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(54) Title: LYSINE BASED POLYMER COMPRISING COMPOSITION FOR USE IN CHEMICAL PRETREATMENT OF METALLIC SUBSTRATES

(57) Abstract: The present invention relates to a method of chemical pretreatment comprising at least step 1), i.e., contacting at least one metallic surface of at least one substrate at least in portion with an aqueous acidic composition AC being suitable to form a coating film at least in portion onto said surface, wherein AC comprises, besides water, at least constituents a1) and a2), i.e., at least one of zirconium, titanium and hafnium cations as constituent(s) a1), and at least one lysine homopolymer and/or copolymer, which bears amide bonds, as constituent(s) a2), to a chemically pretreated substrate obtainable by this method, to the aqueous composition AC as such, to a concentrate usable for its preparation, to a use of composition AC for providing or improving corrosion protection and/or adhesion, to a method of coating an aforementioned chemically pretreated substrate, and to a coated substrate obtainable by said method.

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Lysine based polymer comprising composition for use in chemical pretreatment of metallic substrates

The present invention relates to a method of chemically pretreating metallic surfaces of substrates, to a chemically pretreated substrate obtainable by this method, to a chemical pretreatment composition as such, which is suitable for use in this method, to a concentrate, from which said composition is obtainable, to a use of the chemical pretreatment composition for providing or improving corrosion protection and/or adhesion, to a method of coating an aforementioned chemically pretreated substrate, and to a coated substrate obtainable by said method.

Background of the invention

Before substrates having metallic surfaces are being lacquered, i.e., before permanent coating layers are applied onto their surfaces, they are nowadays typically subjected to an anti-corrosive chemical pretreatment by using a suitable chemical pretreatment composition.

EP 0 319 018 A2 discloses a metal treatment solution comprising a derivative of a polyphenol such as an amine oxide-containing polyphenol. WO 01/66827 A1 relates to a process for the anti-corrosive treatment of in particular non-ferrous metal substrates by use of organic polymer containing aqueous solutions such as poly-4-vinylphenol based polymer containing solutions.

However, use of the treatment solutions disclosed in EP 0 319 018 A2 and WO 01/66827 A1 is not desirable, since the polyphenols described therein, in particular the nitrogen-containing polyphenols, are generally considered to be toxic or at least hazardous and, hence, both ecological and economic disadvantages result, even if they were be able to be used in view of, e.g., regulations applying. In addition, the polyphenols disclosed in EP 0 319 018 A2 and WO 01/66827 A1 do not represent biodegradable materials, in particular due to their aromatic structure, which is also disadvantageous. Further, the method disclosed in WO 01/66827 A1 is disadvantageous, since its use is limited to non-ferrous substrates and, hence, does not include using steel substrates or multi-metallic substrates containing steel.

Environmentally more adapted thin-film pretreatment systems are also well known in the prior art. These are, e.g., based on oxides of zirconium, titanium, cerium, molybdenum, vanadium, tungsten, or other transition metals, and are used as replacement for hazardous components, like chromium and nickel, which were used for decades in trivalent or hexavalent chromate as well as tri-cationic zinc phosphate coatings. In these terms especially zirconium and titanium got used in a wide range of pretreatment applications due to their high chemical stability under the conditions of oxygen or acidic corrosion. For example, aqueous solutions based on metal complex fluorides such as titanium and/or zirconium complex fluorides are used as such chemical pretreatment compositions in order to generate a conversion coating layer on the metallic surfaces of substrates. Optionally, these systems contain further adhesion promotors or corrosion inhibitors such as organosilanes, organo-phosphonates or amino-functional alcohols. Together with the aforesaid inorganic compounds, these additives provide excellent adhesion to the metal surface as well to a following organic coatings such as, e.g., electrodeposition-, powder- or wet-coatings. Moreover, they are able to increase the barrier properties of the layer against the diffusion of corrosive ions against the diffusion and migration of corrosive species to or along the metal surface, which otherwise lead to inhibition of cathodic delamination during corrosive processes.

Even though prior art thin-film pretreatment systems often are able to provide a sufficient corrosion protection on metal substrates such as aluminum alloys, galvanized steels surfaces or zinc-magnesium alloys, they still suffer insufficient corrosion inhibition on steel surfaces, in particular in comparison to chromate or tricationic zinc phosphate conversion coatings. Moreover, prior art thin-film pretreatments often contain nitrogen oxide or phosphorous oxide containing anionic components ($N_xO_y^{z-}$, $P_xO_y^{z-}$) such as nitrates or phosphates, which may lead to eutrophication of water, if released in larger amounts to the environment. Due to this effect, the usage of nitrate and/or phosphate containing systems already faces legal restrictions in some countries, as, e.g., currently in China.

Thus, there is a need to provide chemical pretreatment compositions suitable for formation of thin permanent coating layers on metallic substrates including particularly

ferrous substrates such as steel substrates or multi-metallic substrates including at least portions of steel, which compositions are less toxic and hazardous than prior art compositions, make use of easy accessible constituents, which furthermore have a high degree of biodegradability, but which lead to at least the same, but preferably even to an improved, resistance to corrosion and/or water, and which at the same time also provide an excellent substrate adhesion and an excellent adhesion to any layers applied on top, compared to conventionally used aqueous coating compositions known in the prior art.

Problem

It has been therefore an objective underlying the present invention to provide chemical pretreatment compositions suitable for formation of thin permanent coating layers on metallic substrates including particularly ferrous substrates such as steel substrates or multi-metallic substrates including at least portions of steel, which compositions are less toxic and hazardous than prior art compositions, make use of easy accessible constituents, which furthermore have a high degree of biodegradability, but which lead to at least the same, but preferably even to an improved, resistance to corrosion and/or water, and which at the same time also provide an excellent substrate adhesion and an excellent adhesion to any layers applied on top, compared to conventionally used aqueous coating compositions known in the prior art.

Solution

This objective 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 chemical pretreatment of at least one metallic surface of at least one substrate comprising at least step 1) and optionally one or more of steps 2) and 3), namely

1) contacting the at least one metallic surface of the at least one substrate at least in portion with an aqueous preferably acidic composition AC being suitable to form a coating film at least in portion onto said surface,

wherein the aqueous preferably acidic composition AC comprises, besides water, at least constituents a1) and a2), which are different from one of another, namely

at least one of zirconium, titanium, and hafnium cations as constituent(s) a1), and

at least one lysine homopolymer and/or copolymer, which preferably bears amide bonds, as constituent(s) a2),

2) optionally rinsing the coating film obtained after step 1) at least once with at least one aqueous rinsing composition ARC, which is different from aqueous preferably acidic composition AC, and

3) optionally curing or drying the optionally rinsed coating film obtained after step 1) or 2) to give a cured or dried coating layer.

A further subject-matter of the present invention is a substrate, which is a chemically pretreated substrate being obtainable by the inventive method of chemical pretreatment as defined hereinbefore and hereinafter.

A further subject-matter of the present invention is an aqueous preferably acidic composition AC as defined hereinbefore and hereinafter in connection with step 1) comprising besides water at least one of zirconium, titanium, and hafnium cations as constituent(s) a1), and at least one lysine homopolymer and/or copolymer, which preferably bears amide bonds, as constituent(s) a2).

A further subject-matter of the present invention is a concentrate, from which the aqueous preferably acidic composition AC is at least obtainable by dilution with water and, optionally, further, by pH adjustment.

A further subject-matter of the present invention is a use of at least one lysine homopolymer and/or copolymer as defined hereinbefore and hereinafter as constituent a2) of composition AC, preferably when incorporated into an aqueous composition AC, more preferably into an inventive aqueous preferably acidic composition AC defined hereinbefore and hereinafter, for providing or improving corrosion resistance of metallic surfaces of substrates and/or for providing or improving adhesion of metallic surfaces of substrates to one or more further coating layers present thereon.

A further subject-matter of the present invention is a method of coating of at least one chemically pretreated metallic surface of at least one substrate, wherein chemical pretreatment of the at least one metallic surface has been carried out according to the inventive method of chemical pretreatment as defined hereinbefore and hereinafter or by making use of an inventive aqueous preferably acidic composition AC, the method of coating further comprising at least step 4), namely

4) applying at least one coating material composition comprising at least one film-forming polymer and/or resin onto the optionally rinsed film obtained after step 1) or 2) as defined hereinbefore and hereinafter or onto the dried or cured, preferably dried, film, which in turn is obtainable from drying or curing the film obtainable from optional step 3) as defined hereinbefore and hereinafter.

A further subject-matter of the present invention is a substrate, which is a coated substrate being obtainable by the inventive method of coating as defined hereinbefore and hereinafter.

It has been in particular surprisingly found that composition AC can be used as chemical pretreatment composition, which is suitable for forming a thin permanent coating layer such as a conversion coating layer on metallic substrates including particularly ferrous substrates such as steel substrates or multi-metallic substrates including at least portions of steel.

Furthermore, it has been in particular surprisingly found that composition AC is less toxic and hazardous than prior art compositions and allows making use of easy-accessible constituents, in particular in form of lysine homopolymer and/or copolymer

constituent(s) a2), which has a high degree of biodegradability, since it is based on naturally occurring amino acid lysine.

Moreover, it has been in particular surprisingly found that composition AC can be effectively used as chemical pretreatment composition in a chemical pretreatment method and that the chemically pretreated substrates as such or chemically pretreated substrates bearing further coating layers such as an electrodeposition coating layer, shown an excellent corrosion resistance. It has been in particular surprisingly found in this regard, that this effect is a result of the presence of the lysine homopolymer and/or copolymer in composition AC.

Further, it has been in particular surprisingly found that composition AC can be effectively used as chemical pretreatment composition in a chemical pretreatment method and that the chemically pretreated substrates shown an excellent substrate adhesion and, in addition, an excellent adhesion to any layers applied on top, in particular to an electrodeposition coating layer applied on top of the chemical pretreatment layer. It has been in particular surprisingly found in this regard, that this effect is a result of the presence of the lysine homopolymer and/or copolymer in composition AC.

In addition, it has been found that the aforementioned surprising effects as far as corrosion resistance and adhesion are concerned, can be observed on various kinds of metallic surfaces, not only on aluminum alloys, but also on steel including zinc-coated (galvanized) steel. Therefore, it has been surprisingly found that composition AC can be effectively used not only for forming conversion layers on steel, but also on multi-metallic substrates.

Finally, it has been found that composition AC can also be used as cleaning composition, e.g., in a cleaning step preceding step 1), in addition to its suitability as a chemical pretreatment composition. This allows to use one single composition only for the whole pretreatment method. If composition AC is used as cleaning composition it preferably comprises at least one surfactant such as at least one non-ionic surfactant.

Detailed description of the invention

The term "comprising" in the sense of the present invention, in connection for example with the inventively used or inventive aqueous composition AC, preferably has the meaning of "consisting of". With regard, e.g., to said composition referred to hereinbefore, it is possible – in addition to all mandatory constituents present therein – for one or more of the further optional constituents identified hereinafter to be also included therein. All constituents may in each case be present in their preferred embodiments as identified below.

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

Pretreatment method including chemical pretreatment step 1)

A first subject-matter of the present invention is a method of chemical pretreatment of at least one metallic surface of at least one substrate comprising at least step 1) and optionally one or more of steps 2) and 3). The method may comprise further steps performed prior to step 1) and/or after each of steps 1), 2) and 3).

Chemical pretreatment is a term known by a person skilled in the art and in particular is part of a pretreatment method.

The term "pretreatment" as used herein is preferably used in accordance with the term "surface pretreatment" as defined in Römpp Lexikon "Lacke und Druckfarben" (Publisher: Ulrich Zorll, Editor: Hans-Jürgen P. Adler – Stuttgart; New York: Thieme, 1998; term: "Oberflächenvorbehandlung" page 417). On metallic substrates or substrates having metallic surfaces, according to DIN 50902: 1994-07, the first step(s) of a surface treatment is/are often one or more (chemical) cleaning step(s) with aqueous or non-aqueous cleaning compositions (also called "surface preparation step"). Consequently, as it will be outlined hereinafter, the method may comprise one or more further optional steps performed prior to step 1).

The term “chemical pretreatment” is used in accordance with EN ISO 4618:2006 (E/F/D) (term: 2.41 “chemical pre-treatment”), which represents any chemical process applied to a surface prior to the application of a coating material. According to this standard, e.g., treatments like chromatizing (chromating) and phosphatizing and oxalating, which can be subsumed under the term “conversion treatment”, belong to the chemical pretreatment and thus are to be distinguished from (subsequent) coating steps, wherein coating materials, i.e., coating compositions such as powder coating compositions, electrodeposition coating compositions, aqueous or non-aqueous liquid coating materials are applied. Besides conversion treatments such as chromatizing (chromating) and phosphating, the chemical surface pretreatment may be achieved with passivation compositions and thin-film forming compositions in general, including the aqueous composition AC, which is mandatorily used as chemical pretreatment composition in step 1). Hence, step 1) of the method represents a chemical pretreatment step and the aqueous composition AC used therein represents a chemical pretreatment composition.

In accordance with the above internationally valid definitions of a “pretreatment” of metallic substrates, the pretreatment method according to the present invention preferably encompasses surface preparing cleaning steps besides the chemical pretreatment step 1).

Preferably, the pretreatment method does not contain any step involving any treatment with chromium ions such as Cr(VI) ions and/or Cr(III) ions.

Preferably, the chemical pretreatment step 1) is the only chemical pretreatment step of the pretreatment method. Hence, preferably, other chemical pretreatment compositions than the aqueous composition AC applied in step 1) are not used.

Preferably, the film obtained after step 1) or after optional steps 2) and/or 3) has a coating weight in a range of from 0.5 to 500 mg/m², more preferably of from 1 to 400 mg/m², even more preferably of from 2 to 350 mg/m², determined in each case as tracer element(s) such as Ti, Zr and/or Si via XRF measurements according to the method disclosed in the ‘method’ section. Preferably, the cured or dried coating layer obtained after optional step 3) preferably has a dry film thickness below 0.5 µm.

Substrate

The substrate used in step 1) contains at least one metallic surface. The term "metallic surface" in the sense of the present invention preferably means that the surface of the substrate used is at least partially made of at least one metal, i.e., that at least one region of said surface is made of at least one metal and/or alloy thereof. Preferably, the overall surface of the substrate is made of at least one metal and/or alloy thereof, more preferably, the whole substrate is made of at least one metal and/or alloy thereof, i.e., the substrate consists of at least one metal and/or alloy thereof. If a substrate comprises areas of different metals, such substrate is herein denoted as "multi-metallic substrate" as a subclass of metallic substrates. Such multi-metallic substrates can be subjected to step 1) of the chemical pretreatment method and can be coated in the same treatment bath

The at least one metallic surface of the substrate may be optionally pre-coated, but preferably is not pre-coated.

Preferably, the substrate used is an electrically conductive substrate, which is used customarily and known to the skilled person. The substrate can have all sorts of geometry and shape such as coils, foils and sheets as well as represent parts such as automotive parts including vehicle parts such as wheel parts. Particularly suitable substrates are parts of vehicle bodies or complete bodies of automobiles for production.

Preferably, the at least one surface of the substrate is at least partially made of at least one metal and/or alloy thereof, more preferably is made at least partially of at least one of steel, steel alloys, aluminum, aluminum alloys, zinc, zinc alloys including zinc magnesium alloys, and mixtures thereof, even more preferably is made at least partially of at least one of steel and steel alloys. Examples of steel and/or steel alloys are bare steel, cold rolled steel (CRS), hot rolled steel (HRS), galvanized steel (zinc plated steel) such as hot dip galvanized steel (HDG), electrolytically galvanized steel (EG), alloy galvanized steel and aluminized steel such as, for example, Galvalume®, Galvannealed® or Galfan®, as well as steel coated at least in portion with at least one

kind of zinc-aluminum-magnesium alloy (ZM). Examples of aluminum alloys are aluminum magnesium alloys, aluminum magnesium silicon alloys, aluminum copper alloys, aluminum zinc alloys, and aluminum zinc copper alloys. Examples of zinc alloys are Zn/Mg alloys and Zn/Ni alloys as well as Zn/Mg/Al alloys.

Optional steps performed prior to step 1)

As mentioned hereinbefore and in accordance with the above internationally valid definition of a "pretreatment" of metallic substrates, the pretreatment method according to the present invention preferably encompasses surface preparing cleaning steps besides the chemical pretreatment step 1).

Prior to step 1) one or more of the following optional steps can be performed in this order:

Step A-1): cleaning and optionally subsequently rinsing the surface of the substrate,

Step B-1): subjecting the surface of the substrate to acidic or alkaline pickling, i.e., etching, and subsequently rinsing the surface of the substrate,

Step C-1): contacting the surface of the substrate with an aqueous composition comprising at least one mineral acid, said aqueous composition being different from compositions AC and ARC or alternatively with an aqueous alkaline composition or pH-neutral aqueous composition, each of these compositions being also different compositions AC and ARC, and

Step D-1): rinsing the surface of the substrate obtained after the contact according to step C-1) and/or B-1).

Alternatively, steps A-1) and B-1) may be performed in one step, which is preferred. Preferably, both steps A-1) and B-1) are performed. Optional step C-1) preferably serves to remove oxides, undesired alloy components, the skin, brushing dust etc. from the surface of the substrate and to thereby activate the surface for the subsequent conversion treatment in step 1). Preferably, the at least one mineral acid of the composition in step C-1) is sulfuric acid and/or nitric acid, more preferably sulfuric acid. As it will be outlined hereinafter, in step A-1) a cleaning composition can be used, which is different from or identical to composition AC.

Rinsing step D-1) and the optional rinsing being part of step A-1) are preferably performed by using deionized water or tap water. Preferably, step D-1) is performed by using deionized water.

For cleaning step A-1) it is possible to also the aqueous composition AC as cleaning composition. Preferably, in this case, cleaning step is performed by spraying.

Step 1)

According to step 1) the at least one metallic surface of the at least one substrate is contacted at least in portion with an aqueous composition AC being suitable to form a coating film at least in portion onto said surface. Aqueous composition AC represents a chemical pretreatment composition. By performing step 1) a conversion film (or conversion coating film or passivation film) is formed on the surface of the substrate, which has been in contact with the aqueous composition AC. In case a cleaning step has been performed prior to step 1), preferably the cleaned portion of the surface of the substrate is subjected to step 1).

The term “at least in portion” preferably means in this context, in accordance with the general understanding of said term, that in some cases it might be desired or sufficient to contact not the whole surface of the substrate with the chemical pretreatment composition AC. If only part of the metallic surface is contacted with the respective composition, it is typically the same part for all steps of the method. However, generally, it is desired to contact the whole surface of the metallic substrate with the respective compositions.

The “contacting” according to step 1) can be a spraying, a dipping (immersing) or a roll coating (rolling) step. The composition AC can also be applied by flooding the surface or even manually by wiping or brushing. Preferred is spraying, or dipping.

The treatment time, i.e., the period of time the surface is contacted with the aqueous composition AC in step 1), is preferably from 1 seconds to 20 minutes, more preferably from 15 or 30 seconds to 10 minutes, and most preferably 45 seconds to 5 minutes, as for example 1 to 3 minutes.

The temperature of the aqueous composition AC used in step 1) is preferably of from 5 to 50 °C, more preferably of from 15 to 45 °C or to 40 °C and most preferably from 25 to 35 °C.

The aqueous composition AC can be used as a dip coat bath. However, it can also be applied by virtually any conventional coating procedure like, e.g., spray coating, roll coating, brushing, wiping etc. as outlined above in connection with step 1). Spraying and dipping are preferred.

Preferably, the film obtainable after step 1) – preferably after drying according to optional step 3) – has a coating weight determined by XRF (X-ray fluorescence spectroscopy) of 0.5 to 500 mg/m^2, more preferably 1 to 400 mg/m^2, even more preferably 2 to 350 mg/m^2, still more preferably 3 to 300 mg/m^2, of silicon, zirconium, titanium and/or hafnium ions, each calculated as metal or element.

Aqueous composition AC used in step 1)

The aqueous composition AC comprises, besides water, at least constituents a1) and a2), which are different from one of another. At least one of zirconium, titanium and hafnium cations is present as constituent(s) a1), and at least one lysine homopolymer and/or copolymer is present as constituent(s) a2). The aqueous composition AC used in step 1) represents a “pretreatment composition” or “chemical pretreatment composition”.

Preferably, the aqueous composition AC is an aqueous acidic composition, more preferably has a pH value in a range of from 0.1 to <7.0, still more preferably of from 0.5 to 6.5, even more preferably of from 1.0 to 6.0, yet more preferably of from 1.5 or 2.0 to 5.5, still more preferably of from 2.5 or 3.0 to 5.25, most preferably of from 3.5 or 4.0 to 5.0. The pH value can be in particular adjusted by using a suitable pH adjusting constituent, in particular sodium and/or potassium hydroxide and/or sodium and/or potassium and/or ammonium carbonate for alkaline adjustment, or can be in particular adjusted in case acidic adjustment is needed by at least one inorganic acid

such as phosphoric and/or sulfuric and/or boric acid and/or nitric acid and/or by at least one organic acid such as methyl sulfonic acid.

The aqueous composition AC can be a dispersion or solution. Preferably, it is a solution. Solubility is determined at a temperature of 20°C and atmospheric pressure (1.013 bar).

Preferably, the aqueous composition AC used in step 1) has a temperature in a range of from 5 to 50 °C, more preferably of from 15 to 45 °C or to 40 °C and most preferably from 25 to 35 °C.

The aqueous composition AC used in step 1) is preferably

free or essentially free of any chromium ions such as Cr(VI) cations and/or Cr(III) cations, more preferably is free of chromium ions or comprises a maximum amount of chromium ions of <10 mg/L, calculated as metal, and/or is preferably
free or essentially free of any nickel ions such as Ni(II) cations and/or Ni(III) cations, more preferably is free of nickel ions or comprises a maximum amount of nickel ions of <10 mg/L, calculated as metal, and/or is preferably
free or essentially free of any boron ions such as B(III) cations and/or B(IV) cations, more preferably is free of boron ions or comprises a maximum amount of boron ions of <10 mg/L, calculated as boron, and/or is preferably
free or essentially free of any nitrate anions, more preferably is free of nitrate anions or comprises a maximum amount of nitrate anions of <10 mg/L, calculated as nitrate, and/or is preferably
free or essentially free of any phosphate anions, more preferably is free of phosphate anions or comprises a maximum amount of phosphate anions of <10 mg/L, calculated as phosphate.

“Essentially free” in this context means in each case that at least on purpose none of the aforementioned constituents is added, but it may not be ruled out that any residues of any of the constituents may be present as impurities and/or may be present in amounts being naturally present in water.

The term “aqueous” with respect to the aqueous composition AC used in step 1) in the sense of the present invention preferably means that the composition is a composition containing at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-% in particular at least 80 wt.-%, most preferably at least 90 wt.-% of water, based on its total content of organic and inorganic solvents including water. Thus, the aqueous composition may contain at least one organic solvent besides water - however, in an amount lower than the amount of water present. Preferably, the aqueous composition AC does not or essentially does not contain any organic solvent(s).

Preferably, the aqueous composition AC contains at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-% in particular at least 80 wt.-%, most preferably at least 90 wt.-% of water, in each case based on its total weight.

Preferably, the aqueous composition AC is free or is essentially free of organic solvents. “Essentially free” in this context means that at least on purpose organic solvents are not added, but it may not be ruled out that any of these may be present as impurities. Preferably, the amount of organic solvent(s) present in the aqueous composition AC does not exceed 5 wt.-%, yet more preferably does not exceed 2.5 wt.-%, even more preferably is lower than 2.0 wt.-%, most preferably is at most 1.0 wt.-% or at most 0.5 wt.-% or at most 0.1 wt.-%, in each case based on the total weight of the composition.

Constituent a1)

At least one of zirconium, titanium and hafnium cations, preferably at least one of zirconium and titanium cations, more preferably at least zirconium cations, is present as constituent(s) a1) in the aqueous composition AC.

Preferably, the aqueous composition AC comprises the at least one of zirconium, titanium and hafnium cations in an amount in a range of from 1 or 5 to 4 000 mg/L, more preferably of from 7.5 to 2 000 mg/L, even more preferably of from 10 to 1 500 mg/L, still more preferably of from 12.5 to 1 000 mg/L, yet more preferably of from 15 to 750 mg/L, even more preferably of from 20 to 500 mg/L in each case calculated as metal.

Preferably, a precursor metal compound is used to generate the at least one metal cation being present in composition AC as constituent a1). Preferably, the precursor metal compound is water-soluble. Solubility is determined at a temperature of 20°C and atmospheric pressure (1.013 bar). Particularly preferred zirconium, titanium and/or hafnium compounds for use as precursor compounds are the complex fluorides of these metals. The term “complex fluoride” includes the single and multiple protonated forms as well as the deprotonated forms. It is also possible to use mixtures of such complex fluorides. Complex fluorides in the sense of the present invention are complexes of metal cations such as zirconium, titanium and/or hafnium cations formed with fluoride ions in the composition, e.g., by coordination of fluoride anions to zirconium, titanium and/or hafnium cations in the presence of water. In case complex fluorides of at least one of zirconium, titanium and/or hafnium cations have been used as precursor compounds, the aqueous composition further comprises fluoride anions as constituent a3).

Additionally, or alternatively, zirconium can also be added in form of zirconyl compounds as, e.g., zirconyl nitrate, zirconyl acetate, zirconium carbonate and/or zirconium nitrate, the latter one being particularly preferred, in particular when the aqueous composition is acidic. The same applies to titanium and hafnium.

The content of the at least one metal cation a1) can be monitored and determined by the means of ICP-OES (optical emission spectroscopy with inductively coupled plasma). Said method is described hereinafter in the ‘method’ section.

Constituent a2)

At least one lysine homopolymer and/or copolymer, preferably lysine homopolymer, is present as constituent(s) a2) in the aqueous composition AC.

Preferably, the at least one lysine homopolymer and/or copolymer is present in composition AC an amount in a range of from 1 to 500 000 mg/L, more preferably of from 2 to 300 000 mg/L, even more preferably of from 3 to 200 000 mg/L, still more preferably of from 4 to 100 000 mg/L, yet more preferably of from 5 to 50 000 mg/L,

even more preferably of from 6 to 20 000 mg/L, yet more preferably of from 7 to 15 000 mg/L, even more preferably of from 7.5 to 10 000 mg/L, yet more preferably of from 8 to 5 000 mg/L, still more preferably of from 9 to 2 500 mg/L or to 2 000 mg/L, yet more preferably of from 10 to 1 000 mg/L, most preferably of from 15 or 20 to 500 mg/L.

Preferably, the at least one lysine homopolymer and/or copolymer being present as constituent(s) a2) in composition AC has a weight average molecular weight in a range of from 500 to 300 000 g/mol or to 20 000 g/mol, more preferably of from 750 to 200 000 g/mol or to 15 000 g/mol, even more preferably of from 1 000 to 100 000 g/mol or to 10 000 g/mol, still more preferably of from 1 500 to 75 000 g/mol or to 7 500 g/mol, yet more preferably of from 2 000 to 50 000 g/mol or to 5 000 g/mol.

The inventively used lysine homopolymer and/or copolymers (it is herein also referred to lysine polymers in general or polylyines in this context) at least contain structural units derived from the amino acid lysine. The inventively used lysine polymers, in particular polylysine homopolymers, may differ in terms of stereochemistry (D/L): since the L-form of the amino acid lysine is the naturally occurring form, the inventively used lysine polymers preferably at least contain structural units derived from the amino acid lysine in L-configuration. In addition, the inventively used lysine polymers, in particular polylysine homopolymers, may differ in their link positions (α/ε; with respect the carbon atoms bearing the amino groups within lysine): since the ε-position is the naturally occurring form, the inventively used lysine polymers preferably at least contain structural units derived from the amino acid lysine with ε-link positions. Most preferred are ε-poly-L-lysine polymers, in particular corresponding homopolymers. The at least one lysine homopolymer and/or copolymer, preferably lysine such as ε-polylysine, in particular such as ε-poly-L-lysine (EPL) is preferably produced as a polymer containing at least 10 and up to 100, more preferably at least 15 and up to 75, even more preferably at least 20 and up to 50, still more preferably >20 such as at least 25 and up to 40 such as up to 30 lysine units such as L-lysine units. The precursor amino acid lysine contains two amino groups, one at the α-carbon and one at the ε-carbon. ε-poly-L-lysine is, e.g., used as a natural preservative, which has an antimicrobial effect against I particular yeast, fungi, gram-positive bacteria and gram-negative bacteria. It can be used in food products, chemical and pharmaceutical industries.

The at least one lysine homopolymer and/or copolymer, preferably lysine homopolymer (lysine homopolypeptide), preferably is cationically charged and, hence, belongs to the group of cationic polymers, since at pH 7, polylysines contain a positively charged hydrophilic amino group.

Preferably, the inventively used lysine homopolymer and/or copolymers bears amide bonds, which have been preferably formed by reaction of the carboxyl group of one lysine monomer with an amino group of another lysine monomer, wherein the amino group of the other lysine monomer preferably is connected to its ε-carbon atom. In case of a copolymer, suitable monomers for its preparation, besides lysine, are preferably selected from monomers having at least one amino group and/or carboxyl group.

Preferably, the at least one lysine homopolymer and/or copolymer bears amino groups, more preferably resulting at least in part from the lysine monomers used for its preparation.

The inventively used lysine homopolymer and/or copolymers, in particular homopolymers, can be for example produced by natural fermentation, e.g., in strains of bacteria in the genus streptomyces, which is also used for the commercial production of ε-polylysine such as ε-poly-L-lysines. It usually has a high temperature resistance and does not under high temperatures (e.g., at 121°C for 30 minutes). The inventively used lysine homopolymer and/or copolymer, in particular homopolymer such as ε-polylysine further preferably has a strongly water solubility with a maximum solubility of at least 500 g/L. The inventively used lysine homopolymer and/or copolymer, in particular homopolymer such as ε-polylysine further has a wide pH usage range (pH values 2 to 9), which can compensate for the low activity of other preservatives in neutral and alkaline conditions.

A method for preparation of inventively used lysine homopolymer and/or copolymers and suitable lysine homopolymer and/or copolymers as such are disclosed WO 2022/136613 A1.

Preferably, constituent a2) is a non-aromatic polymer.

Optional constituent a3)

Preferably, the aqueous composition AC further comprises fluoride anions including complex fluoride anions as constituent a3), preferably in an amount in a range of from 5 or 10 to 2 000 mg/L, more preferably of from 15 to 1 500 mg/L, even more preferably of from 20 to 1 000 mg/L, still more preferably of from 25 to 500 or to 200 mg/L, in each case calculated as fluorine. Preferably, the complex fluorides contain zirconium.

Preferably, the aqueous composition AC comprises fluoride anions being present therein as complex fluoride anions as constituent a3), which are preferably coordinated to at least one of zirconium, titanium and hafnium cations in the presence of water, more preferably at least one of zirconium and titanium cations, still more preferably zirconium cations, being also present in the composition as constituent(s) a1), more preferably in an amount of from 1 or 50 mg/L to 4 000 mg/L, still more preferably of from 10 or 100 mg/L to 2 000 or to 1 500 mg/L, yet more preferably in an amount of from 50 or 100 mg/L to 500 or 250 mg/L, calculated in each case as H_2MF_6 with M = Zr, Ti and/or Hf. Alternatively, fluoride anions being present as constituent a3) may be generated by adding other water-soluble fluorine compounds, e.g., fluorides (other than complex fluorides of Ti, Zr and/or Hf) as well as hydrofluoric acid to the composition. The free fluoride content is determined by means of a fluoride ion sensitive electrode according to the method disclosed in the 'methods' section.

Optional constituent a4)

Optionally and preferably, the aqueous composition AC further comprises at least one organosilane and/or a hydrolysis and/or condensation product thereof as constituent(s) a4), preferably in an amount in a range of from 0 or 5 to 20 000 or to 15 000 mg/L, more preferably of from 0 or 10 to 10 000 or to 5 000 mg/L, even more preferably of from 0 or 15 to 1 000 or to 500 mg/L, still more preferably of from 0 or 20 to 250 or to 200 mg/L, in each case calculated as elemental silicon.

The term "organosilanes" includes, e.g., organoalkoxysilanes and organosilanols. Examples of hydrolysis and/or condensation products of organosilanes are organosiloxanes and polyorganosiloxanes as well as polyorganosilanols. For the purposes of this invention, "polyorganosiloxanes" are preferably understood to mean

those compounds which can be condensed from at least two organosilanols and do not form a polydimethylsiloxane. The term “organo” in “organosilane” preferably means that at least one organic group is present, which is connected directly to a silicon atom via a carbon atom and can consequently not be subjected to hydrolysis.

Preferably, optional constituent a4) has at least one functional group selected from (meth)acrylate groups, alkylaminoalkyl groups, alkylamino groups, alkyltetrasulfide groups, amino groups, aminoalkyl groups, carboxyl groups, epoxy groups, glycidoxy groups, hydroxyl groups, isocyanato groups, mercaptoalkyl groups, succinic anhydride groups, imido groups, imino groups, and/or ureido groups (urea groups).

Examples of organosilanes are, e.g., (3-aminopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, bis (trimethoxysilylpropyl) amine, bis (triethoxysilylpropyl) amine, N-2-aminoethyl-3-aminopropyltrimethoxysilane, (3-butylaminopropyl)trimethoxysilan, bis(3-triethoxysilylpropyl)disulfide, bis(3-triethoxysilylpropyl)tetrasulfide), bis(3-trimethoxysilylpropyl)disulfide, bis(3-trimethoxysilylpropyl)tetrasulfide), 1,2-bis(triethoxysilyl)ethane, (3-mercaptopropyl)trimethoxysilane, (3-mercaptopropyl)triethoxysilane, (3-methylaminopropyl)triethoxysilan, (3-methylaminopropyl)trimethoxysilan, (3-glycidyloxypropyl)trimethoxysilane and/or (3-glycidyloxypropyl)triethoxysilane, and/or vinyltrimethoxysilane. The organosilane is preferably present in a hydrolyzed form thereof.

Preferably, the aqueous composition AC comprises at least one organosilane and/or a hydrolysis and/or condensation product thereof as constituent(s) a4) with at least one amino group, urea group, imido group, imino group and/or ureido group per organosilane unit, more preferably with at least one or more such as at least two amino groups per organosilane unit. Particularly preferred is 2-aminoethyl-3-aminopropyltrimethoxysilane, 2-aminoethyl-3-aminopropyltriethoxysilane, bis (trimethoxysilylpropyl) amine and/or bis (triethoxysilylpropyl) amine.

Further optional constituents including optional constituents a5) and a6)

Optionally, the aqueous composition AC further comprises at least one kind of metal cations selected from the group of cations of metals of the 1st to 3rd subgroup (copper, zinc and scandium groups) and 5th to 8th subgroup (vanadium, manganese and iron groups) of the periodic table of the elements including the lanthanides as well as the 2nd main group of the periodic table of the elements (alkaline earth metal group), lithium and bismuth and/or tin. More preferably the aqueous composition AC further optionally comprises at least one kind of metal cations selected from the group consisting of cations of cerium and other lanthanides, chromium, iron, calcium, cobalt, copper, magnesium, manganese, molybdenum, nickel, niobium, tantalum, yttrium, vanadium, lithium, bismuth, zinc and tin, and mixtures thereof. Most preferred are copper and/or zinc cations.

Optionally and preferably, the aqueous composition AC further comprises

zinc cations as constituent a5), preferably in an amount in a range of from 0 or 5 to 5 000 mg/L, more preferably of from 0 or 10 to 2 500 mg/L, even more preferably of from 0 or 25 to 1 000 or to 500 mg/L, in each case calculated as metal, and/or

copper cations as constituent a6), preferably in an amount in a range of from 0 or 1 to 1 000 mg/L, more preferably of from 0 or 1 to 500 mg/L, even more preferably of from 0 or 2 to 100 mg/L, still more preferably of from 0 or 2.5 to 50 mg/L, in each case calculated as metal.

Optionally, the aqueous composition AC further comprises at least one pH-value adjusting constituent, preferably selected from the group consisting of nitric acid, sulfuric acid, methanesulfonic acid, acetic acid, aqueous ammonia, sodium hydroxide and sodium carbonate, wherein methanesulfonic acid and sodium carbonate are preferred. Depending on the pH value of the aqueous composition, the above constituent can be present in their fully or partially deprotonated form or in protonated forms.

Optionally, the aqueous composition AC further comprises at least one organic solvent, preferably selected from the group consisting of methanol, ethanol, ethylene glycol n-

butyl ether, ethylene glycol n-propyl ether, propylene glycol n-propyl ether, propylene glycol n-butyl ether and mixtures thereof. Methanol and ethanol can be, e.g., present as reaction products of the organosilane hydrolysis.

Optionally, the aqueous composition AC further comprises at least one organic acid, preferably at least one organic acid having at least two carboxylic acid groups and/or at least one organic acid having at least one carboxylic acid groups and at least one further functional group having at least one donor atom such an OH-group, e.g., lactic acid, in particular when the aqueous composition is alkaline. The presence of such a compound may be helpful for stabilization of the at least one metal cation being present in the composition as a1) such as Zr cations.

The aqueous composition may further comprise at least one of the following constituents: one or more waxes, one or more wetting agents and one or more defoamers and/or rheology additives.

Optionally, the aqueous composition AC may comprise at least one water-soluble polymer different from constituent a2) such as a water-soluble polymer having at least one kind of functional groups selected from acid groups, hydroxyl groups, and mixtures thereof. Preferably, the at least one water-soluble polymer if present is a homopolymer or copolymer obtainable from polymerization of at least one kind of ethylenically unsaturated monomers, wherein at least part of said monomers bear at least one kind of functional groups selected from acid groups, hydroxyl groups, and mixtures thereof, more preferably is a homopolymer or copolymer obtainable from polymerization of at least one kind of vinyl monomers and/or (meth)acrylic monomers, wherein at least part of said monomers bear at least one kind of functional groups selected from acid groups, hydroxyl groups, and mixtures thereof.

Optionally, the aqueous composition AC further comprises at least one surfactant, in particular when it is also used as and/or represents a cleaning composition, besides its suitability as a chemical pretreatment composition.

The term surfactant (surface active agent) as used herein is preferably used in accordance with the term “tenside” as defined in Römpp Lexikon “Lacke und

Druckfarben" (Publisher: Ulrich Zorll, Editor: Hans-Jürgen P. Adler – Stuttgart; New York: Thieme, 1998; term: "tenside" pages 557 and 558). Surfactants act in a demulsifying manner. Suitable surfactants are known to a person skilled in the art and, e.g., disclosed in WO 2020/200838 A1.

Preferably, the at least one surfactant is selected from non-ionic, anionic and/or cationic surfactants, most preferably from non-ionic surfactants.

Suitable non-ionic surfactants include in particular alkylphenol alkoxylates, especially alkylphenol ethoxylates, having C_6 to C_{14} alkyl chains and a degree of alkoxylation of 5 to 30 mol per mole of phenol, alkylpolyglucosides having an alkyl chain length of C_8 to C_{22}, preferably C_{10} to $C1_8$, and containing 1 to 20, preferably 1 to 5, glucoside units, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates, N-alkylglucamides or else block copolymers consisting of ethylene oxide, propylene oxide and/or butylene oxide, and alkoxylated C_8 to C_{22} alcohols such as fatty alcohol alkoxylates, oxo-process alcohol alkoxylates and Guerbet alcohol alkoxylates, where the alkoxylation may take place with ethylene oxide, propylene oxide, butylene oxide and/or a mixture of these, as a block copolymer or random copolymer. The alcohols preferably have 8 to 18 carbon atoms; the degree of alkoxylation ranges typically between 2 to 50 mol, preferably 3 to 20 mol, of at least one of the stated alkylene oxides per mole of alcohol. The alkylene oxide head group may additionally contain the following so-called end-capping groups as a modification: benzyl, methyl and/or tert-butyl capping.

Depending on application, the following anionic surfactants in particular can be used: fatty alcohol sulfates having alkyl chain lengths of 8 to 22, preferably 10 to 18, carbon atoms, for example lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate or stearyl sulfate, alkyl ether sulfates having alkyl chain lengths of 8 to 22, preferably 10 to 18, carbon atoms, and linear C_8 to C_{20} alkylbenzenesulfonates or else alkanesulfonates and soaps, such as sodium or potassium salts of C_8 to C_{24} carboxylic acids. Cationic surfactants employed, depending on application, are in particular quaternary mono- and di-(C_7-C_{25} alkyl)dimethylammonium compounds, ester quats, especially quaternary esterified mono-, di- and trialkanolamines esterified with C_8-C_{22} carboxylic acids, and C_7 to C_{25} alkylamines, N,N-dimethyl-N-(hydroxy-C_7-C_{25} alkyl)ammonium salts and/or imidazoline quats.

As outlined above, however, the at least one surfactant preferably is at least one non-ionic surfactant. Within the majority of applications, the foaming tendency of anionic surfactants is too high, while cationic surfactants often attach to the metallic surface, and may consequently give rise to problems within the deposition of conversion coating films to be subsequently applied.

Preferably, the aqueous composition AC comprises the at least one surfactant as the at least one constituent a3) in an amount of from 0 or 0.3 to 10.0 g/L, more preferably of from 0 or 0.4 to 5.0 g/L, even more preferably of from 0 or 0.5 to 3.5 g/L.

Optional step 2)

In optional step 2) the film obtained after step 1) is rinsed at least once with at least one aqueous rinsing composition ARC, which is different from aqueous composition AC. Preferably, composition ARC consists or essentially consists of water only. The term “rinsing” preferably means, in accordance with the general understanding of this term, a removal excessive parts of the aqueous composition AC, which was contacted with the surface in the step directly preceding the optional rinsing step.

Tap water and/or deionized water can be used for rinsing in optional step 2). As outlined hereinbefore, optional step 2) can be performed more than once. It is hence possible, e.g., to perform a rinsing in step 2) once with tap water followed by rinsing with deionized water or vice versa.

Optional step 3)

In optional step 3) the film obtained after step 1) or after optional step 2) is dried or cured to give a cured or dried coating layer.

Drying and/or curing may be performed in particular, when in a step 4) as outlined hereinafter, a coating material composition is subsequently applied. However, step 3) is only optional and, hence, further method steps such as step 4) may be carried out without drying and/or curing the film obtained after having performed step 1) or rinsing

step 2). In particular, it is possible to apply a coating material composition such as an electrodeposition coating material composition in a step 4) as outlined hereinafter onto a wet film obtained after having performed step 1) or rinsing step 2).

The drying or curing step 3) may be preferably performed (if performed at all), e.g., at a temperature in the range of 15°C to 180°C, more preferably at a temperature in the range of 25°C to 150°C, in particular at a temperature in the range of 50°C to 130°C. "Drying" in the sense of the present invention means physical drying by evaporation of in particular water originally present in the composition(s) used, whereas "curing" further includes a chemical reaction between at least two constituents originally present in the composition(s) and/or between at least one constituent originally present in the composition(s) and a suitable functional group present on the metallic surface or in the conversion film, e.g., due to the presence of polymer a2) in composition AC. Once a film is dried, the resulting product can be regarded as a layer.

Preferably, a conversion layer formed after drying or curing, preferably drying, the film obtainable after step 3), has a coating weight determined by XRF (X-ray fluorescence spectroscopy) of: 0.5 to 500 mg/m², more preferably of from 1 to 400 mg/m², even more preferably of from 2 to 350 mg/m², determined in each case as tracer element(s) such as Ti, Zr and/or Si via XRF measurements.

Preferably, the dry layer thickness of a a conversion layer formed after drying or curing, preferably drying, the film obtainable after step 3), is below 0.5 µm. Preferably, the obtained cured or dried coating layer obtained after step 3) has a dry film thickness in a range of from 1 nm to <500 nm, more preferably of from 10 nm to 250 nm, in particular of from 80 to 150 nm.

Substrate obtainable by chemical pretreatment method

A further subject-matter of the present invention is a substrate, which is a chemically pretreated substrate being obtainable by the inventive method of chemical pretreatment as defined hereinbefore and hereinafter.

All preferred embodiments described above herein in connection with the chemical pretreatment method and preferred embodiments thereof are also preferred embodiments of the substrate obtainable by this method.

Aqueous composition AC

A further subject-matter of the present invention is an aqueous composition AC as defined hereinbefore and hereinafter in connection with step 1) and as used in step 1) of the chemical pretreatment method comprising besides water at least one of zirconium, titanium, and hafnium cations as constituent(s) a1), and at least one lysine homopolymer and/or copolymer as constituent(s) a2).

All preferred embodiments described above herein in connection with the inventive chemical pretreatment method, the substrate obtainable therefrom, and preferred embodiments thereof are also preferred embodiments of the inventive composition AC.

In particular, when the aqueous composition is used as cleaning composition, it preferably comprises at least one surfactant as optional and preferred constituent.

Concentrate

A further subject-matter of the present invention is a concentrate, from which the aqueous composition AC is at least obtainable by dilution with water and, optionally, further, by pH adjustment.

All preferred embodiments described above herein in connection with the inventive chemical pretreatment method, the substrate obtainable therefrom, and the inventive composition AC, and preferred embodiments thereof are also preferred embodiments of the inventive concentrate.

The concentrate used to produce the aqueous composition AC typically contains the constituents of the aqueous composition AC to be produced in the desired proportions, but at a higher concentration. Such concentrate is diluted with water to the desired concentrations of the constituents as disclosed hereinbefore to form composition AC.

If necessary, the pH value of the composition may be adjusted after dilution as well as outlined hereinbefore. Of course, it is also possible to further add any of the optional constituents of the composition to the water used for dilution or to add any of the optional or some of the necessary constituents after diluting the concentrate with water. It is, however, preferred that the concentrate already contains all necessary constituents.

Preferably, the aqueous composition AC is obtainable from a concentrate by dilution with water, preferably with deionized water, such that the concentrate is present in the composition after dilution in an amount of from 5 to 60 g/L, more preferably 10 to 40 g/L, even more preferably of from 15 to 30 g/L, based on the total weight of the composition (obtained after dilution of the concentrate).

Preferably, the concentrate is diluted with water in a weight ratio of 1:5000 to 1:10, more preferred 1:1000 to 1:10, most preferred in a ratio of 1:300 to 1:10 and even more preferred 1:150 to 1:50 to produce the composition AC.

Preferably, composition AC can be prepared from a concentrate by dilution of the concentrate with water.

Use

A further subject-matter of the present invention is a use of at least one lysine homopolymer and/or copolymer as defined hereinbefore and hereinafter as constituent a2) of composition AC, preferably when incorporated into an aqueous composition AC, more preferably into an inventive aqueous composition AC defined hereinbefore and hereinafter, for providing or improving corrosion resistance of metallic surfaces of substrates and/or for providing or improving adhesion of metallic surfaces of substrates to one or more further coating layers present thereon.

All preferred embodiments described above herein in connection with the inventive chemical pretreatment method, the substrate obtainable therefrom, the inventive composition AC, and the concentrate, and preferred embodiments thereof are also preferred embodiments of the inventive use.

Coating method

A further subject-matter of the present invention is a method of coating of at least one chemically pretreated metallic surface of at least one substrate, wherein chemical pretreatment of the at least one metallic surface has been carried out according to the inventive method of chemical pretreatment as defined hereinbefore and hereinafter or by making use of an inventive aqueous composition AC, the method of coating further comprising at least step 4), namely

4) applying at least one coating material composition comprising at least one film-forming polymer and/or resin onto the optionally rinsed film obtained after step 1) or 2) as defined hereinbefore and hereinafter or onto the dried or cured, preferably dried, film, which in turn is obtainable from drying or curing the film obtainable from optional step 3) as defined hereinbefore and hereinafter.

The method of coating according to the present invention comprises at least step 4) and is performed after having carried out the inventive chemical pretreatment method as defined hereinbefore and hereinafter. The method of coating may, however, comprise one or more further additional optional steps.

All preferred embodiments described above herein in connection with the inventive chemical pretreatment method, the substrate obtainable therefrom, the inventive composition AC, the concentrate and the inventive use, and preferred embodiments thereof are also preferred embodiments of the inventive coating method.

The coating material composition used in step 4) is different from each of compositions AC, and ARC.

The coating material composition can be, e.g., an electrodeposition coating composition, a primer coating composition, a basecoat composition, or a topcoat including a clearcoat composition. It is, of course, possible to apply more than one composition subsequently to form a multilayer coating system, which is conventionally used, e.g., in the automotive industry.

Preferably, the coating material composition applied in step 4) is an electro-depositable, preferably a cathodically depositable, coating material composition, wherein the at least one film-forming polymer and/or resin present therein preferably is an electro-depositable, preferably a cathodically depositable, polymer.

Alternatively, and also preferably, the coating material composition applied in step 4) is a powder coating composition, which comprises at least one of a polymer and/or a resin selected from polyesters, epoxy resins, poly(meth)acrylate homopolymer and poly(meth)acrylate copolymers.

Substrate obtainable by coating method

A further subject-matter of the present invention is a substrate, which is a coated substrate being obtainable by the inventive method of coating as defined hereinbefore and hereinafter.

All preferred embodiments described above herein in connection with the inventive chemical pretreatment method, the substrate obtainable therefrom, the inventive composition AC, the concentrate, the inventive use, and inventive coating method, and preferred embodiments thereof are also preferred embodiments of the inventive coated substrate.

METHODS

1. Free fluoride content determination

The free fluoride content is determined by means of a fluoride ion selective electrode. The electrode is calibrated using at least three master solutions with known fluoride concentrations. The calibration process results in the building of calibration curve. Then the fluoride content is determined by using of the curve.

2. ICP-OES

The amounts of certain elements in a sample under analysis, such as of zirconium, titanium, hafnium etc., is determined using inductively coupled plasma atomic emission spectrometry (ICP-OES) according to DIN EN ISO 11885 (date: September 1, 2009). A sample is subjected to thermal excitation in an argon plasma generated by a high-frequency field, and the light emitted due to electron transitions becomes visible as a spectral line of the corresponding wavelength and is analyzed using an optical system. There is a linear relation between the intensity of the light emitted and the concentration of the element in question. Prior to implementation, using known element standards (reference standards), the calibration measurements are carried out as a function of the particular sample under analysis. These calibrations can be used to determine concentrations of unknown solutions such as the concentration of the amount of titanium, zirconium, and hafnium.

3. Coating weight

XRF (X-ray fluorescence spectroscopy) is used for determining the coating weight in mg/m² of certain (tracer) element(s) such as Ti, Zr and/or Si in a layer such as the conversion layer resulting from applying the chemical pretreatment composition to a substrate.

4. VDA621-415 corrosion test

VDA 621-415 (predecessor of VDA 233-102) is a cyclic corrosion test with a weekly cycle for determination of the corrosion resistance of the investigated sample. The samples have been scratched all the way down parallel to the longitudinal side. The test was used for steel substrates. The weekly cycle consists of 1) a salt spray phase (24 h 5% NaCl salt spray at 35°C), 2) a first condensed water climate phase (96 h

warm and humid period at 40°C with 85% RH (relative humidity)) and 3) a second condensed water climate phase (48 h at ambient conditions, i.e., at 25°C with 50% RH). The whole duration of the test is 10 weeks. The undermining (undercreep; creepage) (overall average) has then been determined after having performed the test according to DIN EN ISO 4628-8. Further, stone chip resistance after 10 weeks has been determined as well according to DIN EN ISO 20567-1, method C.

5. Copper catalyzed acetic acid salt spray (CASS) mist testing to DIN EN ISO 9227

The copper catalyzed acetic acid salt spray mist test is used for determining the corrosion resistance of a coating on a substrate and has been used for aluminum and/or aluminum alloys. The samples have been scratched all the way down parallel to the longitudinal side. In accordance with DIN EN ISO 9227 (07-2017) the samples under analysis are in a chamber in which there is continuous misting of a 5% strength common salt solution, the salt solution being admixed with acetic acid and copper chloride, at a temperature of 50 °C over a duration of 504 hours with controlled pH. The spray mist deposits on the samples under analysis, covering them with a corrosive film of salt water. The samples were then investigated for their level of undermining (creepage) in accordance with DIN EN ISO 4628-8 (03-2013), since the substrate corrodes along the score line during the CASS mist test.

6. Adhesion test 1

A cross hatch adhesion test (crosscut test) according to DIN EN ISO 2409:2020-12 was performed after the substrates investigated had been subjected to a humidity test (CH; condensation atmosphere with constant high humidity) for 240 h according to DIN EN ISO 6270-2:2018-04.

7. Boiling test

Dry and wet adhesion are measured for coated panels and compared with each other via the boiling test and by means of a crosscut test. A crosscut test for measuring the dry adhesion is done according to DIN EN ISO 2409:2020-12 before performing the boiling test. Afterwards the panels are boiled in deionized water at 100 °C (212 °F) for two hours. After two hours, the panels are stored under lab conditions at ambient temperature for one hour. A crosscut test for measuring the wet adhesion is then

performed according to DIN EN ISO 2409:2020-12. The adhesion is determined in each case by pulling the paint film over the crosscut using a tape.

8. Adhesion test 2

By adhesion test 2 dry and wet adhesion are measured for coated panels and compared with each other via the GMW 14704 test and by means of a crosscut test. A crosscut test for measuring the dry adhesion is done first according to DIN EN ISO 2409:2020-12. Afterwards the panels are dipped in deionized water at 62 to 63°C for 48 hours. Then the panels are stored under lab conditions at ambient temperature for one hour. A crosscut test for measuring the wet adhesion is then performed according to DIN EN ISO 2409:2020-12. The adhesion is determined in each case by pulling the paint film over the crosshatch using a tape.

EXAMPLES

The following examples further illustrate the invention, but are not to be construed as limiting its scope.

1. Chemical pretreatment compositions

1.1 *Chemical pretreatment composition CPC1*

For preparation of CPC1 a commercially available product, i.e., Gardo® TP 9906, was used as precursor, which is an acidic aqueous composition that contains fluoride anions and zirconium cations. Said precursor was added to a 100 L batch to prepare a chemical pretreatment bath such that a concentration of zirconium cations of 100 mg/L, calculated as metal, resulted. 30 mg/L of commercial organosilane containing product Oxsilan®9810/3 was then added to the bath, calculated as silicate. Then, a polylysine homopolymer PL1 having a M_w of 3090 g/mol was added such that a polymer concentration of 20 mg/L resulted. PL1 was synthesized as disclosed in WO 2022/136613 A1 and used in this form without any further processing. The preparation of PL1 was performed according to the procedure of polylysine-5 of Table 1 in WO 2022/136613 A1. After reaching the target pressure, however, distillation was continued for another period of time compared to polylysine-5. Further, 10 mg/L copper cations were added to the bath, calculated as metal. The bath temperature was then adjusted to 30 °C. The pH-value and the free fluoride content of the resulting bath were subsequently adjusted through addition of a diluted sodium bicarbonate solution to a pH value of 4.8 and a concentration of free fluoride anions in a range of from 30 to 40 mg/L, calculated as fluorine. Before being used for chemical pretreatment of substrates, the bath was aged for at least 12 hours to obtain a chemical equilibrium.

1.2 *Chemical pretreatment composition CPC2*

CPC2 was prepared in the same manner as CPC1 except of the fact that PL1 was added in an amount such that a polymer concentration of 200 mg/L resulted.

1.3 *Chemical pretreatment composition CPC3*

CPC3 was prepared in the same manner as CPC2 except of the fact that Oxsilan®9810/3 has not been used for preparing the bath.

1.4 *Chemical pretreatment composition CPC4*

CPC4 was prepared in the same manner as CPC3 except of the fact that PL1 was added in an amount such that a polymer concentration of 500 mg/L resulted.

1.5 *Comparative pretreatment composition REF 1*

In addition, a comparative chemical pretreatment composition REF1 was used, which had been prepared in the same manner as CPC1 except of not having included the polylysine homopolymer PL1 therein as described hereinbefore in connection with CPC1.

1.6 *Comparative pretreatment composition REF2*

In addition, a comparative chemical pretreatment composition REF2 was used, which had been prepared in the same manner as CPC3 except of not having included the polylysine homopolymer PL1 therein as described hereinbefore in connection with CPC3.

1.7 *Chemical pretreatment composition CPC5*

For preparation CPC5 a commercially available product, i.e., Gardobond® X 4548, was used as precursor, which is an acidic aqueous composition that contains fluoride anions and zirconium cations. Said precursor was added to a 50 L batch to prepare a chemical pretreatment bath such that a concentration of zirconium cations of 35 mg/L, calculated as metal, resulted. 4 g/L of a mixture of non-ionic surfactant Propetal® 120 and deionized water was then added to the bath. Then, a polylysine homopolymer PL2 having a M_w of 3700 g/mol was added such that a polymer concentration of 400 mg/L resulted. PL2 was synthesized as disclosed in WO 2022/136613 A1 and used in this form without any further processing. The preparation of PL2 was performed according to the procedure of polylysine-6 of Table 1 in WO 2022/136613 A1. After reaching the target pressure, however, distillation was continued for another period of time compared to polylysine-6. The bath temperature was then adjusted to 30 °C. The pH-value and the free fluoride content of the resulting bath were subsequently adjusted through addition of a diluted sodium bicarbonate solution to a pH value of 5.4 and a concentration of free fluoride anions in a range of from 20 to 25 mg/L, calculated as fluorine.

2. Pretreatment including chemical pretreatment method

2.1 Three kinds of substrates were used, namely a hot-dip galvanized steel substrate (HDG substrate; S1), a cold rolled steel substrate (CRS substrate; S2) and an aluminum alloy substrate (AA6014S substrate; S3). Each of the substrates was cleaned by making use of a commercially available phosphate free alkali cleaner having a pH value of about 10.8 at 60 °C for about 3 minutes. Then, spray rinsing with tap water and subsequent spray rinsing with deionized water was performed (for 30 seconds each at ambient temperature).

A contacting step was then carried out, wherein the overall surface of each of the substrates was contacted with one of the chemical pretreatment compositions described hereinbefore in item **1.** for 3 minutes by immersion at 30 °C in order to form a conversion coating film onto the surface of each of the substrates. In a reference example, the contacting step with a chemical pretreatment composition was omitted.

Following the contacting step, a spray rinsing with tap water and subsequently a spray rinsing with deionized water was performed (for 30 seconds each at ambient temperature). Following the rinsing steps, a drying step was performed by warm air drying for 8 minutes in an oven at 120 °C air temperature. Finally, a commercially available electrodeposition (ED) coating material (Cathoguard® 800) was applied on the conversion coated surface of the substrates and baked at 175 °C for 25 minutes. The dry layer thickness of the ED coating was in a range of from 20 µm and 25 µm.

2.2 Four kinds of substrates were used, namely each of S1 to S3 as described above in section **2.1**, as well as a boron steel as substrate S4. Each of the substrates was cleaned via spraying by making use of composition CPC5 described hereinbefore. In run a) spraying was done at a spray pressure of 1-2 bar for 120 s at 45 °C. In an alternative run b) spraying was done at a spray pressure of 1-2 bar for 180 s at 30 °C Then, in each case spray rinsing with tap water and subsequent spray rinsing with deionized water was performed (for 30 seconds each at ambient temperature).

A contacting step was then carried out, wherein the overall surface of each of the substrates was contacted with chemical pretreatment composition CPC5 described hereinbefore for 3 minutes by immersion at 30 °C in order to form a conversion coating film onto the surface of each of the substrates.

Following the contacting step, a spray rinsing with tap water and subsequently a spray rinsing with deionized water was performed (for 30 seconds each at ambient temperature). Following the rinsing steps, a drying step was performed by warm air drying for 8 minutes in an oven at 120 °C air temperature. Finally, one of three different kinds of powder paintings was applied: a commercially available polyester powder paint (Interpon® A2201 from AkzoNobel), another commercially available polyester powder panint (RAL 7035 light gray texture from PPG), or an epoxy and polyester mix powder paint (Interpon® 700 from AkzoNobel) was applied on the conversion coated surface.

3. Investigation of the properties of the chemically pretreated substrates

3.1 The substrates obtained after the method described hereinbefore in item **2.1** had been performed have then been investigated according to the methods described in the 'methods' section. The results are shown in Tables 1.1 and 1.2.

Table 1.1

Chemical pretreatment composition used	*Substrate*	*Cross hatch test after 240 h of humidity test*	*VDA 621-415 test after 10 weeks*		*DIN EN ISO 9227 CASS test after 504 h*
			Stone chip resistance	Creepage [mm]	Creepage [mm]
REF1	HDG	0	2.5±0	2.4±0.05	/
	CRS	0	1.67±0.17	1.67±0.17	/
	AA6014S	0	/	/	1.3±0
CPC1	HDG	0	2.5±0	1.9±0.06	/
	CRS	0	1.5±0	1.37±0.08	/
	AA6014S	0	/	/	1.27±0.2
CPC2	HDG	0	2.5±0	1.8±0.14	/
	CRS	0	1.5±0	1.3±0	/
	AA6014S	0	/	/	1.2±0.14

Table 1.2

Chemical pretreatment composition used	*Substrate*	*Cross hatch test after 240 h of humidity test*	*VDA 621-415 test after 10 weeks*		*DIN EN ISO 9227 CASS test after 504 h*
			Stone chip resistance	Creepage [mm]	Creepage [mm]
REF2	HDG	1	3.5±0	2.3±0.1	/
	CRS	1	2.17±0.13	0.87±0.13	/
	AA6014S	1	/	/	2.13±0.13
CPC3	HDG	1	3.5±0	2.2±0.16	/
	CRS	1	2±0	0.87±0.13	/
	AA6014S	0	/	/	2.13±0.13
CPC4	HDG	1	3±0	2.2±0.16	/
	CRS	1	1.83±0.16	0.87±0.13	/
	AA6014S	0	/	/	1.77±0.14

3.2 The substrates obtained after the method described hereinbefore in item **2.2** had been performed have then been investigated according to the methods described in the 'methods' section. The results are shown in Tables 1.3, 1.4 and 1.5

Table 1.3

Cleaning according to run a)	*Dry adhesion before boiling test*			
	Powder coating composition used: Interpon® A2201			
	AA6014S	HDG	CRS	Boron steel
	Delamination in [%] for dry paint adhesion			
	0%	0%	0%	0%
Chemical pretreatment composition used:				
	Wet adhesion after boiling test			
	Powder coating composition used: Interpon® A2201			
	AA6014S	HDG	CRS	Boron steel
CPC5	Delamination in [%] for wet paint adhesion			
	0%	0%	0%	0%

Table 1.4

Cleaning according to run b)	*Dry adhesion before GMW 14704 test*					
	Powder coating composition used: RAL 7035			Powder coating composition used: Interpon® 700		
	AA6014S	HDG	CRS	AA6014S	HDG	CRS
	Delamination in [%] for dry paint adhesion					
	0%	0%	0%	0%	0%	0%
Chemical pretreatment composition used:						
	Wet adhesion after GMW 14704 test					
	Powder coating composition used: RAL 7035			Powder coating composition used: Interpon® 700		
	AA6014S	HDG	CRS	AA6014S	HDG	CRS
CPC5	Delamination in [%] for wet paint adhesion					
	0%	0%	0%	0%	0%	0%

Table 1.5

Cleaning according to run b)	*Dry adhesion (before humidity test)*					
	Powder coating composition used: RAL 7035			Powder coating composition used: Interpon® 700		
	AA6014S	HDG	CRS	AA6014S	HDG	CRS
	Delamination in [%] for dry paint adhesion					
	0%	0%	0%	0%	0%	0%
Chemical pretreatment composition used:						
	Wet adhesion (after 240 h of humidity test)					
	Powder coating composition used: RAL 7035			Powder coating composition used: Interpon® 700		
	AA6014S	HDG	CRS	AA6014S	HDG	CRS
CPC5	Delamination in [%] for wet paint adhesion					
	0%	0%	0%	0%	0%	0%

CLAIMS

1. A method of chemical pretreatment of at least one metallic surface of at least one substrate comprising at least step 1) and optionally one or more of steps 2) and 3), namely

   1) contacting the at least one metallic surface of the at least one substrate at least in portion with an aqueous acidic composition AC being suitable to form a coating film at least in portion onto said surface,

   wherein the aqueous acidic composition AC comprises, besides water, at least constituents a1) and a2), which are different from one of another, namely

   at least one of zirconium, titanium, and hafnium cations as constituent(s) a1), and

   at least one lysine homopolymer and/or copolymer, which bears amide bonds, as constituent(s) a2),

   2) optionally rinsing the coating film obtained after step 1) at least once with at least one aqueous rinsing composition ARC, which is different from aqueous acidic composition AC, and

   3) optionally curing or drying the optionally rinsed coating film obtained after step 1) or 2) to give a cured or dried coating layer.

2. The method according to claim 1, characterized in that the at least one lysine homopolymer and/or copolymer is present in composition AC an amount in a range of from 1 to 500 000 mg/L, more preferably of from 2 to 300 000 mg/L, even more preferably of from 3 to 200 000 mg/L, still more preferably of from 4 to 100 000 mg/L, yet more preferably of from 5 to 50 000 mg/L, even more preferably of from 6 to 20 000 mg/L, yet more preferably of from 7 to 15 000 mg/L, even more preferably of from 7.5 to 10 000 mg/L, yet more preferably of from 8 to 5 000 mg/L, still more preferably of from 9 to 2 500 mg/L or to 2 000

mg/L, yet more preferably of from 10 to 1 000 mg/L, most preferably of from 15 or 20 to 500 mg/L.

3. The method according to claim 1 or 2, characterized in that the at least one lysine homopolymer and/or copolymer, preferably lysine homopolymer, being present as constituent(s) a2) in composition AC has a weight average molecular weight in a range of from 500 to 300 000 g/mol or to 20 000 g/mol, more preferably of from 750 to 200 000 g/mol or to 15 000 g/mol, even more preferably of from 1 000 to 100 000 g/mol or to 10 000 g/mol, still more preferably of from 1 500 to 75 000 g/mol or to 7 500 g/mol, yet more preferably of from 2 000 to 50 000 g/mol or to 5 000 g/mol.

4. The method according to one or more of the preceding claims, characterized in that the at least one lysine homopolymer and/or copolymer, preferably lysine homopolymer, bears amide bonds, which have been formed by reaction of the carboxyl group of one lysine monomer with an amino group of another lysine monomer, wherein the amino group of the other lysine monomer preferably is connected to its ε-carbon atom, preferably such that the lysine homopolymer formed is a L-lysine homopolymer, more preferably an ε-poly-L-lysine homopolymer, and/or in that the at least one lysine homopolymer and/or copolymer, preferably lysine homopolymer, is a polymer containing at least 10 and up to 100, more preferably at least 15 and up to 75, even more preferably at least 20 and up to 50, still more preferably >20 such as at least 25 and up to 40 such as up to 30 lysine units, wherein the lysine units are preferably L-lysine units, wherein the at least one lysine homopolymer and/or copolymer preferably is a cationically charged polymer, and/or in that the at least one lysine homopolymer and/or copolymer bears amino groups.

5. The method according to one or more of the preceding claims, characterized in that aqueous composition AC comprises the at least one of zirconium, titanium, and hafnium cations in an amount in a range of from 1 or 5 to 4 000 mg/L, more preferably of from 7.5 to 2 000 mg/L, even more preferably of from 10 to 1 500 mg/L, still more preferably of from 12.5 to 1 000 mg/L, yet more preferably of from 15 to 750 mg/L, even more preferably of from 20 to 500 mg/L in each case calculated as metal.

6. The method according to one or more of the preceding claims, characterized in that the aqueous composition AC has a pH value in a range of from 0.1 to <7.0, preferably of from 0.5 to 6.5, more preferably of from 1.0 to 6.0, even more preferably of from 1.5 or 2.0 to 5.5, still more preferably of from 2.5 or 3.0 to 5.25, most preferably of from 3.5 or 4.0 to 5.0.

7. The method according to one or more of the preceding claims, characterized in that the aqueous composition AC further comprises fluoride anions including complex fluoride anions as constituent a3), preferably in an amount in a range of from 5 or 10 to 2 000 mg/L, more preferably of from 15 to 1 500 mg/L, even more preferably of from 20 to 1 000 mg/L, still more preferably of from 25 to 500 or to 200 mg/L, in each case calculated as fluorine.

8. The method according to claim 7, characterized in that the aqueous composition AC comprises fluoride anions being present therein as complex fluoride anions as constituent a3), which are preferably coordinated to at least one of zirconium, titanium and hafnium cations being also present in the composition as constituent(s) a1), more preferably in an amount of from 1 or 50 mg/L to 4 000 mg/L, still more preferably of from 10 or 100 mg/L to 2 000 or to 1 500 mg/L, yet more preferably in an amount of from 50 or 100 mg/L to 500 or to 250 mg/L, calculated in each case as H_2MF_6 with M = Zr, Ti and/or Hf.

9. The method according to one or more of the preceding claims, characterized in that aqueous composition AC further comprises

at least one organosilane and/or a hydrolysis and/or condensation product thereof as constituent(s) a4), preferably in an amount in a range of from 0 or 5 to 20 000 or to 15 000 mg/L, more preferably of from 0 or 10 to 10 000 or to 5 000 mg/L, even more preferably of from 0 or 15 to 1 000 or to 500 mg/L, still more preferably of from 0 or 20 to 250 or to 200 mg/L, in each case calculated as elemental silicon, and/or

zinc cations as constituent a5), preferably in an amount in a range of from 0 or 5 to 5 000 mg/L, more preferably of from 0 or 10 to 2 500 mg/L, even more

preferably of from 0 or 25 to 1 000 or to 500 mg/L, in each case calculated as metal, and/or

copper cations as constituent a6), preferably in an amount in a range of from 0 or 1 to 1 000 mg/L, more preferably of from 0 or 1 to 500 mg/L, even more preferably of from 0 or 2 to 100 mg/L, still more preferably of from 0 or 2.5 to 50 mg/L, in each case calculated as metal.

10. The method according to one or more of the preceding claims, characterized in that step 3) is performed and that the cured or dried coating layer obtained after step 3) preferably has a dry film thickness below 0.5 µm and/or in that the cured or dried coating layer obtained after step 3) preferably has a coating weight in a range of from 0.5 to 500 mg/m², more preferably of from 1 to 400 mg/m², even more preferably of from 2 to 350 mg/m², determined in each case as tracer element(s) such as Ti, Zr and/or Si via XRF measurements.

11. The method according to one or more of the preceding claims, characterized in that if further comprises at least one cleaning step, which is performed prior to step 1), wherein the at least one metallic surface of the at least one substrate is contacted at least in portion with at least one cleaning composition, wherein the cleaning composition is different from or identical to the aqueous acidic composition AC used in step 1), and wherein the cleaning composition preferably comprises at least one surfactant.

12. The method according to one or more of the preceding claims, characterized in that the at least one metallic surface of the at least one substrate is made at least partially of at least one of steel, steel alloys, aluminum, aluminum alloys, zinc, zinc alloys including zinc magnesium alloys, and mixtures thereof, preferably is made at least partially of at least one of steel and steel alloys.

13. An aqueous acidic composition AC as defined in one or more of claims 1 to 9 comprising besides water at least one of zirconium, titanium, and hafnium cations as constituent(s) a1), and at least one lysine homopolymer and/or copolymer, which bears amide bonds, as constituent(s) a2), or a concentrate,

from which said aqueous acidic composition AC is at least obtainable by dilution with water and, optionally, further, by pH adjustment.

14. A use of at least one lysine homopolymer and/or copolymer as defined in one or more of claims 1 to 4, preferably when incorporated into an aqueous composition AC, preferably into an aqueous acidic composition AC according to claim 13, for providing or improving corrosion resistance of metallic surfaces of substrates and/or for providing or improving adhesion of metallic surfaces of substrates to one or more further coating layers present thereon.

15. A method of coating of at least one chemically pretreated metallic surface of at least one substrate, wherein chemical pretreatment of the at least one metallic surface has been carried out according to the method as defined in one or more of claims 1 to 12 or by making use of aqueous acidic composition AC according to claim 13, the method of coating further comprising at least step 4), namely

4) applying at least one coating material composition comprising at least one film-forming polymer and/or resin onto the optionally rinsed film obtained after step 1) or 2) as defined in claim 1 or onto the dried or cured, preferably dried, film, which in turn is obtainable from drying or curing the film obtainable from optional step 3) as defined in claim 1 or 10.

16. A substrate, which is a chemically pretreated substrate being obtainable by the method according to one or more of claims 1 to 12, or a coated substrate being obtainable by the method according to claim 15.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/066201

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C22/34
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)
C23C

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2006 152436 A (NIHON PARKERIZING) 15 June 2006 (2006-06-15) table 3 paragraph [0024] paragraphs [0029], [0056] paragraph [0065] - paragraph [0070] paragraph [0074] - paragraph [0079]	1-16
X	US 2010/068513 A1 (KIKUCHI IKUO [JP] ET AL) 18 March 2010 (2010-03-18) paragraph [0037] paragraph [0106] - paragraph [0109] table 5	1-16

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[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 September 2024	17/09/2024

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/066201

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 104 667 347 A (UNIV TIANJIN) 3 June 2015 (2015-06-03)	1-4,6, 9-11,13, 14,16
A	claims 1-2	5,7,8, 12,15

X	CN 110 004 438 A (PRETTY DISPLAY & DESIGN LTD) 12 July 2019 (2019-07-12) paragraph [0003] - paragraph [0017]	1,2,4-6, 9-16

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/066201

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2006152436 A	15-06-2006	JP 4969831 B2	04-07-2012
		JP 2006152436 A	15-06-2006
US 2010068513 A1	18-03-2010	CN 101563481 A	21-10-2009
		JP 5363117 B2	11-12-2013
		JP WO2008075553 A1	08-04-2010
		KR 20090089434 A	21-08-2009
		MY 153417 A	13-02-2015
		TW 200902760 A	16-01-2009
		US 2010068513 A1	18-03-2010
		WO 2008075553 A1	26-06-2008
CN 104667347 A	03-06-2015	NONE	
CN 110004438 A	12-07-2019	NONE	