that constituent (iv) is present in the first coating material composition F1, preferably when constituent (iii) represents at least partially water.
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9. The method according to any of the preceding claims, characterized in that the parameter(s) selected in step (5) and, optionally, during an at least one-fold repetition as defined in step (9), is/are associated with partial or full exchange and/or lowering or increasing of the amount of at least one constituent that contributes to the total solid content of each of the coating material compositions, preferably that contributes to the total binder solid content of each of the coating material compositions.
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10. The method according to any of the preceding claims, characterized in that the at least one property measured in steps (4) and (8), and optionally measured after an at least one-fold repetition as defined in step (9), and selected in step (11), is at least one property selected from the group consisting of crosslinking density, glass transition temperature, shrinkage, spread, and surface tension of the cured coating films, in particular is at least one property selected from the group consisting of crosslinking density and glass transition temperature of the cured coating films.
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11. The method according to any of the preceding claims, characterized in that the at least one property measured in steps (4) and (8), and optionally measured after an at least one-fold repetition as defined in step (9), and selected in step (11), correlates to at least one characteristic of the cured coating films, preferably correlates to at least one of the characteristics selected from the group consisting of stone chip robustness, hardness, preferably surface hardness, pencil hardness and/or micro hardness, scratch resistance, impact resistance, resistance to UV light exposure, resistance to heat, resistance to moisture, cohesion, adhesion, appearance, color stability, in particular after storage, stability against overspray, flop, levelling and wettability, in particular correlates to at least one of the characteristics selected from the group consisting of stone chip robustness, hardness, preferably surface hardness,
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pencil hardness and/or micro hardness, scratch resistance, impact resistance, resistance to UV light exposure, resistance to heat, resistance to moisture, cohesion, adhesion, and appearance.

- 5 12. The method according to any of the preceding claims, characterized in that evaluation and comparison step (12) as well as step (13) make use of all results of the at least one property selected in step (11), which are present in the preferably electronic database.
- 10 13. The method according to any of the preceding claims, characterized in that the at least one new coating formulation provided in step (13) is different from the first coating material composition F1 and from any of the further coating material compositions obtained after step (5) and from any coating material composition obtained optionally after an at least one-fold repetition as defined in step (9), in at least one of the parameters as defined within step (5) of claim 1.
- 15 14. The method according to any of the preceding claims, characterized in that the at least one new coating formulation provided in step (13) when applied and cured as defined in steps (2) and (3), not only leads to a cured coating film showing an improvement of the at least one property selected in step (11), preferably of at least one property as defined in claim 10 when measured as defined in step (4) and/or (8), but also leads to a cured coating film showing an improvement of at least one characteristic of the cured coating film, said characteristic preferably being a characteristic as defined in claim 11, and being in correlation to said at least one property, wherein the improvement of the at least one property preferably is a lowering of the crosslinking density and/or glass transition temperature of the cured coating films, which results at least in an improvement of the stone chip robustness as at least one characteristics of the cured coating film.
- 20 25 30 15. A use of the method according to any of the preceding claims for investigating the influence of film-forming polymers (i), said polymers having crosslinkable functional groups, and/or of crosslinking agents (ii) having functional groups,

which are reactive at least towards the crosslinkable functional groups of the polymers, and/or of additives (v) and/or of pigments and/or fillers (vi) on properties of cured coating films obtained from applying and curing coating material compositions containing (i) and (ii) and optionally (v) and/or (vi) onto optionally pre-coated surfaces of substrates.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2021/077416

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/00 G01N33/44 G01N33/00
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C09D G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 3 480 261 A1 (PPG IND OHIO INC [US]) 8 May 2019 (2019-05-08) paragraph [0008] - paragraph [0011] abstract; claims 1-15; examples 1-3; table 1	1-15
A	WO 2007/044774 A2 (DU PONT [US]; JOHNSON JEFFERY W [US]; YUAN SAN C [US]) 19 April 2007 (2007-04-19) page 3, line 26 - page 5, line 25 abstract; claims 1-20; figures 1, 2; examples 1-5; table 1	1-15
A	US 2003/155242 A1 (CHUNG DING YU [US]) 21 August 2003 (2003-08-21) paragraph [0007] - paragraph [0009] abstract; claims 1-10; example 1	1-15
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 17 November 2021	Date of mailing of the international search report 02/12/2021
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Glomm, Bernhard
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 816 442 A2 (CIBA GEIGY AG [CH]) 7 January 1998 (1998-01-07) page 2, line 34 - line 55 abstract; claims 1-22; examples 1-4 -----	1-15
A	US 2007/059622 A1 (YU ROBERT C [US] ET AL) 15 March 2007 (2007-03-15) paragraph [0024] - paragraph [0027] abstract; claims 1-20; figures 1-3; examples I - III; tables 1, 2 -----	1-15

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