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(54) Title: USE OF A COMPOSITION FOR INHIBITION OF CORROSION OF METALS OR METAL ALLOYS AND METHOD FOR INHIBITION OF CORROSION OF METALS OR METAL ALLOYS

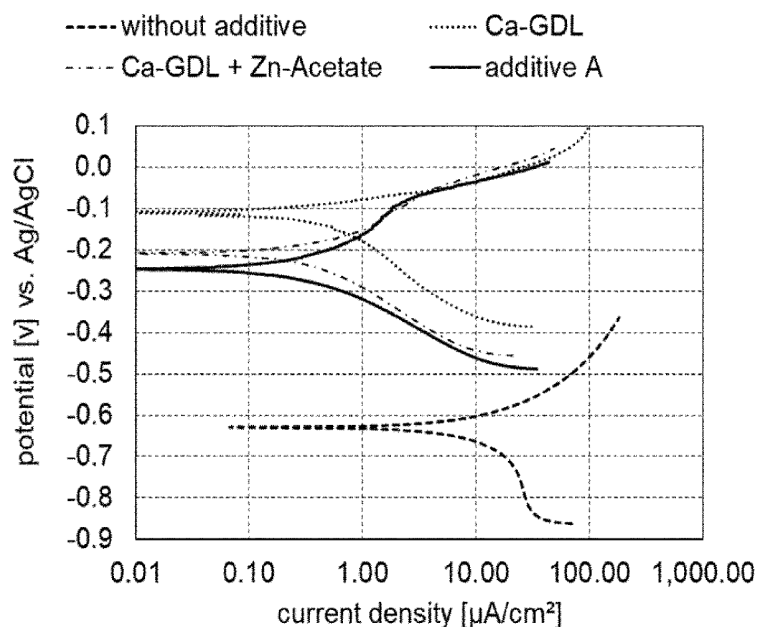


Fig. 1a

(57) Abstract: The present invention relates to the use of a corrosion inhibition composition for protection of metals and/or metallic surfaces from corrosion and a method for inhibition of corrosion of metallic surfaces using the corrosion inhibition composition.

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Use of a composition for inhibition of corrosion of metals or metal alloys and method for inhibition of corrosion of metals or metal alloys

The present invention relates to the use of a corrosion inhibition composition comprising biodegradable and environmentally friendly chemicals for the concurrent protection of a variety of metals and/or metallic surfaces.

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, restore biodiversity and cut pollution by 2050. In particular, the EU plans to reach this goal by investing in environmentally friendly technologies.

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.

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.

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.

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.

Disadvantageously the above described formulations often contain at least one critical chemical that lowers the environmental friendliness.

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.

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.

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.

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

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

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).

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.

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

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. Ivušić et al. (2013) *Materialwissenschaft und Werkstofftechnik* 44 (4), 319–329).

Sanni et al. reported about the corrosion inhibition of aluminum alloy in 0.5 M H₂SO₄ 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).

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.

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) *IJRSET* 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.

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 Zn²⁺ ions in form of zinc sulfate enhances the corrosion inhibition efficiency (IE), which is described as a synergistic effect between glycine and Zn²⁺.

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 Zn²⁺ 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.

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

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.

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.

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.

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.

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.

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.

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).

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.

CN 101 485 839 A discloses a Chinese medicine preparation for the prevention and treatment of infantile malnutrition comprising 200 to 400 weight portion Rhizoma Atractylodis Macrocephalae (stir-fry), 100 to 300 weight portions Fructus Crataegis, 100 to 300 weight portion Fructus Hordei Germinatus (stir-fry), 100 to 300 weight portions Fructus Colocasiae Esculentae, 10 to 80 weight portion Calcium, formed from a raw material like calcium gluconate, 1 to 8 weight portion ferrum, 1 to 8 weight portion Zinc, formed from a raw material like zinc acetate, zinc carbonate, zinc gluconate and zinc lactate, and 0.09 to 0.3 weight portion vitamin A, and a method for the preparation.

CN 104 643 190 A describes a liver-protection beverage comprising following weight parts in every 10000 parts of finished beverage: root of kudzu vine 20 to 1000, Semen Hoveniae (Fructus Hoveniae) 20 to 1000, mung bean 20 to 1000, mulberry fruit 20 to 1000, vitamin C 0.1 to 3, Cobastab1 0.01 to 0.05, Cobastab2 0.01 to 0.05, edible calcium salt 1 to 30, formed from one or more raw materials selected calcium lactate, whey calcium, calcium gluconate, threonic acid or calcium acetate; edible zinc salt 0.01 to 0.1, formed from one or more raw materials selected from zinc lactate, zinc gluconate, zinc sulfate or zinc acetate; chlorophyll copper sodium 0.02 to 0.5, flavoring 1 to 500, and water, as well as a method for making it.

CN 108 420 025 A discloses a composite color protection liquid composed of 3 to 3.5 mg/L zinc gluconate, 40 to 50 mg/L zinc lactate, 260 to 300 mg/L sodium hydrogen carbonate, 260 to 300 mg/L sodium sulfite, and 200 to 250 mg/L zinc acetate.

CN 101 869 142 A describes a method for the preparation of food additives, comprising a composite mineral matter, selected from among others zinc lactate, zinc gluconate, zinc acetate and calcium gluconate.

Mahdavian et al. describe a corrosion inhibition of mild steel in 3.5% sodium chloride solution by zinc complexes, in particular zinc acetate, zinc acetylacetonate or zinc gluconate (Mahdavian (2010) *Corrosion Science* 53, 1194-1200). Furthermore, Mahdavian et al. describe that sodium, zinc and calcium salts of gluconic acid could provide an effective corrosion inhibition for the mild steel immersed in near neutral media.

US 5 531 931 A discloses corrosion inhibition salt deicers comprising a deicing salt as the major component and an inhibitor system comprising either a water-soluble rare earth salt or a water-soluble organic acid salt selected from the group consisting of gluconate salts, ascorbate salts, tartrate salts, and saccharate salts, and preferred cations for the water-soluble organic acid salts, in particular alkali metal cations such as sodium and potassium, alkaline earth cations such as magnesium and calcium, and transition metal cations such as zinc, iron, and the like.

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).

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

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.

The present invention provides the use of an environmentally friendly 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, for protection of metals and/or metallic surfaces from corrosion.

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

Fig. 1 a) – e) depicts corrosion current densities (i_{corr}) in artificial tap water (see ASTM D1384-05) containing either i) no additive or ii) 5% (w/w) calcium gluconate additive (the additive consisting of 5% (w/w) Ca-GDL and 95% (w/w) water) or iii) 5% (w/w) calcium gluconate and zinc acetate additive (the additive consisting of 5% (w/w) Ca-GDL, 0.08% (w/w) zinc acetate and 94,92 % (w/w) water) or iv) 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.

In a first aspect the present invention provides an environmentally friendly corrosion inhibition composition for inhibition of corrosion of metals and/or 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.

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

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.

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.

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

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

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.

In the following “carboxylate anion” includes one or more kinds of carboxylate anions.

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

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

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

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.

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.

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.

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

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

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.

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.

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.
- 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.

Magnesium carboxylates may enhance the advantageous effects.

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

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

In embodiments, the corrosion inhibition composition for metallic surfaces consists of at least one zinc carboxylate, calcium gluconate and optionally at least one magnesium carboxylate, 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.

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.

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.

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.

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.

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.

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

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. 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.

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.

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.

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, tin, solder, titanium, brass and combinations thereof.

Additionally, the present invention comprises a method for inhibition of corrosion of metals and/or 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 metal and/or metallic surface is exposed to the liquid medium or will be exposed to the liquid medium.

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.

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.

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

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.

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

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.

In certain embodiments, the liquid medium is an aqueous medium.

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

In further embodiments, the liquid 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.

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.

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.

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

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

The concentration of additives in the metal contacting liquid 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.

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. 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.

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.

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.

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.

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

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

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.

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.

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 metal and/or metallic surfaces, surrounded by a liquid medium.

In embodiments, the corrosion inhibition composition is a liquid formulation further comprising a liquid medium selected from water and/or an organic and/or inorganic solvent or a mixture thereof.

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.

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

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.

Advantageously, the liquid formulation can be added to a wide range of liquid media to protect metals and/or metallic surfaces from corrosion at different temperatures and different concentrations.

In further embodiments, the corrosion inhibition composition is a solid formulation further comprising 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.

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.

According to the invention, the corrosion inhibition composition is used for the protection of metals and/or metallic surfaces from corrosion.

In embodiments, the corrosion inhibition composition is used for the protection of metals and/or metallic surfaces from corrosion in liquids comprising water, e.g. in an aqueous medium.

In embodiments, the corrosion inhibition composition is used 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,
- 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/or
- Cast magnesium production.

In embodiments, the corrosion inhibition composition is used for protection of metals and/or metallic surfaces from corrosion in fluids containing amines or alkaline formulations.

In certain embodiments, the corrosion inhibition composition 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).

In further embodiments, the recently described embodiments can be combined.

Figures and Examples

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

Fig. 1 shows corrosion current densities (i_{corr}) in artificial tap water (see ASTM D1384-05) containing either i) no additive or ii) 5% (w/w) calcium gluconate additive (the additive consisting of 5% (w/w) Ca-GDL and 95% (w/w) water) or iii) 5% (w/w) calcium gluconate and zinc acetate additive (the additive consisting of 5% (w/w) Ca-GDL, 0.08% (w/w) zinc acetate and 94.92 % (w/w) water) or iv) 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

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

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

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.

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

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

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.

Electrolyte

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.

Specimen

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 3 cm² and is used to calculate current densities from measured currents.

Electrochemical Equipment

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.

Investigation of corrosion efficiency of Ca-GDL

- 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.

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 consisting of 95% (w/w) artificial tap water and 5% (w/w) Ca-GDL and zinc acetate additive (the additive consisting of 5% (w/w) Ca-GDL, 0.08% (w/w) zinc acetate and 94,92 % (w/w) water)
- iv) 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).

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.

Tab. 2 Corrosion current densities and inhibition efficiencies.

Experiment	Mild steel	Cast iron	Zinc	Aluminum	copper

(i)	i_{corr} [$\mu\text{A}/\text{cm}^2$] no additive	43	55.7	15.4	1.4	1.9
(ii)	i_{corr} [$\mu\text{A}/\text{cm}^2$] 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} [$\mu\text{A}/\text{cm}^2$] with additive A	0.4	2.6	0.9	0.4	0.4
	IE [%]	99.1	95.3	94.2	71.4	78.9
(iv)	i_{corr} [$\mu\text{A}/\text{cm}^2$] with additive A	0.3	9.7	0.7	0.3	0.6
	IE [%]	99.3	82.6	95.5	78.6	68.4

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) and (iv)) provides high corrosion inhibition efficiency for all investigated metals at the same time.

Tab. 3 Corrosion current densities and inhibition efficiencies of the metal samples in the corrosive electrolyte iv) for 1 h and 8 weeks.

Experiment		Mild steel	Cast iron		Zinc	Aluminum	copper
1 h	i_{corr} [$\mu\text{A}/\text{cm}^2$] with additive A	0.3	9.7		0.7	0.3	0.6
	IE [%]	99.3	82.6		95.5	78.6	68.4
8 weeks	i_{corr} [$\mu\text{A}/\text{cm}^2$] with additive A	0.4	3.9		2.1	0.12	0.6
	IE [%]	99.1	93.0		86.4	91.4	68.4

The corrosion inhibition composition according to the invention (experiment (iv)) provides even after 8 weeks a high corrosion inhibition efficiency for all investigated metals (see **Tab. 3**).

Claims

1. Use of 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,
for protection of metals and/or metallic surfaces from corrosion.
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.
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.
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.
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. Use according to one of the claims 1 to 6, wherein the corrosion inhibition composition is a liquid formulation further comprising a liquid medium, selected from water, at least one organic solvent or a mixture thereof.

8. Use according to claim 7, wherein the concentration of the corrosion inhibition composition is in the range of 0.01% to 50% (w/w) of the total liquid formulation.
9. Use according to one of the claims 1 to 6, wherein the corrosion inhibition composition is a solid formulation comprising the at least one further component, wherein the at least one further component is selected from carrier materials, complexing agents, softener and surfactants.
10. Method for inhibition of corrosion of metals and/or 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 metal and/or metallic surface is exposed to the liquid medium or will be exposed to the liquid medium.
11. Method according to claim 10, wherein the concentration of the corrosion inhibition composition in the liquid medium is in the range of 0.01% to 20% (w/w).
12. Method according to claim 10 or 11, 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.
13. Method according to one of the claims 10 to 12, wherein the corrosion inhibition composition additionally comprises at least one magnesium carboxylate.
14. Method according to one of the claims 10 to 13, wherein the corrosion inhibition composition additionally comprises a chelating agent.
15. Method according to one of the claims 10 to 14, wherein the metal and/or 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.

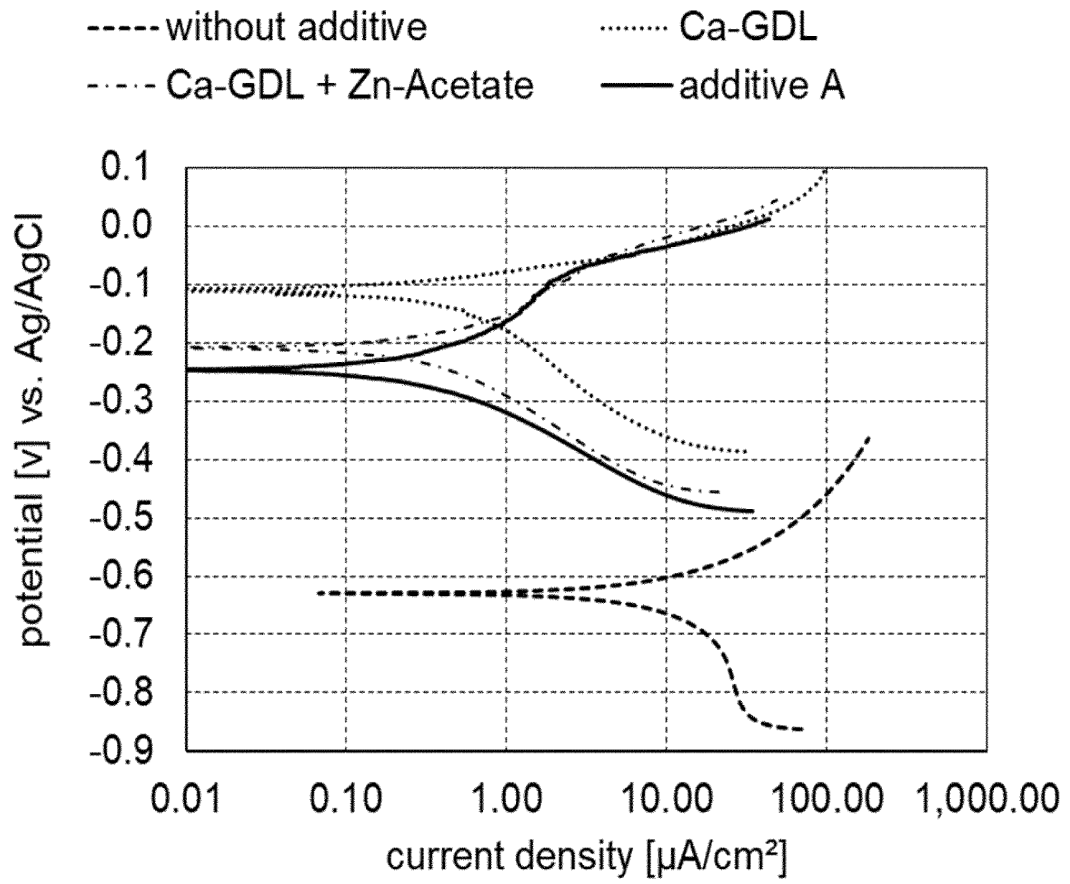


Fig. 1a

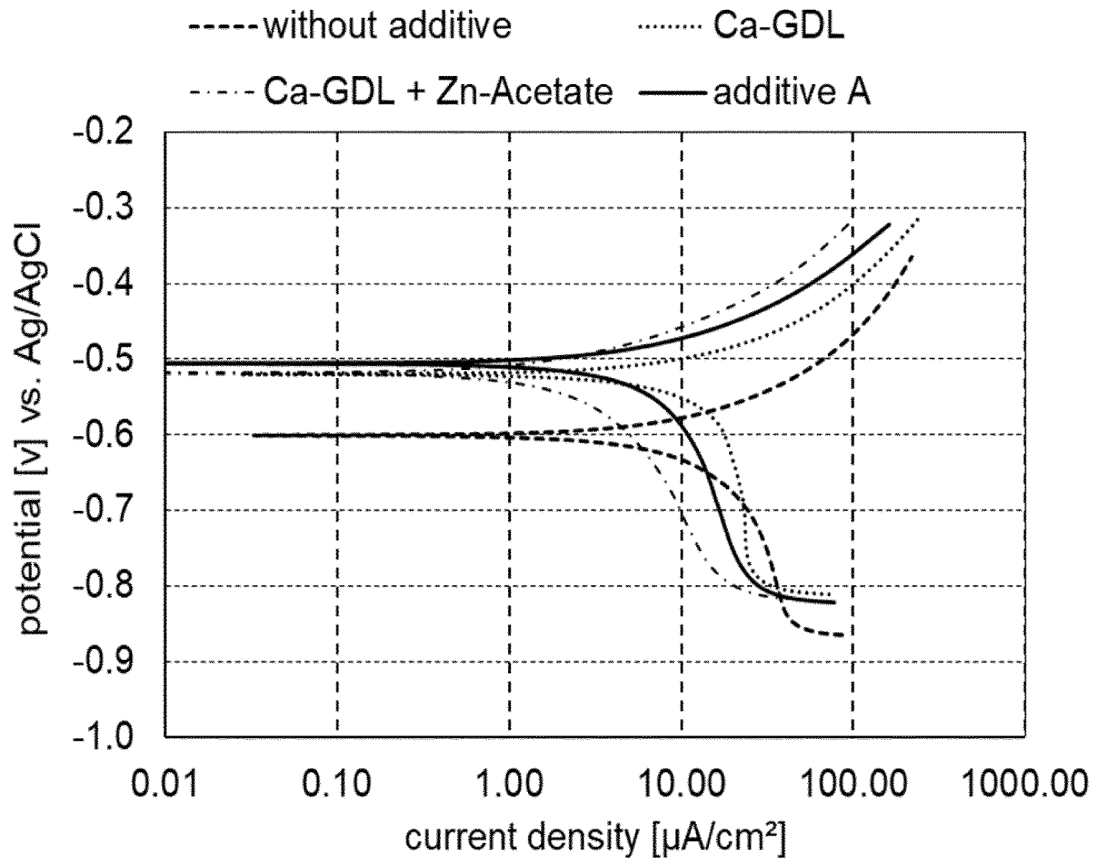


Fig. 1b

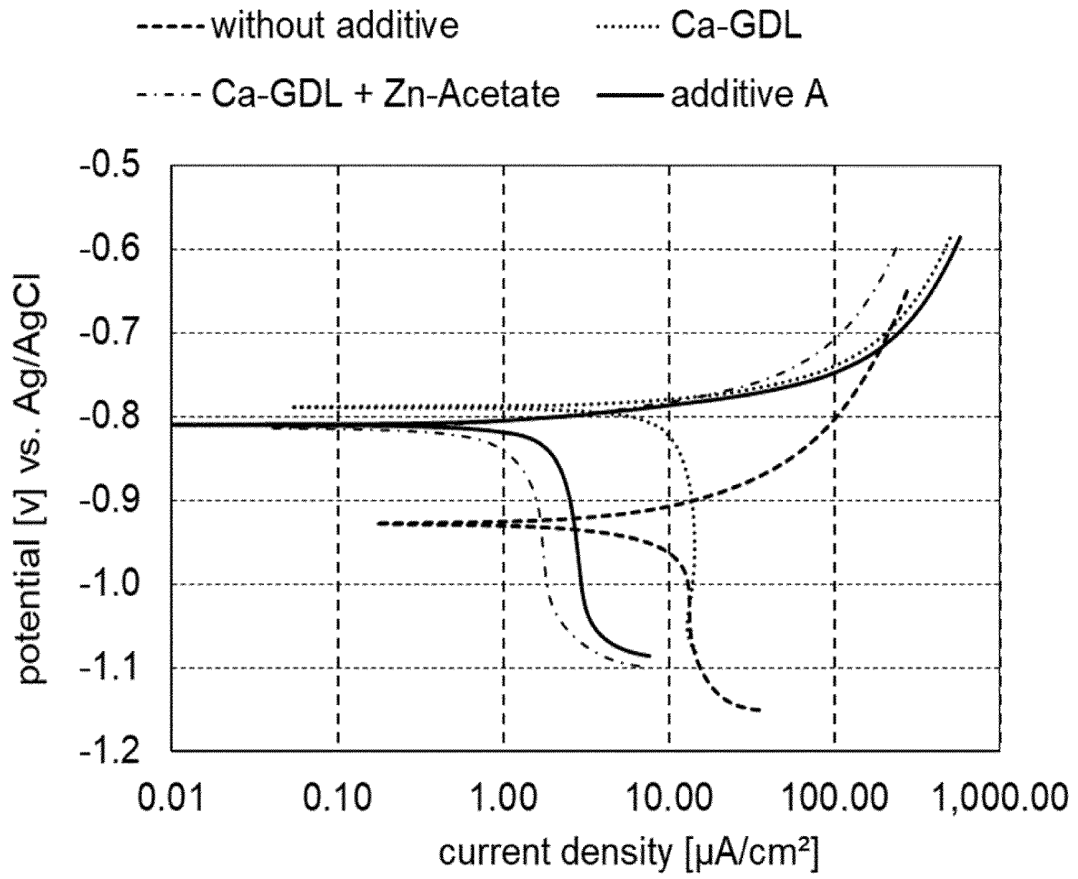


Fig. 1c

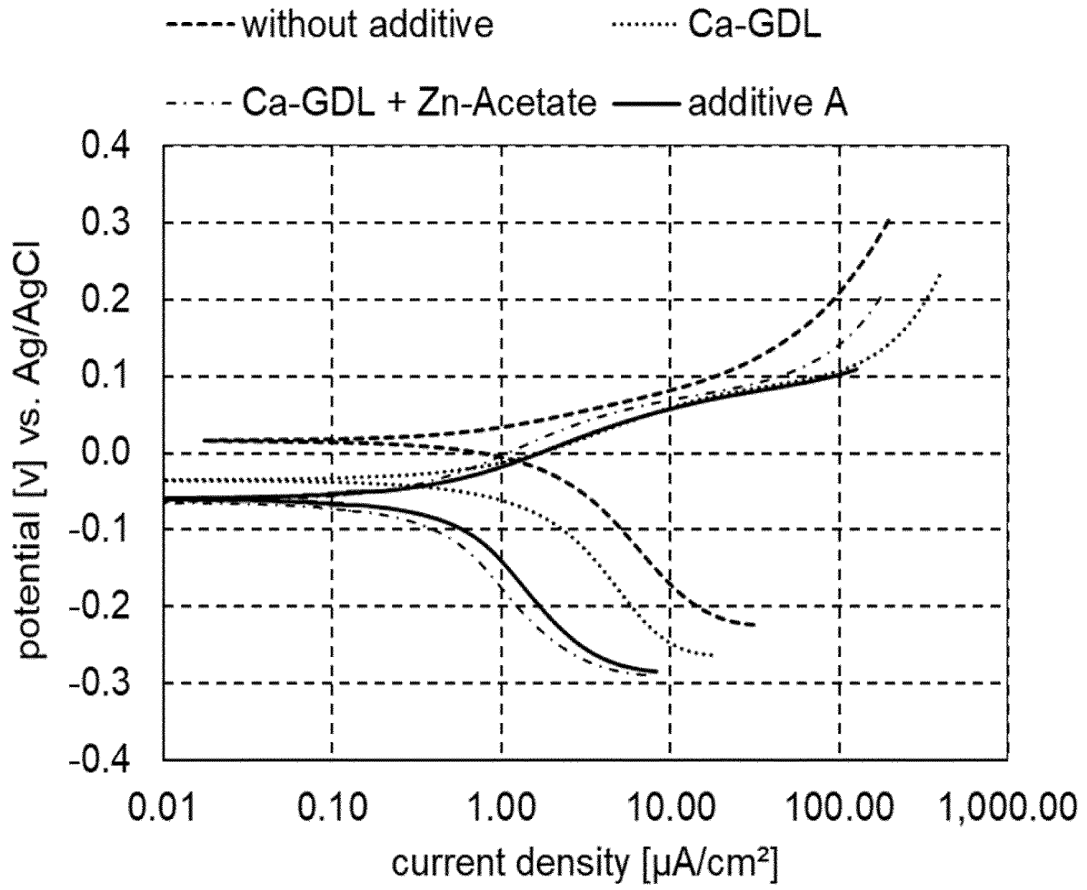


Fig. 1d

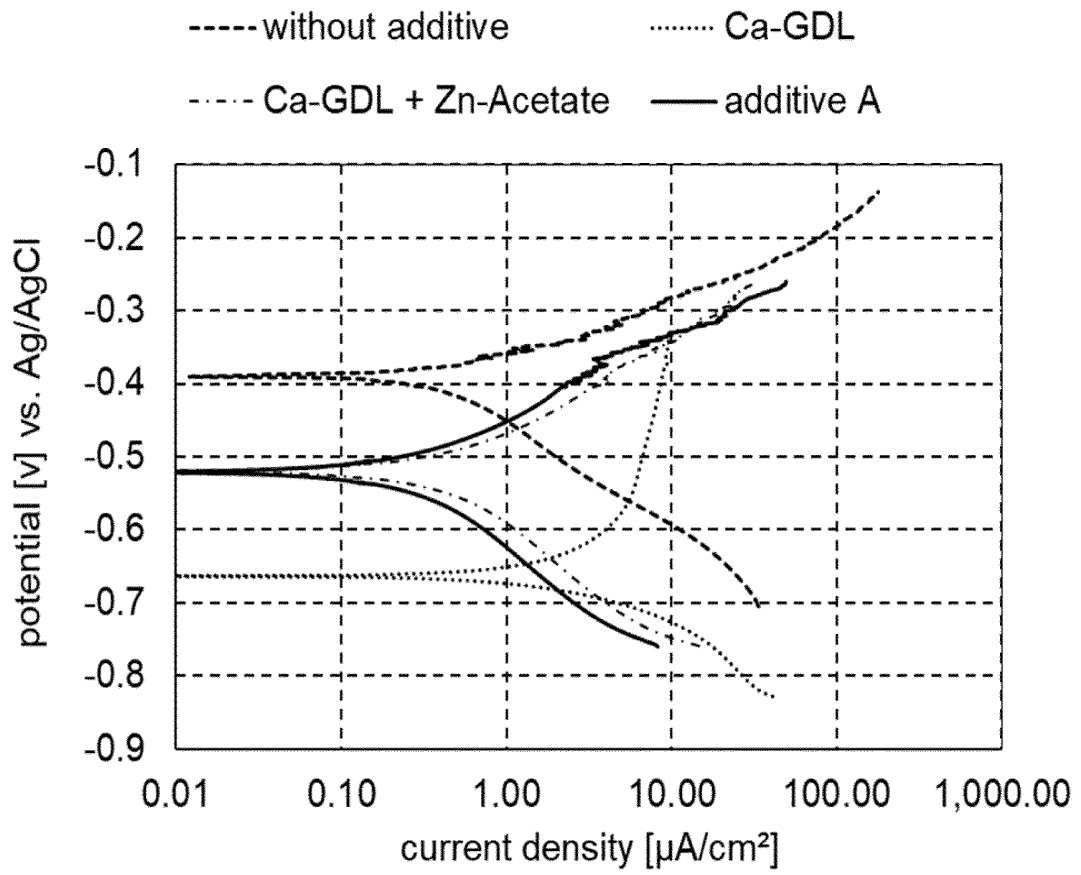


Fig. 1 e

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2021/063804

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C23F11/12 C23F11/10 C23C22/68 C23F11/08
 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)
 C23F 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.
A	CN 107 829 092 A (UNIV LIAONING NORMAL) 23 March 2018 (2018-03-23) abstract; claims 1-5 -----	1-15
A	SAREMI M ET AL: "Effect of Calcium Gluconate Concentration and Hydrodynamic Effect on Mild Steel Corrosion Inhibition in Simulated Cooling Water", CORROSION, NATIONAL ASSOCIATION OF CORROSION ENGINEERS, NACE, US, vol. 65, no. 12, 1 December 2009 (2009-12-01), pages 778-784, XP001552073, ISSN: 0010-9312, DOI: 10.5006/1.3319104 the whole document ----- -/--	1-15

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 9 August 2021	Date of mailing of the international search report 19/08/2021
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Handrea-Haller, M
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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2021/063804

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>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</p> <p style="text-align: center;">-----</p>	1-15
A	<p>US 5 531 931 A (KOEFOOD ROBERT S [US]) 2 July 1996 (1996-07-02) the whole document</p> <p style="text-align: center;">-----</p>	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2021/063804

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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