

(19)



(11)

EP 3 916 127 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
01.12.2021 Bulletin 2021/48

(51) Int Cl.:
C23F 11/12 (2006.01) **C23F 11/10** (2006.01)
C23C 22/68 (2006.01)

(21) Application number: 20176457.8

(22) Date of filing: 26.05.2020

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(71) Applicants:

- **AloxX GmbH**
8002 Zürich (CH)
- **Otto-von-Guericke-Universität Magdeburg**
39106 Magdeburg (DE)

(72) Inventors:

- **HEYN, Andreas**
39106 Magdeburg (DE)
- **ZWINSELMAN, Jan Johan**
8002 Zürich (CH)

(74) Representative: **Kailuweit & Uhlemann**
Patentanwälte
Partnerschaft mbB
Bamberger Straße 49
01187 Dresden (DE)

Remarks:
Amended claims in accordance with Rule 137(2) EPC.

(54) **COMPOSITION AND METHOD FOR INHIBITION OF CORROSION OF METALS OR METAL ALLOYS**

(57) The present invention relates to a corrosion inhibition composition for metallic surfaces, a method for inhibition of corrosion of metallic surfaces using the cor-

rosion inhibition composition, a liquid and a solid formulation comprising the corrosion inhibition composition and their use.

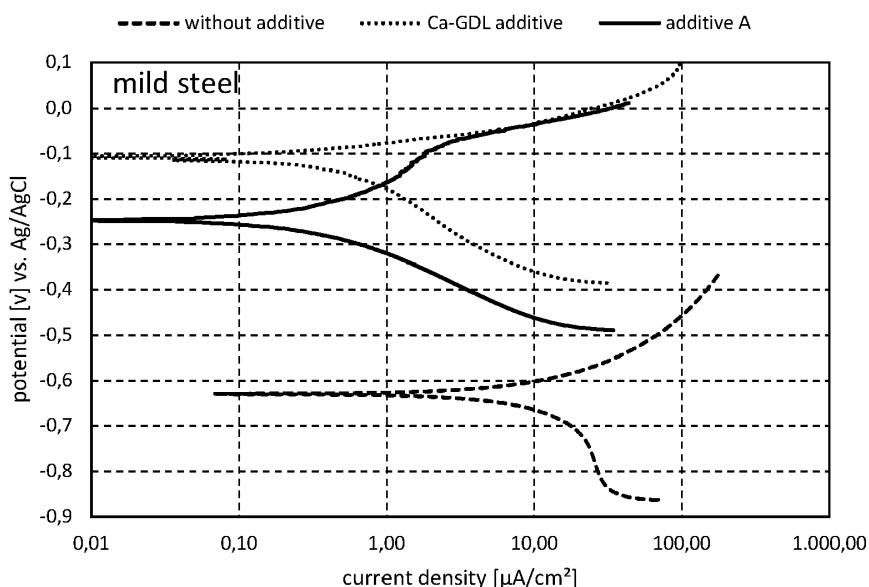


Fig. 1a

Description

[0001] The present invention relates to novel corrosion inhibitors consisting of biodegradable and environmentally friendly chemicals for the concurrent protection of a variety of metals and/or metallic surfaces.

[0002] The application of metals, such as iron, aluminum, copper and alloys of these metals, in aqueous systems and hence in the presence of water and oxygen constantly requires strong methods for sufficient corrosion inhibition. Conventional corrosion inhibitors are often based on more or less toxic chemicals, typically hazardous compounds (e.g. triazoles or reactive amines) exhibiting an enormous problem in safety and environmentally friendly application, which leads to an increased demand for biodegradable, non-toxic and generally recognized as safe (GRAS) chemicals as novel corrosion inhibitors. This demand is increased by the "European Green Deal", a guideline for increasing the sustainability of the EU's economy, which comprises actions to boost the efficient use of resources by moving to a clean, circular economy and restore biodiversity and cut pollution by 2050. In particular, the EU plans to reach this goal by investing in environmentally friendly technologies.

[0003] In order to replace hazardous compounds a certain number of corrosion inhibitors have been published in the past years, yet often complex mixtures of different inhibiting compounds have been proposed. Most common are mixtures of silicates, phosphates, gluconates and molybdates.

[0004] CN 104403523 A describes a mining spray rod with high corrosion resistance formed by a layer composed of polyester resin, quaternary ammonium salt, an amine, sodium gluconate and aluminum hydroxide.

[0005] In CN 102642934 A, a corrosion inhibitor is used for protection of carbon steel in normal running processes, consisting of tungstate or molybdate, alkali or alkali earth metal gluconate, rare earth salt, zinc salt and stabilizer.

[0006] Another method for inhibiting corrosion of steel is described by US 2002/0195590 A1, where a mixture of sodium sebacate, potassium sebacate, dicyclohexylammonium nitrite, sodium nitrite, zinc gluconate, sodium gluconate, and calcium nitrite is used to prevent corrosion of steel reinforcements embedded in concrete.

[0007] Disadvantageously the above described formulations often contain at least one critical chemical that lowers the environmentally friendliness.

[0008] Organic and/or inorganic zinc salts act as cathodic inhibitors, by reducing the corrosion rate due to retarding cathodic reactions. Such cathodic inhibitors cause formation of insoluble compounds precipitating on the cathodic sites in form of a barrier film. The effective cathode area is one of the factors of galvanic corrosion, therefore its reduction results in decrease of corrosion rate.

[0009] However, some organic and/or inorganic zinc salts, e.g. zinc sulfate, are known as non-stable substances in alkaline aqueous media, since formation of zinc hydroxide will occur. Zinc hydroxide itself is water insoluble and will precipitate from the solution.

[0010] Zinc salts, especially organic and/or inorganic zinc salts, can be kept dissolved in aqueous solutions by adding a chelating agent to the solution. Amino acids and their salts, especially their metal salts, EDTA or various phosphorus-containing chemicals are well known chelating agents, used in compositions for corrosion inhibition of carbon steel.

[0011] Again, these chelating agents often exhibit environmentally unfriendly or even hazardous effects on organisms.

[0012] Other studies show that the efficiency of corrosion inhibition of sodium gluconate can be enhanced by combining the gluconate with inorganic Zn^{2+} salts.

[0013] Manjula et al. firstly described a synergistic effect of sodium gluconate and inorganic Zn^{2+} salts in a DTPMP system for the corrosion inhibition of carbon steel immersed in an aqueous solution containing chloride ions (P. Manjula et al. (2009) E-Journal of Chemistry 6 (3), 887-897).

[0014] Furthermore, Almaraj et al. showed that the performance of sodium gluconate as corrosion inhibitor of carbon steel in an aqueous system, containing 60 ppm Cl^- is enhanced when adding inorganic Zn^{2+} ions, e.g. zinc sulphate (A. J. Amalraj et al. (2001) Anti-Corrosion Methods and Materials 48 (6), 371-375). In this publication, an optimized system is proposed, showing good inhibition effects, when steel is immersed into an aqueous solution comprising 150 ppm of sodium gluconate and 50 ppm of Zn^{2+} ions. The inhibition efficiency proved best for a mass ratio of sodium gluconate and Zn^{2+} ions in the range of 1:1 to 3:1.

[0015] Furthermore, organic zinc salts, such as zinc gluconate, show promising effects on corrosion inhibition of carbon steel.

[0016] Alar et al. evaluated the effect of zinc gluconate on the corrosion inhibition of carbon steel in various water types and showed that low concentrations of zinc gluconate in the range of 0.1 to 3 g/l deliver substantial corrosion inhibition in different aqueous systems (F. Ivisic et al. (2013) Materialwissenschaft und Werkstofftechnik 44 (4), 319-329).

[0017] Sanni et al. reported about the corrosion inhibition of aluminum alloy in 0.5M H_2SO_4 solution in the presence of 0,5 to 2% w/v zinc gluconate and show an increasing inhibition efficiency for concentrations of zinc gluconate up to 1.5% w/v, which decreases again at higher concentrations (O. Sanni et al. (2013) Polish Journal of Chemical Technology 15 (4), 60-64).

[0018] The inhibiting effect on corrosion of copper and zinc in natural seawater has been studied by Wrubl et al. (C. Wrubl et al. (1983) Br. Corros. J. 18 (3), 142-147). The inhibition efficiency of zinc gluconate on copper was shown to

reach its maximum (60%) at a zinc gluconate concentration of $4 \cdot 10^{-3}$ mol/l and then drops rapidly with increasing concentration of zinc gluconate. For the corrosion inhibition of zinc similar results have been obtained.

[0019] Another promising agent for corrosion protection of carbon steel, zinc, tin and copper is represented by aminoacetic acid, also known as glycine. Raja et al. describe glycine as an effective corrosion inhibitor in acidic, neutral or decalcified carbonated medium by forming a protective film on these materials (A. S. Raja et al. (2014) IJIRSET 3 (4), 11455-11467). Glycine can function as anodic, cathodic or mixed type of inhibitor, depending on the nature of metal and the corrosive environment.

[0020] Thangakani et al. report on the usage of glycine as an efficient corrosion inhibiting amino acid, for the protection of carbon steel (J. A. Thangakani et al. (2014) Int. J. Nano. Corr. Sci. Eng. 1 (1), 50-62). The addition of inorganic Zn^{2+} ions in form of zinc sulfate enhances the corrosion inhibition efficiency (IE), which is described as a synergistic effect between glycine and Zn^{2+} .

[0021] The same effect is described by Raja et al., who reported on the usage of a formulation consisting of 250 ppm of glycine and 50 ppm of Zn^{2+} ions coming from zinc sulfate (S. A. Raja et al. (2013) Eur. Chem. Bull. 2 (3), 130-136). This formulation offers a good IE of 82% for carbon steel.

[0022] There are also reports on other organic metal salts in corrosion inhibiting compositions.

[0023] US 3 589 859 A describes the addition of small amounts of gluconate salts to cooling water systems for the inhibition of oxidative corrosion of carbon steel. Furthermore, US 3 589 859 A discloses the combination of gluconate salts with other corrosion inhibitors, such as benzoate salts and salicylate salts, results in synergistic improvement of such inhibition. The corrosion inhibition efficiency also increases with increasing temperatures.

[0024] US 2014/0241939 A1 discloses a corrosion inhibition composition for cooling water applications made of carbon steel, comprising a carboxylic acid and its water-soluble salts in combination with Zn^{2+} ions. A water-soluble zinc salt, such as zinc chloride, zinc sulphate or zinc oxide, is added to the cooling water system, in combination with a carboxylic acid, such as gluconic acid or saccharinic acid. The concentration of the carboxylic acid in the cooling water is in the range 30 to 300 ppm. Carboxylic acids with more than two carboxyl groups are not suitable.

[0025] AU 1 434 804 A discloses an aqueous corrosion inhibition composition for steel substrates, comprising a water-soluble salt of a hydroxy carboxylic acid, e.g. gluconate, and a water-soluble zinc salt of another acid. The zinc salt can be selected from chloride, sulphate, acetate or fluoride.

[0026] GB 1 455 247 A discloses a composition for inhibition of corrosion comprising an amino- or hydroxyalkyl phosphonic acid, a water-soluble zinc salt, such as zinc chloride, and at least one carboxylic acid, selected from heptagluconic acid, gluconic acid, aliphatic amino carboxylic acids, aromatic carboxylic acids or their water-soluble salts. It is not possible to mix all the components together to achieve a stable composition. Hence, first the zinc salt and the phosphonic acid are mixed and the carboxylic acid is added right before the application.

[0027] US 5 130 052 A discloses a method for protection from corrosion for metallic surfaces, selected from Fe, Cu, Al or their alloys, in aqueous systems. For this, a water-soluble rare earth chelating complex is added to the aqueous system. This complex is initially built from an organic chelate building complex and a rare earth metal. The complex can be combined with an organic zinc-chelating compound, made from zinc cations and organic acids, such as sulfonic acids, citric acid or tetra acetic acid.

[0028] US 4 512 915 A discloses a corrosion inhibition composition for metallic substrates, selected from Fe, Ni, Cu, Al or their alloys, in aqueous systems. The composition comprises zinc gluconate or glucoheptonate and at least one inorganic polyphosphate, e.g. alkali metal hexamethaphosphate or -tripolyphosphate. The optimized system comprises zinc gluconate and sodium hexametaphosphate 1:1 in a total concentration of 530 ppm in water.

[0029] Touir et al. published a study about the effect of sodium gluconate anion on the corrosion and scale inhibition of ordinary steel in simulated cooling water and postulated that an increase of the sodium gluconate concentration leads to an increase of the corrosion potential towards the positive direction (R. Touir et al. (2008) Corrosion Science 50 (6), 1530-1537).

[0030] Still the above-described formulations suffer from not being applicable to a variety of metals but to selected metals only. More disadvantageously only a limited range of concentrations is suitable to show inhibiting effects.

[0031] Especially the protection of cast iron is challenging, since most inhibitors that show effective protection of mild steel, do not inhibit corrosion of cast iron (see for example: Florence et al. (2005) Indian Journal of Chemical Technology 12, 472-476).

[0032] In addition, an efficient inhibition of corrosion for cast iron and aluminum has concurrently not been published.

[0033] Therefore, it is an object of the present invention to provide an environmentally friendly, effective composition for the concurrent inhibition of corrosion of a variety of metals or metal alloys. Furthermore, it is an object of the present invention to provide a process for inhibiting concurrent corrosion of different metals, metal alloys or metal containing surfaces.

[0034] The present invention provides an environmentally friendly corrosion inhibition composition for metallic surfaces comprising at least one zinc carboxylate and calcium gluconate, wherein the mass ratio of the at least one zinc carboxylate and the calcium gluconate is in the range of 1:10 to 1:600.

[0035] The present invention also provides a method for inhibition of corrosion of metals, metal alloys or metal containing surfaces by applying this corrosion inhibition composition to the metal, metal alloy or metal containing surface by addition of the corrosion inhibition composition to a liquid medium, the metal, metal alloy or metal containing surface is exposed to or will be exposed to.

5 [0036] Fig. 1 a) - e) depicts corrosion current densities (i_{corr}) in artificial tap water (see ASTM D1384-05) containing either no additive or 5% (w/w) calcium gluconate additive (the additive consisting of 5% (w/w) Ca-GDL and 95% (w/w) water) or 5% (w/w) additive A (the additive consisting of 4% (w/w) calcium gluconate, 1% (w/w) magnesium gluconate, 0.08% (w/w) zinc acetate and 94.92% (w/w) water) for a) mild steel, b) cast iron, c) zinc, d) aluminum and e) copper.

10 [0037] In a first aspect the present invention provides an environmentally friendly corrosion inhibition composition for metallic surfaces comprising at least one zinc carboxylate and calcium gluconate, wherein the mass ratio of the at least one zinc carboxylate and the calcium gluconate is in the range of 1:10 to 1:600.

[0038] In preferred embodiments, all or at least one of the carboxylates are water-soluble and/or emulsifiable.

[0039] As mentioned above, zinc salts are known to act as cathodic corrosion inhibitors for certain metals only, e.g. only for mild steel. Furthermore, salts of carboxylic acids are known additives for the protection of metals from corrosion.

15 [0040] However, only certain concentrations lead to a desired effect and only specific metals can be protected. In some cases, aqueous solutions of the metal salts alone even show a higher corrosion rate on specific metals than pure water.

[0041] Surprisingly, metal salts of carboxylic acids show an increased corrosion inhibition efficiency not only for steel, but for a broad variety of metals or metal alloys concurrently, when mixed in a combination according to the invention.

20 [0042] According to the invention, the corrosion inhibition composition for metallic surfaces comprises at least one zinc carboxylate and calcium gluconate.

[0043] In terms of the invention, "at least one zinc carboxylate" means that the carboxylate anion of the zinc carboxylate may be of one structural kind or it might be a mixture of two or more different structural kinds of carboxylate anions.

[0044] In the following "carboxylate anion" includes one or more kinds of carboxylate anions.

25 [0045] In preferred embodiments, all or at least one of the carboxylates are water-soluble and/or emulsifiable.

[0046] In certain embodiments, the carboxylate anions of the zinc carboxylate are selected from the group comprising gluconate, bisglycinate, glycinate, citrate, acetate, nitrate, ascorbate, DL-hydrogenaspartate, L-hydrogenaspartate, malate and mixtures of these. In certain embodiments, the zinc carboxylate is zinc gluconate.

[0047] In certain embodiments, the carboxylates are water-soluble and/or water-emulsifiable.

30 [0048] In terms of the invention, "water-soluble" means that the carboxylate can be dissolved in water or aqueous solutions at acidic, neutral or basic pH value without precipitation, providing a clear solution.

[0049] In terms of the invention "water-emulsifiable" carboxylate means, that the salt can be kept in water or aqueous solutions at acidic, neutral or basic pH value by adding an emulsifying agent, without precipitation, providing a clear solution.

35 [0050] As stated in the prior art, a synergistic effect of Zn^{2+} ions of organic and/or inorganic sources on other metal salts, such as sodium gluconate, can be observed for a mass ratio of Zn^{2+} ions/ sodium gluconate in a very narrow range of mass ratio.

[0051] At higher mass ratios, the inhibition efficiency might even drop again.

40 [0052] Surprisingly, the range of possible concentrations of calcium gluconate within the liquid medium surrounding the metallic surface, increases, when combined with a zinc carboxylate.

[0053] According to the invention, the mass ratio of the at least one zinc carboxylate and the calcium gluconate is in the range of 1:10 to 1:600, preferably in the range of 1:50 to 1:100.

[0054] Surprisingly, a corrosion inhibition composition according to the present invention with said mass ratio shows constantly good results in corrosion inhibition for a broad variety of metals.

45 [0055] Surprisingly, the corrosion inhibition composition according to the invention allows a symbiosis of zinc carboxylates and calcium gluconate in an advantageous manner:

- a) On the one hand, zinc carboxylates, that are not soluble in water, will be kept in solution by an emulsifying effect of the calcium gluconate, at neutral and even at basic pH values.
- 50 b) On the other hand, the corrosion inhibiting effect of a carboxylate in aqueous solution, which is used to protect only very specific metal surfaces, can now be applied to a large variety of metal surfaces concurrently. Even a concurrent protection of aluminum and cast iron is given.

[0056] Magnesium carboxylates may enhance the advantageous effects.

55 [0057] In certain embodiments, the corrosion inhibition composition according to the invention additionally comprises at least one magnesium carboxylate.

[0058] In certain embodiments, the carboxylate anions of the magnesium carboxylate are selected from the group comprising gluconate, bisglycinate, glycinate, citrate, acetate, nitrate, ascorbate, DL-hydrogenaspartate, L-hydro-

naspartate, malate and mixtures of these.

[0059] In certain embodiments, the corrosion inhibition composition according to the invention comprises additionally a chelating agent. In terms of the invention, "chelating agents" are chemical compounds that react with metal ions to form a stable, water-soluble complex. They are also known as chelants, chelators or sequestering agents.

5 [0060] In certain embodiments, chelating agents have a ring-like centre, which forms at least two bonds with the metal ion allowing it to be excreted. Chelating agents are known in the art. In certain embodiments, the chelating agent is selected from metal salts.

10 [0061] To avoid turbid solutions of the corrosion inhibition composition a chelating agent can be added. Surprisingly, the addition of a chelating agent to the composition not only provides clear aqueous solutions of the composition. In some cases, the corrosion inhibition efficiency of the composition even increases.

[0062] In certain embodiments, the mass ratio of the at least one zinc carboxylate to the sum of calcium gluconate plus the chelating agent, preferably to the sum of all, magnesium and calcium carboxylates plus the chelating agent, is in the range of 1:5 to 1:200, preferably in the range of 1:10 to 1:100, more preferably in the range of 1:20 to 1:100.

15 [0063] In certain embodiments, the chelating agent is different from the zinc carboxylate and calcium gluconate, or in certain embodiments, different from the at least one zinc carboxylate and from calcium gluconate and from the at least one magnesium carboxylate in the corrosion inhibition composition according to the invention.

[0064] In further embodiments, the chelating agent is selected from amino acids or metal gluconates.

[0065] In the documents depicting the state of the art, the inhibition of corrosion using zinc salts or other metal salts showed satisfying results for a limited number of metals only.

20 [0066] Furthermore, most environmentally friendly corrosion inhibitors used in the state of the art effectuate ionization of copper in presence of other metal salts in aqueous solution. Advantageously, ionization of copper is prevented when using the corrosion inhibition composition according to the invention and in addition to it, a high protection of other metallic surfaces is provided.

25 [0067] Surprisingly, the corrosion inhibition composition according to the invention shows high corrosion inhibition efficiency for a wide range of metals and/or metallic surfaces concurrently.

[0068] In accordance to the invention, the term "metallic surface" comprises surfaces of metals and/or metal alloys, as well as of any other metal and/or metal alloy containing material.

30 [0069] In certain embodiments, the metal in the metallic surface is selected from the group comprising cast iron, copper, aluminum, cast aluminum, steel, mild steel, zinc, magnesium, cast magnesium, magnesium dichromate, tin, solder, titanium, brass and combinations thereof.

[0070] Additionally, the present invention comprises a method for inhibition of corrosion of metallic surfaces comprising the steps

35 a) Providing a corrosion inhibition composition comprising

- at least one zinc carboxylate and
- calcium gluconate,

40 wherein the mass ratio of the at least one zinc carboxylate and the calcium gluconate is in the range of 1:10 to 1:600, and

45 b) Addition of the corrosion inhibition composition to a liquid medium, wherein the metallic surface is exposed to the liquid medium or will be exposed to the liquid medium.

[0071] In a first step, a corrosion inhibition composition is provided. According to the invention the composition comprises

- at least one zinc carboxylate and
- calcium gluconate.

50 [0072] According to the invention, the mass ratio of the at least one zinc carboxylate and the calcium gluconate is in the range of 1:10 to 1:600, preferably in the range of 1:50 to 1:100.

[0073] A further explanation can be found in the paragraph describing the corrosion inhibition composition according to the invention.

55 [0074] In certain embodiments of the invention, the composition additionally comprises at least one magnesium carboxylate. Further embodiments of the corrosion inhibition composition can be found in the respective paragraph above.

[0075] According to the invention, in a second step b) the corrosion inhibition composition is added to the liquid medium, wherein the metallic surface is exposed to or contacted with the liquid medium or will be exposed to or contacted with the liquid medium.

[0076] In certain embodiments, the corrosion inhibition composition is part of a superordinate composition added to the liquid medium for various purposes, e.g. cleaning purposes or paint/coating purposes.

[0077] In certain embodiments, the liquid medium is an aqueous medium.

[0078] In certain embodiments, the liquid medium comprises a water-soluble organic and/or inorganic solvent.

5 [0079] In further embodiments, the fluid medium comprises water and an organic and/or inorganic solvent and at least one surface tension modifying additive selected from emulsifiers, surfactants and/or detergents. In embodiments, the liquid medium is a water/oil emulsion or an oil/water emulsion.

10 [0080] Advantageously, the corrosion inhibition composition according to the invention can be added to aqueous liquid media and organic and/or inorganic solvents containing emulsions. It can also be part of a solid composition, which can be added to a liquid medium for various purposes. More advantageously, the corrosion inhibition composition according to the invention is highly compatible with amines or alkaline formulations, which are often used in standard corrosion inhibition compositions.

15 [0081] This offers a broad field of application for the composition according to the invention. Examples for potential applications are:

- Hydraulic fluids (HF-A; HF-C),
- House-hold and/or institutional cleaners,
- Dishwashing tablets/powder/liquid,
- Chelating agent for aqueous systems,
- Paint and/or coating (liquid and/or powder coating),
- Deicing fluid for airfield runways,
- Deicing fluid aircrafts,
- Deicing fluids for roads and/or parking areas,
- Corrosion additive package for deicing fluids,
- Aluminum drawing and rolling process,
- Aluminum and magnesium tapping processes,
- Copper drawing and rolling processes,
- Lubricants,
- Automotive coolants,
- Metal working fluids,
- Coolant fluids for (sea-) containers and display cabinets in supermarkets,
- Solar fluids,
- Heating systems,
- Heat transfer fluids,
- Off-shore drilling fluids,
- Temporary corrosion inhibitor for copper, brass, ferrous, aluminum magnesium,
- Cast iron production,
- Cast aluminum production and
- Cast magnesium production.

40 [0082] In certain embodiments, the liquid medium, the metal will be exposed to, comprises amines or alkaline formulations.

[0083] In certain embodiments, the liquid medium and the corrosion inhibition composition or the superordinate composition are mixed thoroughly before exposing the metallic surface to the liquid medium.

45 [0084] The concentration of additives in the metal contacting medium often plays an important role for the efficiency of corrosion inhibition. Too low concentrations may not have a sufficient effect on corrosion inhibition, whereas other studies show that concentrations exceeding a certain value can lead to decreased inhibition effects.

[0085] As stated in the prior art, each metal or metal alloy often requires a defined corrosion inhibitor composition with defined dosages of each ingredient and defined concentrations of additives to achieve sufficient inhibition efficiency.

50 Additionally, prior art corrosion inhibitors often exhibit sufficient efficiency at very low concentrations in the metal contacting medium, e.g. water. This aspect strongly generates the problem of over-dosage, since smaller volumes or amounts of metal surrounding media (e.g. 10 to 20 liters of water in a dishwasher) require very little amounts of additives. Advantageously, the current invention allows a high variability in the total concentration of additives in the liquid medium the metallic surface is or will be exposed to.

55 [0086] In certain embodiments, the concentration of the corrosion inhibition composition in the liquid medium, with or without a superordinate composition, is in the range of 0.01% to 20% (w/w), more preferably in the range of 0.05% to 15% (w/w), most preferably in the range of 0.1% to 10% (w/w); to achieve sufficient corrosion inhibition to a large variety of metallic surfaces.

[0087] Corrosion inhibition compositions according to the invention were tested at different concentrations and different mass ratios of organic and/or inorganic zinc salts and metal salts for protection of surfaces of copper, aluminum, mild steel, zinc and cast iron and investigated optically. All metallic surfaces showed no corrosion but preserved their metallic gloss.

[0088] To evaluate the performance of additive formulations electrochemical measurements were conducted to obtain corrosion current densities (i_{corr}) in artificial tap water (see ASTM D1384-05) with and without corrosion inhibition compositions according to the invention. Specimen from different metals are immersed in the specific electrolytes for 1 hour. After that period, the specimen was continuously polarized with 1 mV/s from cathodic to anodic direction based on the open circuit potential. From the resulting current density-potential-plot i_{corr} was determined by using Tafel extrapolation of the cathodic and anodic branch of the curve (see ASTM G3-14 (Reapproved 2019): Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing). The higher i_{corr} , the higher the corrosion rate or the metal loss.

[0089] For an evaluation of the protection capabilities of an additive or inhibitor, the inhibition efficiency (IE) was calculated using formula 1

$$IE [\%] = 100 * (i_{corr1} - i_{corr2})/i_{corr1} \quad (1),$$

wherein i_{corr1} is the corrosion current density of the specific sample in the non-inhibited electrolyte and i_{corr2} the corrosion current density of the specific sample in the inhibited electrolyte.

[0090] Surprisingly, all investigated compositions showed increased corrosion inhibition efficiency to a broad variety of metals or metallic surfaces respectively, such as aluminum, mild steel, zinc, copper or even cast iron.

[0091] Advantageously, this effect opens the possibility for a wide range of applications such as addition of the corrosion inhibition composition to coolants, cleaning systems, deicing systems and/or lubrication solvents to prevent corrosion of the metallic surfaces, surrounded by a liquid medium.

[0092] Another object of the invention is a liquid formulation comprising a corrosion inhibition composition according to the invention and a liquid medium selected from water and/or an organic and/or inorganic solvent or a mixture thereof.

[0093] In certain embodiments, the concentration of the corrosion inhibition composition in the liquid medium is in the range of 0.01% to 50% (w/w), preferably in the range of 0.05% to 50% (w/w), more preferred in the range of 0.05% to 20% (w/w), regarding the total mass of the liquid formulation.

[0094] In embodiments, the liquid medium comprises water and at least one water-soluble organic solvent.

[0095] In certain embodiments, the liquid medium comprises water and at least one organic solvent and at least one surface tension modifying additive such as emulsifiers, surfactants and/or detergents.

[0096] Advantageously, the liquid formulation according to the invention can be added to a wide range of liquid media to protect metallic surfaces from corrosion at different temperatures and different concentrations.

[0097] Another object of the invention is a solid formulation comprising a composition according to the invention and at least one further component, wherein the at least one further component is selected from carrier materials, complexing agents, such as magnesium gluconate; softener and surfactants.

[0098] In certain embodiments, the solid formulation is selected from powder, suspension, grouted powder and particles. In embodiments, the concentration of the corrosion inhibition composition in the solid formulation is in the range of 0.05% to 99% (w/w), preferably in the range of 0.05% to 50% (w/w), more preferred in the range of 0.05% to 20% (w/w), regarding the total mass of the solid formulation.

[0099] Another object of the invention is the use of a corrosion inhibition composition according to the invention, a liquid formulation according to the invention or a solid formulation according to the invention for the protection of metals and/or metallic surfaces from corrosion.

[0100] In embodiments, the corrosion inhibition composition according to the invention, the liquid formulation according to the invention or the solid formulation according to the invention is used for the protection of metals and/or metallic surfaces from corrosion in liquids comprising water, e.g. in an aqueous medium.

[0101] Another object of the invention is the use of a corrosion inhibition composition according to the invention, a liquid and/or a solid formulation according to the invention for protection of metals and/or metallic surfaces from corrosion in

- Hydraulic fluids (HF-A; HF-C),
- House-hold and/or institutional cleaners,
- Dishwashing tablets/powder/liquid,
- Chelating agent for aqueous systems,
- Paint and/or coating (liquid and/or powder coating),
- Deicing fluid for airfield runways,
- Deicing fluid for aircrafts,

- Deicing fluids for roads and/or parking areas,
- Corrosion additive package for deicing fluids,
- Aluminum drawing and rolling processes,
- Aluminum and magnesium tapping processes,
- 5 • Copper drawing and rolling processes,
- Lubricants,
- Automotive coolants,
- Metal working fluids,
- Coolant fluids for (sea-) containers and display cabinets in supermarkets,
- 10 • Solar fluids,
- Heating systems,
- Heat transfer fluids,
- Off-shore drilling fluids
- Temporary corrosion inhibitor for copper, brass, ferrous, aluminum magnesium,
- 15 • Cast iron production,
- Cast aluminum production and/or
- Cast magnesium production.

[0102] Another object of the invention is the use of a corrosion inhibition composition, a liquid and/or a solid formulation according to the invention for protection of metals and/or metallic surfaces from corrosion in fluids containing amines or alkaline formulations.

[0103] In certain embodiments, the corrosion inhibition composition, the liquid and/or solid formulation according to the invention is added to the liquid, the metallic surface is or will be exposed to, in an amount that the concentration of the corrosion inhibition composition in the liquid is in the range of 0.01% to 20% (w/w), more preferably in the range of 0.05% to 15% (w/w), most preferably in the range of 0.1% to 10% (w/w).

[0104] In further embodiments, the recently described embodiments can be combined.

Figures and Examples

[0105] The present invention will now be further explained by the following non-limiting figures and examples.

[0106] **Fig. 1** shows corrosion current densities (i_{corr}) in artificial tap water (see ASTM D1384-05) containing either no additive or 5% (w/w) calcium gluconate additive (the additive consisting of 5% (w/w) Ca-GDL and 95% (w/w) water) or 5% (w/w) additive A (the additive consisting of 4% (w/w) calcium gluconate, 1% (w/w) magnesium gluconate, 0.08% (w/w) zinc acetate and 94.92% (w/w) water) for a) mild steel, b) cast iron, c) zinc, d) aluminum and e) copper.

Examples

[0107] Investigations on corrosion inhibition efficiency have been provided using the metal coupons according to Tab. 1.

40 Tab. 1 Specification and densities of metal coupons (UNS: Unified Numbering System for metals and/or alloys. It specifies exactly the composition of the metal in question).

UNS code	Trade name	Density (g/cm ³)
G10100	C1010 Mild Steel	7.87
C11000	CDA 110 ETP Copper	8.89
A91100	Al 1100 Aluminum	2.71
Z15001	Zinc	7.13
F12801	Grey Cast Iron Type G-2 CL40	6.97

Electrochemical measurements

General procedure

[0108] Electrochemical measurements are conducted to obtain corrosion current densities (i_{corr}) in artificial tap water [see ASTM D1384-05] with and without corrosion inhibition compositions. Specimen of different metals are immersed

in the specific electrolytes for 1 hour. After that period, the specimen is continuously polarized with 1 mV/s from cathodic to anodic direction based on the open circuit potential. From the resulting current density-potential-plot i_{corr} is determined by using Tafel extrapolation of the cathodic and anodic branch of the curve (see ASTM G3-14). The higher i_{corr} , the higher the corrosion rate or the metal loss.

5 [0109] For an evaluation of the protection capabilities of an additive or inhibitor, the inhibition efficiency (IE) is calculated using formula 1

$$IE [\%] = 100 * (i_{corr1} - i_{corr2})/i_{corr1} \quad (1),$$

10 wherein i_{corr1} is the corrosion current density of the specific sample in the non-inhibited electrolyte and i_{corr2} the corrosion current density of the specific sample in the inhibited electrolyte.

15 Electrolyte

15 [0110] For testing of one specific composition, the relevant composition or formulation is mixed together with the corrosive water (tap water) before the experiment to obtain a specific concentration. For each test, 200 ml of fresh solution is made and used.

20 Specimen

20 [0111] The tested metallic samples are commercially obtained coupons of mild steel (C1010), cast iron (GCL40), zinc, copper and aluminum (AL1100) (also see Tab. 1). Before the test, each specimen is ground with abrasive paper grit 600, rinsed and dried in air. The actual value of the exposed surface area in the corrosion tests is 3cm² and is used to calculate current densities from measured currents.

25 Electrochemical Equipment

30 [0112] For the performance testing, electrochemical equipment is used consisting of a glass vessel for the electrolyte, a counter electrode made of a platinum mesh and a KCl-saturated Ag/AgCl reference electrode with an electrode potential of $E = 197$ mV vs. standard hydrogen electrode (SHE). For conducting the polarization measurements, the potentiostat "Reference 1000" (Gamry) and the software "Gamry Frameworks" is used. For evaluation of the corrosion current density by Tafel extrapolation the software "Gamry Echem Analyst" is used.

35 Investigation of corrosion efficiency of Ca-GDL

40 [0113]

- a) Ca-GDL = (D,L)-calcium gluconate, analytical grade, Sigma Aldrich,
- b) Mg-CDL = (D,L)-magnesium gluconate, analytical grade, Sigma Aldrich,
- c) Zn-acetate = zinc acetate, analytical grade, Sigma Aldrich.

45 [0114] Comparative experiments are performed with all metal samples in a corrosive electrolyte for 1 h in

- i) Artificial tap water without additive,
- ii) Solution consisting of 95% (w/w) artificial tap water and 5% (w/w) Ca-GDL additive (the additive consisting of 5% (w/w) Ca-GDL and 95% (w/w) water)
- iii) Solution of 99.5% (w/w) artificial tap water and 5% (w/w) additive composition (formulation: 0.08% (w/w) Zn acetate, 1.0% (w/w) Mg-GDL, 4.0% (w/w) Ca-GDL).

50 [0115] The resulting current density-potential-plots are shown in **Fig. 1 (a)-(e)**. The resulting values for corrosion inhibition efficiency are shown in Tab. 2.

55 **Tab. 2** Corrosion current densities and inhibition efficiencies.

Experiment		Mild steel	Cast iron	Zinc	Aluminum	copper
(i)	i_{corr} [$\mu A/cm^2$] no additive	43	55.7	15.4	1.4	1.9

(continued)

Experiment		Mild steel	Cast iron	Zinc	Aluminum	copper
(ii)	i_{corr} [$\mu A/cm^2$] with Ca-GDL additive	0.3	23.8	8.8	4.1	1.4
	IE [%]	99.3	57.3	42.9	-192.9.9	26.3
(iii)	i_{corr} [$\mu A/cm^2$] with additive A	0.3	9.7	0.7	0.3	0.6
	IE [%]	99.3	82.6	95.5	78.6	78.4

[0116] The tap water (experiment (i)) shows high corrosion rates. Partial corrosion inhibition can be achieved by adding Ca-GDL (experiment (ii)), still zinc, copper and aluminum show strong corrosion. Only the corrosion inhibition composition according to the invention (experiment (iii)) provides high corrosion inhibition efficiency for all investigated metals at the same time.

Claims

1. Corrosion inhibition composition for metallic surfaces comprising

- at least one zinc carboxylate and
- calcium gluconate,

wherein the mass ratio of the at least one zinc carboxylate and the calcium gluconate is in the range of 1:10 to 1:600.

2. Corrosion inhibition composition according to claim 1, wherein the carboxylate anion in the zinc carboxylate is selected from the group comprising gluconate, bisglycinate, glycinate, citrate, acetate, nitrate, ascorbate, DL-hydrogenaspartate, L-hydrogenaspartate, malate and mixtures of these.

3. Corrosion inhibition composition according to claim 1 or 2 additionally comprising at least one magnesium carboxylate.

4. Corrosion inhibition composition according to any of the claims 1 to 3 additionally comprising a chelating agent.

5. Corrosion inhibition composition according to any of the claims 1 to 4, wherein the metal in the metallic surface is selected from the group comprising cast iron, copper, aluminum, cast aluminum, steel, mild steel, zinc, magnesium, cast magnesium, magnesium dichromate, tin, solder, titanium, brass and combinations thereof.

6. Method for inhibition of corrosion of metallic surfaces comprising the steps

a) Providing a corrosion inhibition composition comprising

- at least one zinc carboxylate and
- calcium gluconate,

wherein the mass ratio of the at least one zinc carboxylate and the calcium gluconate is in the range of 1:10 to 1:600, and

b) Addition of the corrosion inhibition composition to a liquid medium,

wherein the metallic surface is exposed to the liquid medium or will be exposed to the liquid medium.

7. Method according to claim 6, wherein the concentration of the corrosion inhibition composition in the liquid medium is in the range of 0.01% to 20% (w/w).

8. A liquid formulation comprising a corrosion inhibition composition according to any of the claims 1 to 5 and a liquid medium, selected from water, at least one organic solvent or a mixture thereof.

9. A liquid formulation according to claim 8, wherein the concentration of the corrosion inhibition composition is in the range of 0.01% to 50% (w/w) of the total liquid formulation.

10. A solid formulation comprising a corrosion inhibition composition according to any of the claims 1 to 5 and at least one further component,
 wherein the at least one further component is selected from carrier materials, complexing agents, softener and surfactants.

5

11. Use of a corrosion inhibition composition according to any of the claims 1 to 5 or a liquid formulation according to claim 8 or 9 or a solid formulation according to claim 10 for protection of metals and/or metallic surfaces from corrosion.

10

12. Use according to claim 11 for protection of metals and/or metallic surfaces from corrosion in liquids comprising water.

Amended claims in accordance with Rule 137(2) EPC.

1. Use of a corrosion inhibition composition comprising

15

- at least one zinc carboxylate and
- calcium gluconate,

wherein the mass ratio of the at least one zinc carboxylate and the calcium gluconate is in the range of 1:10 to 1:600, for protection of metals and/or metallic surfaces from corrosion,

20

wherein metallic surfaces comprise surfaces of metals and/or metal alloys, and of any other metal and/or metal alloy containing material.

25

2. Use of a corrosion inhibition composition for protection of metals and/or metallic surfaces from corrosion according to claim 1, wherein the carboxylate anion in the zinc carboxylate is selected from the group comprising gluconate, bisglycinate, glycinate, citrate, acetate, ascorbate, DL-hydrogenaspartate, L-hydrogenaspartate, malate and mixtures of these.

30

3. Use of a corrosion inhibition composition for protection of metals and/or metallic surfaces from corrosion according to claim 1 or 2 additionally comprising at least one magnesium carboxylate.

4. Use of a corrosion inhibition composition for protection of metals and/or metallic surfaces from corrosion according to any of the claims 1 to 3 additionally comprising a chelating agent.

35

5. Use of a corrosion inhibition composition for protection of metals and/or metallic surfaces from corrosion according to any of the claims 1 to 4, wherein the metal in the metallic surface is selected from the group comprising cast iron, copper, aluminum, cast aluminum, steel, mild steel, zinc, magnesium, cast magnesium, tin, solder, titanium, brass and combinations thereof.

40

6. Use according to one of the claims 1 to 5 for protection of metals and/or metallic surfaces from corrosion in liquids comprising water.

7. Method for inhibition of corrosion of metals and/or metallic surfaces comprising the steps

a) Providing a corrosion inhibition composition comprising

45

- at least one zinc carboxylate and
- calcium gluconate,

wherein the mass ratio of the at least one zinc carboxylate and the calcium gluconate is in the range of 1:10 to 1:600, and

50

b) Addition of the corrosion inhibition composition to a liquid medium,

55

wherein the metal and/or metallic surface is exposed to the liquid medium or will be exposed to the liquid medium,

wherein metallic surfaces comprise surfaces of metals and/or metal alloys, and of any other metal and/or metal alloy containing material.

8. Method according to claim 6, wherein the concentration of the corrosion inhibition composition in the liquid medium

is in the range of 0.01% to 20% (w/w).

5 9. Use of a liquid formulation comprising a corrosion inhibition composition according to any of the claims 1 to 5 and a liquid medium, selected from water, at least one organic solvent or a mixture thereof for protection of metals and/or metallic surfaces from corrosion, wherein metallic surfaces comprise surfaces of metals and/or metal alloys, and of any other metal and/or metal alloy containing material.

10 10. Use of a liquid formulation for protection of metals and/or metallic surfaces from corrosion according to claim 8, wherein the concentration of the corrosion inhibition composition is in the range of 0.01% to 50% (w/w) of the total liquid formulation.

15 11. Use according to claim 9 and 10 for protection of metals and/or metallic surfaces from corrosion in liquids comprising water.

20 12. Use of a solid formulation comprising a corrosion inhibition composition according to any of the claims 1 to 5 and at least one further component,

25 wherein the at least one further component is selected from carrier materials, complexing agents, softener and surfactants,

20 for protection of metals and/or metallic surfaces from corrosion,

25 wherein metallic surfaces comprise surfaces of metals and/or metal alloys, and of any other metal and/or metal alloy containing material.

30 13. Use according to claim 12 for protection of metals and/or metallic surfaces from corrosion in liquids comprising water.

25

30

35

40

45

50

55

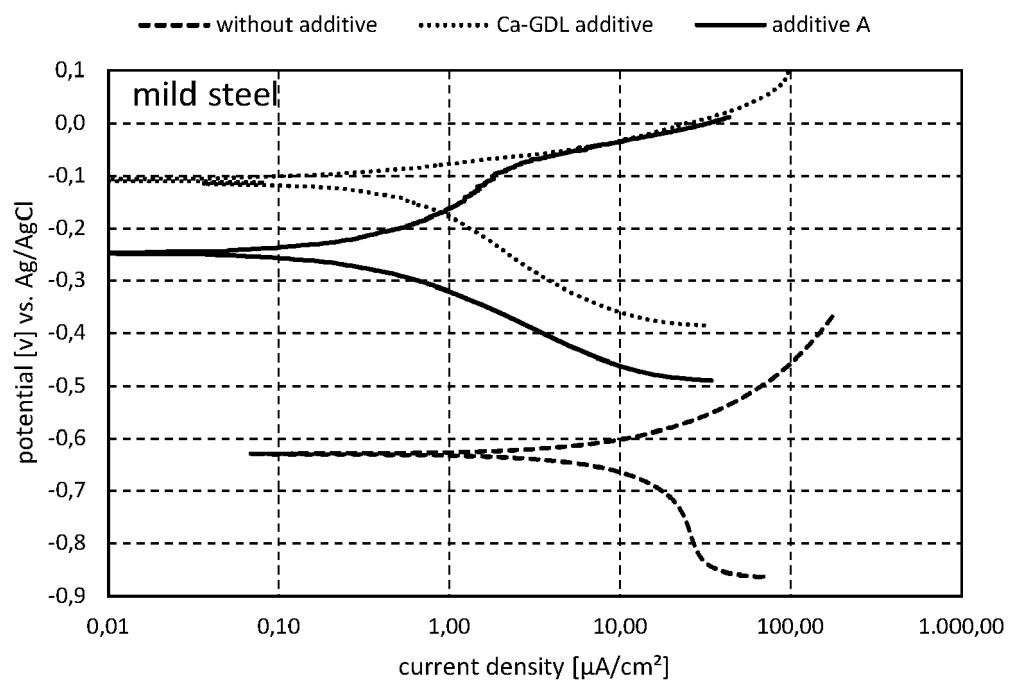


Fig. 1a

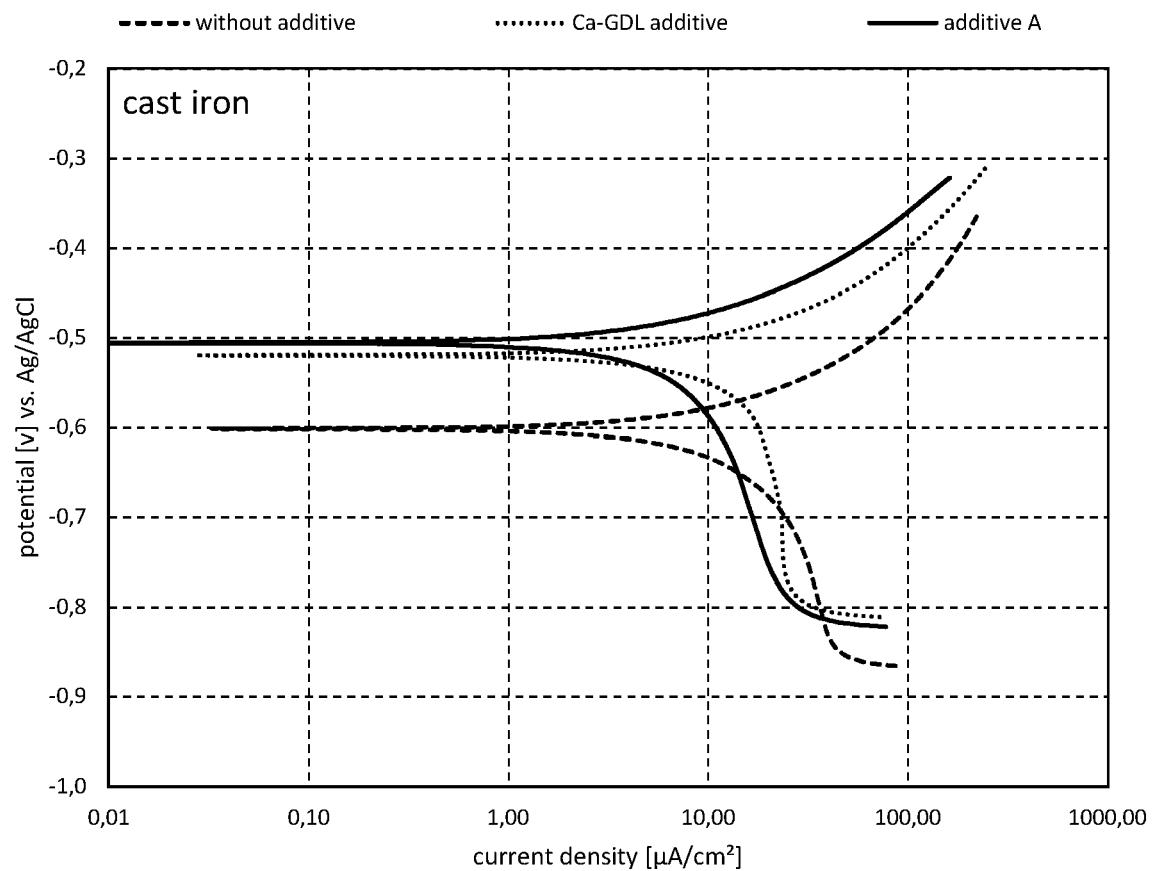


Fig. 1b

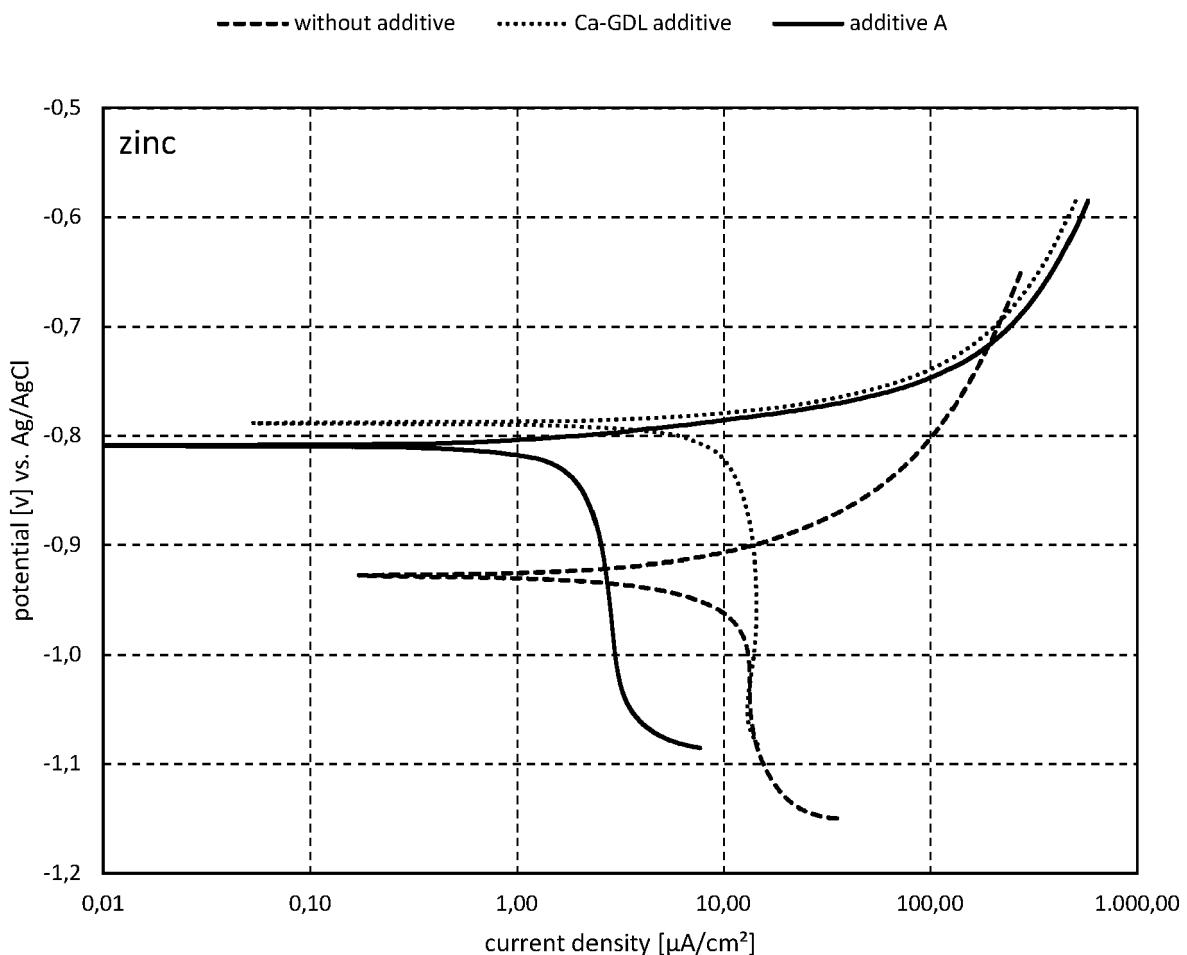


Fig. 1c

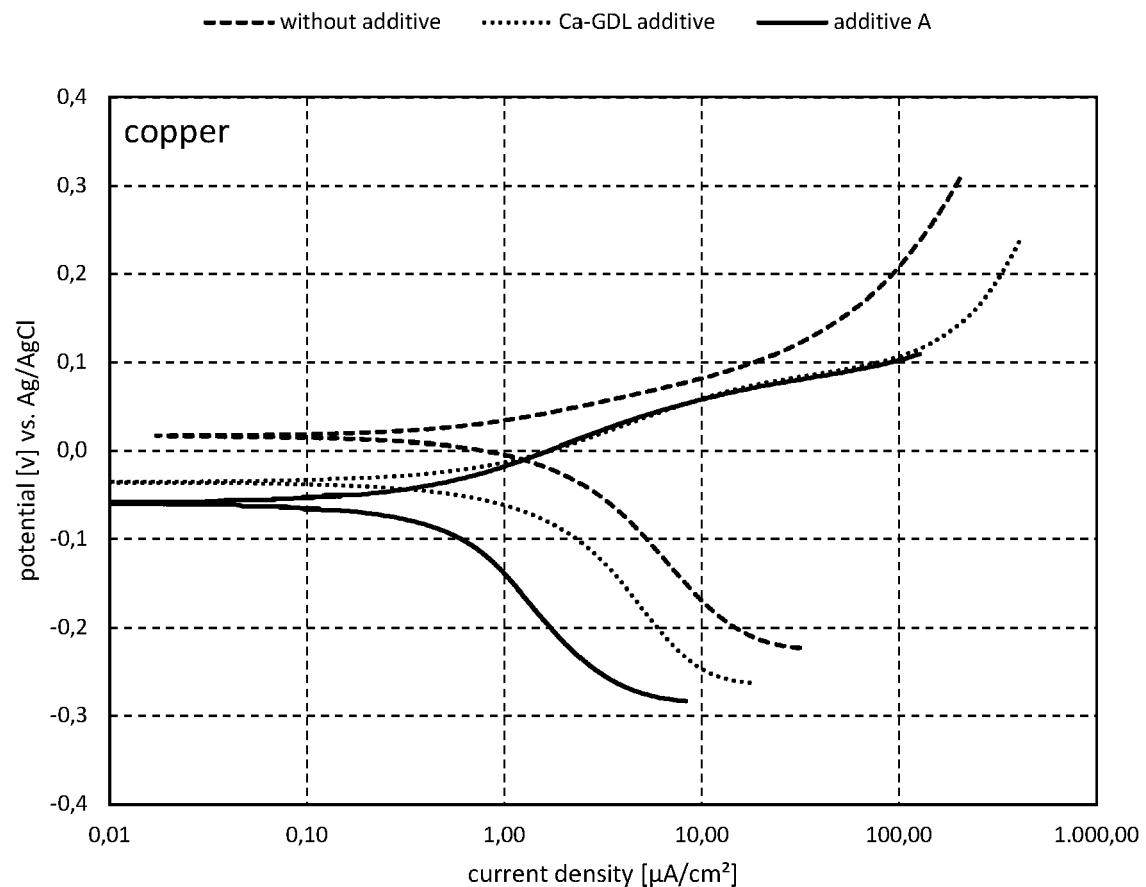


Fig. 1d

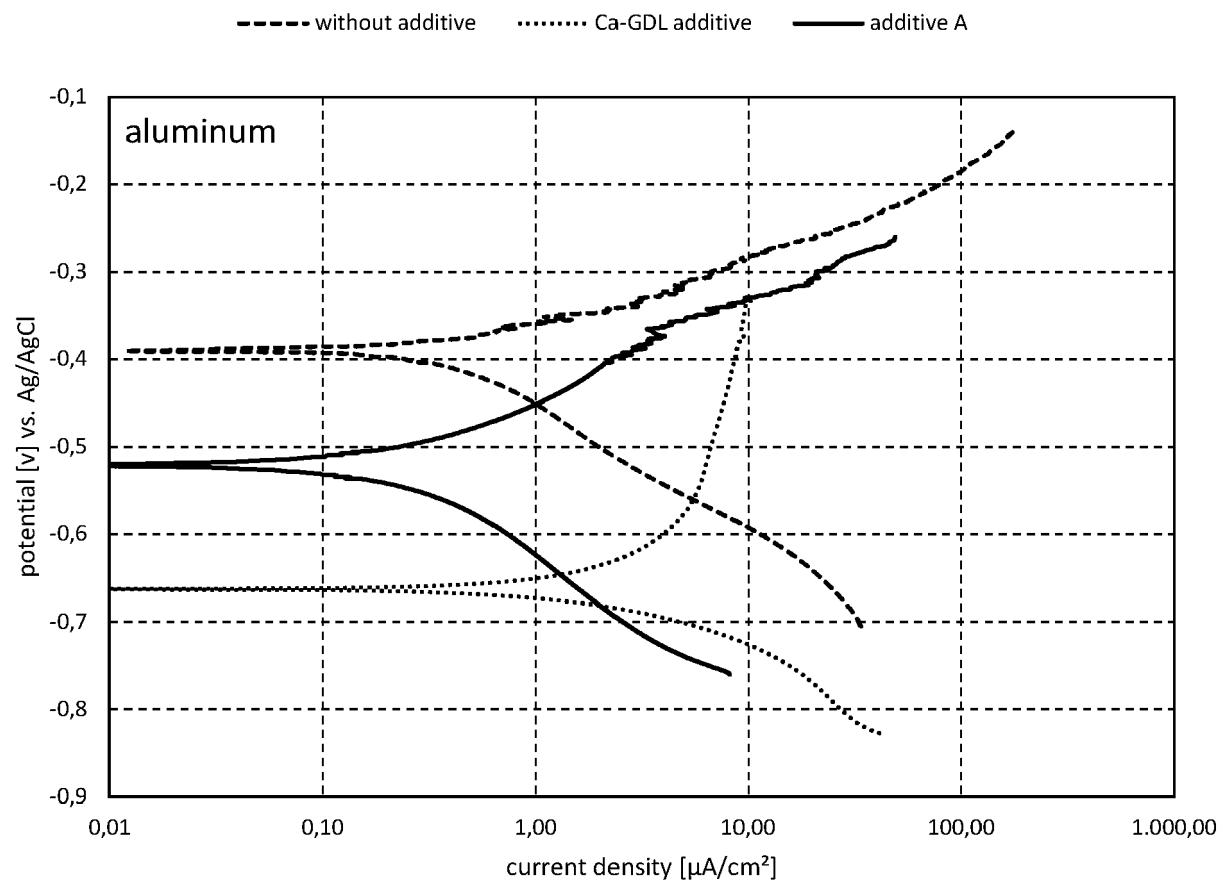


Fig. 1 e



EUROPEAN SEARCH REPORT

Application Number

EP 20 17 6457

5

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
10 X	CN 101 485 839 A (BEIJING TIANKE RENXIANG MEDICAL SCI TECH CO LTD [CN]) 22 July 2009 (2009-07-22) * abstract; claims 1-6; examples 1-3 *	1,2,8-10	INV. C23F11/12 C23F11/10 C23C22/68
15 X	CN 104 643 190 A (ZHOU GUOPING) 27 May 2015 (2015-05-27) * claims 1-4; example 1 *	1,2,8,9	
20 X	CN 108 420 025 A (NINGXIA ZHONGXI DATE IND CO LTD) 21 August 2018 (2018-08-21) * claim 8 *	1,2,8,9	
25 X	CN 101 869 142 A (BEIJING LONGEVITY VITA BIO TECH CO LTD) 27 October 2010 (2010-10-27) * abstract; claims 1-6; example 3 *	1,2,10	
30 A	MAHDAVIAN M ET AL: "Corrosion inhibition of mild steel in sodium chloride solution by some zinc complexes", CORROSION SCIENCE, OXFORD, GB, vol. 53, no. 4, 7 December 2010 (2010-12-07), pages 1194-1200, XP028153310, ISSN: 0010-938X, DOI: 10.1016/J.CORSCI.2010.12.013 [retrieved on 2010-12-17] * the whole document *	1-12	TECHNICAL FIELDS SEARCHED (IPC)
35 A	US 5 531 931 A (KOEFOED ROBERT S [US]) 2 July 1996 (1996-07-02) * the whole document *	1-12	C23F C23C
40			
45			
50 2	The present search report has been drawn up for all claims		
55	Place of search Munich	Date of completion of the search 6 October 2020	Examiner Handrea-Haller, M
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 20 17 6457

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

06-10-2020

10	Patent document cited in search report	Publication date	Patent family member(s)		Publication date
	CN 101485839 A	22-07-2009	NONE		
15	CN 104643190 A	27-05-2015	NONE		
	CN 108420025 A	21-08-2018	NONE		
20	CN 101869142 A	27-10-2010	NONE		
	US 5531931 A	02-07-1996	CA 2165759 A1	01-07-1996	
			US 5531931 A	02-07-1996	
25					
30					
35					
40					
45					
50					
55					

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- CN 104403523 A [0004]
- CN 102642934 A [0005]
- US 20020195590 A1 [0006]
- US 3589859 A [0023]
- US 20140241939 A1 [0024]
- AU 1434804 A [0025]
- GB 1455247 A [0026]
- US 5130052 A [0027]
- US 4512915 A [0028]

Non-patent literature cited in the description

- P. MANJULA et al. *E-Journal of Chemistry*, 2009, vol. 6 (3), 887-897 [0013]
- A. J. AMALRAJ et al. *Anti-Corrosion Methods and Materials*, 2001, vol. 48 (6), 371-375 [0014]
- F. IVUSIC et al. *Materialwissenschaft und Werkstofftechnik*, 2013, vol. 44 (4), 319-329 [0016]
- O.SANNI et al. *Polish Journal of Chemical Technology*, 2013, vol. 15 (4), 60-64 [0017]
- C. WRUBL et al. *Br. Corros. J.*, 1983, vol. 18 (3), 142-147 [0018]
- A. S. RAJA et al. *IJIRSET*, 2014, vol. 3 (4), 11455-11467 [0019]
- J. A. THANGAKANI et al. *Int. J. Nano. Corr. Sci. Eng.*, 2014, vol. 1 (1), 50-62 [0020]
- S. A. RAJA et al. *Eur. Chem. Bull.*, 2013, vol. 2 (3), 130-136 [0021]
- R. TOUIR et al. *Corrosion Science*, 2008, vol. 50 (6), 1530-1537 [0029]
- FLORENCE et al. *Indian Journal of Chemical Technology*, 2005, vol. 12, 472-476 [0031]