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McCormick

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(54) **STABLE ACID INHIBITOR FORMULATIONS
WITH IMPROVED PERFORMANCE,
LOWER TOXICITY AND MINIMAL
ENVIRONMENTAL ISSUES**

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(57) **ABSTRACT**

(76) **Inventor: David R. McCormick**, Clawson, MI
(US)

Correspondence Address:
HENKEL CORPORATION
THE TRIAD, SUITE 200
2200 RENAISSANCE BLVD.
GULPH MILLS, PA 19406 (US)

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Aqueous concentrates of non-toxic corrosion inhibitors, preferably storage-stable, useful in acidic cleaning solutions for cleaning the surfaces of metal that contacts food or potable water, the concentrates comprising at least one polymer, which may be protein-derived or synthetic; at least one iodine ion providing compound; an acidifier; and optionally, at least one anionic, nonionic or amphoteric surfactant; at least one coupling agent; and a pH adjuster; the concentrates being substantially free of nonylphenol derivatives and compounds containing elemental iodine and providing an improved acid inhibition and less foaming than similar compositions comprising nonylphenol derivatives and elemental iodine when mixed with aqueous acidic cleaners; acidic solutions prepared therefrom; and methods of their use.

**STABLE ACID INHIBITOR FORMULATIONS
WITH IMPROVED PERFORMANCE, LOWER
TOXICITY AND MINIMAL ENVIRONMENTAL
ISSUES**

FIELD OF THE INVENTION

[0001] This invention relates to corrosion inhibitors for use in acidic cleaning and pickling compositions. More particularly, the invention relates to storage-stable aqueous concentrates for non-toxic corrosion inhibitors useful in acidic pickling solutions for cleaning the surfaces of metal used in potable water wells, cooling towers, food process equipment and electrolysis membranes and other units holding, delivering or otherwise coming into contact with, food or potable water.

BACKGROUND OF THE INVENTION

[0002] Water wells containing potable water require periodic cleaning in order to remove scale from the well casings, well screens, pump bowls, etc. Typically, this scale is removed using an acid solution, generally a solution of hydrochloric acid. However, when such acid cleaning agents are used, several of the components forming the pumping mechanism are subject to attack by the acid, in particular, the well screen which is usually made of 304 stainless steel, the well casing which is usually made of mild steel, and especially the pump bowl which is usually cast iron. Other facilities requiring non-toxic, acid cleaning include water storage tanks, conduits, plumbing, boilers, cooling towers, food process equipment and electrolysis membranes and other units holding, delivering or otherwise coming into contact with, food or potable water and the like.

[0003] The hydrochloric acid is usually present in the cleaners in a concentration range of from 10 to 20% by weight, which, upon repeated use, can be quite damaging to the above parts. In order to protect these parts from the acid during the cleaning cycle, inhibitors have been added to the acid cleaning mixtures. However, these inhibitors have generally been of two types, namely, a toxic inhibitor such as diethylthiourea or a nontoxic inhibitor such as gelatin. The use of toxic inhibitors is, of course, quite undesirable, while the use of gelatin alone is also unsatisfactory due to the difficulty of dissolving the gelatin in the cold water and the fact that the gelatin may not protect the metal parts of the well properly, especially the cast iron pump bowl.

[0004] The use of proteins such as gelatin to inhibit the corrosion of metals in acid solution is well known; see for example, Desai, et al., *Werkstoffe Korrosion* 14, 739-42 (1963) that describes the use of gelatin to inhibit the organic acid corrosion of brass. Desai, et al., *J. Inst. Chem. Calcutta* 45, Part IV, 135-7 (1973) describes the use of gelatin as an inhibitor to protect aluminum alloys against acetic acid and chlorosubstituted acetic acids. Talati, et al., *Vidya*, 12(2), 182-192 (1969) discloses the use of gelatin to reduce the corrosion of aluminum and aluminum magnesium alloys when exposed to organic acids. Koshel, et al., *Australas Corros. Eng.*, 18(8), 17-19 (1974) describes the use of casenium purum, dextrin, tannin, gelatin, or carboxymethyl cellulose to prevent weight loss due to corrosion of aluminum in hydrochloric acid. Talati, et al., *Acta. Cienc. Indica.*, 2(3), 219-225 (1976) describes the use of inhibitors such as gelatin, glue, gum tragacanth, agar-agar, acacia, etc., to prevent the corrosion of aluminum alloys in chloroacetic acids.

[0005] A number of patents and publications describe the use of gelatin as an inhibitor against the corrosion attack by acids on iron or steel substrates. British Pat. No. 1,052,771 describes the use of gelatin, an arsenate, and a wetting agent with inorganic acids, such as phosphoric acid, to inhibit corrosion on iron or steel. Beloglazov, *Uchenye Zapiski Permsk. Univ.* 13, No. 3, 85-92 (1959) describes the use of inhibitors such as gelatin, casein, glycerol, etc., to protect steel against sulfuric acid. Machu, et al., *Werkstoffe Korrosion*, 13, 745-752 (1962) discloses the inhibition of acid corrosion in sulfuric acid by the addition of gelatin to protect a number of metals including iron metals. Beloglazov, *Uch. Zap. Permsk. Gos. Univ.*, 19, No. 1, 37-41 (1961) discloses the use of agents such as gelatin and casein in acid solutions to prevent hydrogenation and a change in fatigue strength of steel. Cabrera, et al., *Cuba Azucar*, Apr., Jun., 13-20 (1977) describe the use of both ammoniated and untreated molasses to protect steel against corrosion during acid cleaning. Cabrera, et al., *Cuba Azucar*, Jul.-Sep., 20-26 (1976) describes the use of distillery slops for preventing the acid corrosion of steel. The use of hydrolysates of gelatin to protect certain metals from acid corrosion has also been described. For example, published Japanese Patent Application 74-35,244 describes the use of gelatin or its hydrolysate to prevent the acid corrosion of copper zinc alloys. U.S. Pat. No. 3,505,184 describes the use of hydrolyzed protein as an inhibitor in a zinc electrodeposition bath. Published Czechoslovakian Patent Application 153,709 discloses the use of protein hydrolysate to inhibit the corrosion of steel in 39% HCl. U.S. Pat. No. 4,209,418 describes the use of gelatin mixed with benzimidazole compounds (which are toxic), as providing corrosion inhibition for aqueous carboxylic acid metal cleaning solutions. Ammoniated ethylenediamine tetraacetic acid (EDTA) and/or ammoniated citric acid are preferred as the carboxylic acids. Minor amounts of ethylquinolinium iodide and/or 2-thio-4,6-dimethyl pyrimidine hydrochloride may be present, although no other ingredients are disclosed. Both of these minor additives, or their analogs, are listed as toxic substances in the Chemical Abstracts Service Registry, the iodide having No. 634-35-5.

[0006] U.S. Pat. No. 4,851,149 discloses a corrosion inhibitor for use in acidic cleaners containing PVP and/or natural polymer. This patent also teaches use of components containing elemental iodine as well as the use of nonylphenol derivatives. The use of elemental iodine and nonylphenol derivatives is becoming less attractive to customers due to environmental, health and safety issues. According to the EPA, nonylphenol is moderately soluble and resistant to natural degradation in water. There is therefore a continued need for an inhibited acid solution for cleaning potable water wells and other units in which the inhibitor is substantially nontoxic, effective, and readily soluble, with the added benefit of being more environmentally acceptable, meaning containing fewer substances such as elemental iodine and/or nonylphenol or nonylphenol derivatives.

SUMMARY OF THE INVENTION

[0007] In an attempt to develop acid inhibitors useful in acid cleaners that do not contain elemental iodine and nonylphenol derivatives, Applicants unexpectedly discovered a new formulation that performed better than formulations taught by the '149 patent. The new formulation when mixed with an aqueous acidic cleaner provides greater

protection against corrosion of metals exposed to the cleaner. The new formulation also causes less gassing off of iodine containing fumes and less undesirable foaming of the cleaner bath.

[0008] It is accordingly an object of the invention to provide a more environmentally acceptable acid inhibitor comprising substantially no added elemental iodine, nonylphenol and/or nonylphenol derivatives. It is a further object of the invention to provide such an inhibitor with improved corrosion inhibiting performance and less foaming than the prior art nonyl phenol and elemental iodine containing inhibitors.

[0009] It is another object of the invention to provide an aqueous acid inhibitor concentrate that is stable after storage at room temperature (21 deg. C.) for at least 12, preferably 14, 16, 18, 20, 22, 24, 26, 28, 30, 35, 40, 45, 50, 55, 65, 75, 100 weeks.

[0010] It is also an object of the invention to provide an aqueous acid inhibitor concentrate that has improved stability when exposed to temperatures colder than (-4 or 10 deg. C.) and hotter than (49 deg. C.) room temperature (21 deg. C.). It is a further object of the invention to provide an aqueous acid inhibitor concentrate having improved freeze/thaw stability, that is upon re-warming to room temperature after freezing, the concentrate shows little or no separation that cannot be eliminated by mixing.

[0011] One embodiment of the invention provides an aqueous, storage stable, corrosion inhibitor concentrate, comprising: at least one polymer, which may be protein-derived or synthetic; at least one iodine ion providing compound; optionally, at least one anionic, nonionic or amphoteric surfactant; optionally, at least one coupling agent; an acidifier; and a pH adjuster comprising at least one alkaline source; wherein the aqueous corrosion inhibitor concentrate is storage stable. In a preferred embodiment (A) is a protein-derived polymer and (B) is a salt containing iodide anion. In a further embodiment, the acidifier comprises a polyprotic acid, preferably a phosphoric acid. In another further embodiment, the acidifier and pH adjuster form a buffer system in the concentrate. Alternatively, the acidifier and pH adjuster may be replaced with a salt, of a weak acid or polyprotic acid, that affords the same combination of available ions when dispersed in water. By way of non-limiting example, phosphoric acid and sodium hydroxide may be replaced with a suitable amount of monosodium phosphate. The salt is preferably added after dissolution of the polymer in the water.

[0012] In a preferred embodiment, the aqueous, storage stable, corrosion inhibitor concentrate comprises: about 1 to about 50% by weight of a gelatin hydrolysate; about 0.1 to about 15% by weight of ethylene diamine dihydroiodide; optionally, about 1 to about 20% by weight of at least one surfactant selected from the group consisting of anionic, nonionic, and amphoteric surfactants; optionally, at least one coupling agent; from about 0.5 to about 5% by weight of an acidifier; and an amount of pH adjuster comprising an alkaline source sufficient to give the concentrate a pH in the range of about 6.5 to about 3. In a particularly preferred embodiment, the aqueous corrosion inhibitor concentrate comprises an amount of gelatin hydrolysate is between about 10 to about 15% by weight; the amount of ethylene diamine dihydroiodide is between about 2 and about 8% by

weight; the amount of surfactant is between about 2 to about 16% by weight; the amount of acidifier is between about 1.5 and 2.5% by weight and the pH adjuster comprising an alkaline source is present in an amount sufficient to give the concentrate a pH in the range of about 6.0 to about 3.5.

[0013] In a particularly preferred embodiment of the aqueous, storage stable, corrosion inhibitor concentrate, the concentrate comprises less than 1.0 wt % nonylphenol derivatives and less than 0.1 wt % of compounds containing elemental iodine.

[0014] Another embodiment of the invention provides an aqueous, storage stable, corrosion inhibitor concentrate, substantially free of nonylphenol and nonyl phenol derivatives, comprising: (A) at least one polymer, which may be protein-derived or synthetic; (B) at least one iodine ion providing compound; (C) at least one anionic, nonionic or amphoteric surfactant and/or a pH adjuster comprising at least one alkaline source; (D) optionally, at least one coupling agent; and (E) an acidifier; wherein component (C) is present in an amount effective to render the aqueous corrosion inhibitor concentrate more storage stable, than similar concentrates in the absence of component (C). In a further embodiment, (E) is a phosphoric acid. In a preferred embodiment, the aqueous corrosion inhibitor concentrate has a pH of 2.7 to 6. In another aspect of this embodiment, the aqueous, storage stable, corrosion inhibitor concentrate, substantially free of nonylphenol and nonyl phenol derivatives comprises (C) a pH adjuster comprising at least one alkaline source. In a preferred embodiment, the concentrate comprises: (A) about 1 to about 50% by weight of a gelatin hydrolysate; (B) about 0.1 to about 15% by weight of ethylene diamine dihydroiodide; (C) optionally, in addition to said pH adjuster, about 1 to about 20% by weight of at least one surfactant selected from the group consisting of anionic, nonionic, and amphoteric surfactants; (D) optionally, at least one coupling agent; and (E) from about 0.5 to about 5% by weight of an acidifier.

[0015] In another embodiment of the invention the aqueous, corrosion inhibitor concentrate, comprises at least one polymer, which may be protein-derived or synthetic; at least one iodine ion providing compound; optionally, at least one anionic, nonionic or amphoteric surfactant; optionally, at least one coupling agent; and an acidifier; said concentrate comprising less than 1.0 wt % nonylphenol derivatives and less than 0.1 wt % of compounds containing elemental iodine, wherein said concentrate provides greater metal corrosion protection in acid cleaner solutions than a substantially identical concentrate containing amounts of nonylphenol phenol or its derivatives greater than or equal to 1.0 wt % and amounts compounds containing elemental iodine greater than 0.1 wt % . Preferably the polymer is a protein-derived polymer and the at least one iodine ion providing compound is a salt containing iodide anion. In a further aspect of this embodiment, the aqueous corrosion inhibitor concentrate comprises: about 1 to about 50% by weight of a gelatin hydrolysate; about 0.1 to about 15% by weight of ethylene diamine dihydroiodide; optionally, about 1 to about 20% by weight of at least one surfactant selected from the group consisting of anionic, nonionic, and amphoteric surfactants; optionally, at least one coupling agent; and from about 0.5 to about 5% by weight of an acidifier. In a preferred embodiment according to this further aspect, the concentrate further comprises a pH adjuster comprising at

least one alkaline source, said aqueous corrosion inhibitor concentrate having improved shelf life as compared to a substantially identical concentrate prepared in the absence of said alkaline source.

[0016] In yet another aspect of the invention an aqueous corrosion inhibited acid cleaning composition is provided in the absence of nonylphenol derivatives and compounds containing elemental iodine, the cleaning composition comprising: from about 1 to about 50% by weight of an acid; and a corrosion inhibiting effective amount of an aqueous concentrate comprising: at least one polymer, which may be protein-derived or synthetic; at least one iodine ion providing compound; optionally, at least one anionic, nonionic or amphoteric surfactant; optionally, at least one coupling agent; and an acidifier; and having a lower metal etch rate than similar compositions comprising nonylphenol derivatives and elemental iodine. In a preferred embodiment, the concentrate used in the acid cleaner further comprises a pH adjuster comprising at least one alkaline source. In a particularly preferred embodiment, the aqueous corrosion inhibited acid cleaning composition comprises a corrosion inhibiting effective amount of an aqueous concentrate comprising: about 1 to about 50% by weight of a gelatin hydrolysate; about 0.1 to about 15% by weight of ethylene diamine dihydroiodide; about 1 to about 20% by weight of at least one surfactant selected from the group consisting of anionic, nonionic, and amphoteric surfactants; optionally, a coupling agent; and about 0.5 to about 5% by weight of an acidifier.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0017] Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, or defining ingredient parameters used herein are to be understood as modified in all instances by the term "about". Unless otherwise indicated, all percentages are percent by weight.

[0018] This invention relates to acid cleaning/pickling compositions for metal surfaces containing a mixture of non-toxic ingredients that inhibit corrosion by the acid in the cleaner, non-toxic aqueous corrosion inhibitor additive concentrates for such acid cleaners which provide improved inhibition of corrosion and less foaming during use than similar prior art products, and methods for using the foregoing. In a preferred embodiment, the aqueous concentrate has improved storage stability, including longer shelf life at room temperature.

[0019] The acid cleaner compositions of this invention are used to remove water insoluble, acid soluble, deposits from metal surfaces that are in contact with, or may be in contact with, potable water or other potable liquids. Such surfaces include water well casings, liquid storage tanks, water heaters, conduits, cooling towers, food process equipment and electrolysis membranes and other units holding, delivering or otherwise coming into contact with, food or potable water.

[0020] For this reason, it is critical that the cleaner ingredients are non-toxic and safe for such use. To realize this, the ingredients are preferably on the GRAS (U.S.F.D.A. Generally Recognized As Safe) list, or even of food grade, where applicable. It also is extremely desirable that the ingredients are biodegradable, where possible.

[0021] The acid cleaner compositions according to this invention, in addition to an acid and water, contain corrosion

inhibitor ingredients which may be in the form of an aqueous concentrate, or which may be mixed separately with the acid and water.

[0022] The aqueous corrosion inhibiting concentrates (and the acid cleaners themselves) of this invention contain as essential ingredients:

[0023] (A) at least one polymer, which may be protein-derived or synthetic;

[0024] (B) at least one iodine ion providing compound;

[0025] (C) at least one anionic, nonionic or amphoteric surfactant (optional),

[0026] (D) at least one coupling agent (optional);

[0027] (E) an acidifier; and

[0028] (F) a pH adjuster comprising least one alkaline source (optional).

[0029] The foregoing ingredients, either individually or in concentrate form, are combined with aqueous acid solutions that have known utility as metal cleaners/picklers. Generally any acid may be used in this invention, provided critically that it is water-soluble, effective for cleaning metal surfaces, non-toxic in the quantity that may remain on the surfaces after water rinsing, and is preferably environmentally safe and/or biodegradable. Examples of known useful acids are: inorganic acids such as hydrochloric (muriatic), sulfuric, boric, nitric, phosphoric, and the like; and organic acids such as formic, citric, acetic, sulfamic, glycolic, benzoic, oxalic, mono-, di- or tri-chloroacetic, various C.sub.2-22 carboxylic acids, and the like. Mixtures of these acids are also useful. The acids in the aqueous solutions are at least minimally present in a cleaner-effective amount, particularly concentrations of 1 to 50% by weight, more preferably in a concentration of 5 to 30% by weight, most preferably 5 to 15% by weight. Hydrochloric acid, sulfamic acid, and/or sodium bisulfate are preferred.

[0030] The corrosion inhibited acid cleaner composition of this invention may be prepared by adding the corrosion inhibitor ingredients to the acid aqueous cleaner solution in any order and under ambient conditions or slightly elevated temperatures, accompanied by simple mixing.

[0031] Because of the difficulties of transporting a large volume of acid solution, it is generally preferable to premix the corrosion inhibitor ingredients to a concentrate and then to prepare the completed corrosion inhibitor acid cleaner at the point of use, or to introduce separately the acid cleaner and corrosion inhibitor concentrate in metered amounts in situ. Since mixing dry solid concentrate into a large aqueous bath, such as the acid cleaner, can result in clumping of the dry solid and other difficulties in producing a homogeneous mixture, it is preferred that the corrosion inhibitor concentrate be aqueous rather than dry. Aqueous corrosion inhibitor concentrates are readily mixed into acid cleaner solutions and provide a desirably homogeneous bath.

[0032] Methods of making aqueous corrosion inhibitor concentrates are within the knowledge of those of ordinary skill in the art. Suitable methods of making the concentrate of the invention are disclosed in U.S. Pat. No. 4,851,149, incorporated herein by reference. It is preferred in preparing concentrates of the instant invention that component (A) be mixed thoroughly with water until dissolved, followed by addition of the remaining ingredients. For concentrates of the invention containing a pH adjuster comprising an alka-

line source, it is preferred that the alkaline source is reserved for addition as the final ingredient.

[0033] The pH of the aqueous corrosion inhibitor concentrates according to the invention is acidic. Desirably, the pH for concentrates according to the invention is less than, in increasing order of preference 7, 6.5, 6.25, 6, 5.75, 5.5, 5.25, 5, 4.75, 4.5, 4.25, 4, 3.75, and independently the pH is more than in increasing order of preference 1.0, 1.25, 1.5, 1.75, 2, 2.25, 2.5, 2.75, 3, 3.25, 3.5. Typical pH ranges of aqueous corrosion inhibitor concentrates for use in an acid cleaner bath are between 1-6, preferably 2-5. In preferred embodiments that show good storage stability and stability to temperature variations, pH generally is less than, in increasing order of preference 6, 5.75, 5.5, 5.25, 5, 4.75, 4.5, 4.25, 4, 3.75, and independently the pH is more than in increasing order of preference 2.5, 2.6, 2.7, 2.75, 2.8, 2.9, 3, 3.25, 3.5.

[0034] It is preferred that concentrates of the invention are storage stable. One known problem in aqueous acid inhibitor concentrates is lack of shelf life. Lack of shelf life in this application meaning undesirable changes, such as phase separation, visible particulate matter, color changes as compared to the fresh concentrate, take place in the aqueous concentrate after manufacture when stored at room temperature for longer than 3 weeks. Nonyl phenol-derived iodophors were introduced in some aqueous corrosion inhibitors to improve stability, but the presence of nonyl phenol derivatives and indeed the elemental iodine with which iodophors complex is becoming a drawback for customers concerned with effluent and other regulation. Customers would prefer to use an aqueous acid inhibitor concentrate that is free of these additives, and which exhibits good shelf life over time as well as stability to varying temperatures.

[0035] In a preferred embodiment, aqueous concentrates of the invention are stable below room temperature (about 21 degrees C.), as well as when frozen and thereafter thawed. The concentrates of the invention generally form highly viscous liquids or soft gels at or below 4 deg. C and freeze at -10 deg. C.

[0036] Stability against temperature variation as well as freeze and thaw stability may conveniently be evaluated by observing whether any phase separation takes place, haziness to the human eye appears and whether the concentrate forms a solid gel which when brought to ambient temperature does not re-liquefy or has phase separation which is not eliminated upon remixing at ambient temperature. Haziness, persistent phase separation and irreversible gellation are indicators of the lack of storage stability of a concentrate. Preferred embodiments of the concentrates are stable to variations in temperature ranging from about -10 degree C. to 21 degree C, more preferably to 49 degree C. In a particularly preferred embodiment, concentrates of the invention are storage stable at 21 degrees C. and most preferably, at 21 and 49 degrees C. for more than 14 weeks. Storage stable as used herein means that after storage, the concentrate has no phase separation and if phase separation is present, the separation can be eliminated upon remixing at ambient temperature. Another indicator of stability is if viscosity of the concentrate has not increased to a viscosity that would negatively effect incorporation of the concentrate into the cleaner or transfer of the concentrate by pumping or pouring, typically a viscosity increase of about 25%. With increasing preference in the order given, the concentrates according to the invention are storage stable as thus defined after storage at 49 deg. C. for at least 30, 60, 100, 150 200, 400, 500, 600, 700 days.

[0037] (A) Protein-derived polymers useful in this invention include: gelatin, gelatin hydrolysates, casein, casein hydrolysates, starch, agar agar, carrageen, algin, pectin; gums such as locust bean, guar, tragacanth, arabic, karaya, acacia, carob bean, and the like; molasses and extracts thereof; potato, corn, or wheat starch; egg albumin, carboxymethylcellulose, carboxyethylcellulose, tannin, dextrin, sorbitol, and the like. To at least some degree, all protein and/or sugar derived polymers are useful, provided that they are (a) non-toxic (preferably on the GRAS list, most preferably food grade), and (b) preferably biodegradable. Protein hydrolysates such as gelatin hydrolysates and casein hydrolysates or their mixtures are preferred, gelatin hydrolysates being most preferred.

[0038] Synthetic polymers useful in this invention are vinyl-based, and must also meet the criteria of non-toxicity and, preferably, must also be environmentally safe and/or degradable. Examples of useful vinyl-based polymers are: polyvinylpyrrolidone (PVP), especially having a viscosity average molecular weight of 5,000 to 50,000, preferably 9,000 to 40,000; polyvinylpolypyrrolidone; vinylpyrrolidone/vinylacetate copolymers with a molecular ratio of 30:70 to 70:30; alkylated vinylpyrrolidone polymers with an average molecular weight of 7,000 to 17,000; vinylpyrrolidone/styrene copolymers; vinylpyrrolidone/quaternized dimethylaminoethylmethacrylate copolymers of varying molecular weight; vinylpyrrolidone/dimethylaminoethylmethacrylate copolymers; poly(methylvinylether/maleic anhydride); poly(octodecylvinyl ether/maleic anhydride); poly(methylvinyl ether); and the like. Of these compounds, vinyl-pyrrolidone polymers are preferred, polyvinylpyrrolidone being most preferred. Mixtures of any of the above polymers are also useful.

[0039] (B) The iodine compounds useful in this invention are those that provide available iodine ions. Iodine ion being understood to mean iodine in an ionically charged, preferably an anionically charged state. Iodine ion providing components are believed to serve two functions, in that they interact with the polymers and increase their desirable corrosion-inhibitive properties, and in that they may also have desirable bactericidal and fungicidal properties. These two functions do not appear to be inter-related. Compounds meeting the above criteria, which are suitable for use in this invention, include iodide salts that dissociate into iodine ions, such as NaI, KI, NH_4I , CuI_2 , FeI_2 , ZnI_2 . Particularly useful iodine ion providing components include NaI, KI, NH_4I , as well as iodic acid and amine iodides of which ethylene-diamine dihydroiodide is most preferred. All of the above iodide producing compounds may be used alone or in any combination.

[0040] It is preferred that elemental iodine, that is iodine in a non-ionized form, be eliminated or substantially eliminated from the formulation. Without being bound by a single theory, Applicants believe the elemental iodine competed with other more effective corrosion inhibitors and/or acted as an oxidizing agent on metal surfaces, and resulted in less than optimum performance of corrosion inhibitors. Compositions of the invention were found to perform better when the amount of elemental iodine was minimized. Another benefit of reducing the amount of elemental iodine present is the decreased gassing off of the iodine, which reduces odor of the acid cleaner bath. Accordingly, concentrates according to the invention comprise less than, in increasing order of preference, 0.1, 0.05, 0.01, 0.005, 0.001 wt % elemental iodine. In addition, the iodine ion providing compounds must be non-toxic and degradable or biodegradable.

able. It is particularly preferred that concentrates of the invention contain no nonylphenol derivatives, e.g. nonylphenoxypoly(ethyleneoxy)-ethanol-iodine complex. Accordingly, concentrates according to the invention comprise less than, in increasing order of preference, 1.0, 0.5, 0.1, 0.05, 0.01, 0.005, 0.001 wt % nonylphenol derivatives.

[0041] (C) The surfactants useful in this invention are those which are non-toxic, environmentally safe (and biodegradable if feasible), and stable in solutions with a pH of 6 or less, preferably pH 5-2. The surfactant is primarily required when an aqueous solution concentrate is prepared, and mainly helps to keep the concentrate ingredients in homogenous phase. It also assists in wetting the metal surface being cleaned. Suitable surfactants are generally anionic, amphoteric or nonionic, particularly polyoxyethylene-solubilized nonionics. Alcohol ethoxylates and polysorbates are particularly useful. Examples of suitable surfactants include, but are not limited to, polyoxyethylene (20 E.O.) sorbitan monolaurate, polyoxyethylene (20 E.O.) sorbitan monostearate and polyoxyethylene (20 E.O.) sorbitan monooleate, alkoxypoly(ethyleneoxy)ethanols, such as ethoxylated tridecyl alcohol and the like. These surfactants also function as a detergent/wetting agent. Without being bound by a single theory, it is thought that the ethoxylates in suitable surfactants may provide additional stability for the aqueous concentrate. It is preferred that use of surfactants containing nonylphenol derivatives, e.g. nonylphenoxy-polyethyleneoxy-ethanol, be reduced or eliminated, due to environmental, health and safety concerns regarding effluent containing nonylphenol derivatives. Accordingly, concentrates according to the invention comprise less than, in increasing order of preference, 1.0, 0.5, 0.1, 0.05, 0.01, 0.005, 0.001 wt % nonylphenol derivatives.

[0042] (D) The coupling agent is an optional ingredient used as a stabilizer for the aqueous concentrate. Useful coupling agents include propylene glycol and/or sodium xylene sulfonate, propylene glycol being preferred.

[0043] (E) The acidifier is used in the aqueous solution concentrate to provide an acidic pH to the aqueous concentrate which, when added to the acidic cleaner, does not interfere with the desired acidic environment provided by the acidic cleaner's other components. Any acid meeting the general ingredient criteria and capable of providing the aqueous solution concentrate, alone or in combination with the pH adjuster (F), a pH as previously described can be used, including the cleaner acids. Phosphoric acid, and/or hydrochloric acid is preferred. For embodiments designed for increased shelf life, that is improved storage stability, a polyprotic acid or a weak acid is preferred, for example phosphoric acid.

[0044] (F) The optional pH adjuster comprises at least one alkaline source. The pH adjuster is used in the aqueous solution concentrate to raise and/or maintain the concentrate pH in the desired pH range for embodiments that show good storage stability and stability to temperature variations. Any alkaline source can be used, provided the ion generated at dissociation of the pH adjuster components does not interfere with the stability of the aqueous concentrate or the performance of the concentrate in the acidic cleaner. The pH adjuster works in combination with (E) and maintains the aqueous solution concentrate within a desired pH range, as previously described herein. Suitable alkaline sources that can be used in the (F) component are those that meet the general ingredient criteria and are capable of balancing the acid of the (E) component, such as ammonium hydroxide,

amines, sodium hydroxide and potassium hydroxide. Preferred alkaline sources include sodium hydroxide and potassium hydroxide, especially sodium hydroxide.

[0045] Alternatively, (E) and (F) may be replaced with a salt, of a weak acid or polyprotic acid, that affords the same combination of available ions when dispersed in water, as would an aqueous solution of (E) and (F). By way of non-limiting example, phosphoric acid and sodium hydroxide may be replaced with a suitable amount of monosodium phosphate. The salt is preferably added after dissolution of the polymer in the water.

[0046] As the Examples show, stability of the aqueous concentrate at low pH remains acceptable for approximately 3 months at room temperature. Improved shelf life at elevated and room temperature and improved stability to cold temperatures, as well as freezing and thawing has been achieved by increasing the pH of the concentrate by the addition of a pH adjuster comprising an alkaline source. In preferred embodiments, designed for improved shelf life and/or freeze/thaw stability when exposed to the above-described conditions, the aqueous concentrate according to the invention contains a pH adjuster, desirably comprising an alkaline source or a buffer system.

[0047] The various ingredients in the compositions and concentrates of this invention are used in the following preferred amounts.

I. Acid Cleaner-Corrosion Inhibitor Composition

[0048] The acid is present in aqueous solution in at least a minimum cleaner-effective amount. Depending upon the acid, the w/w concentration generally will be a maximum of 50%, 1 to 50% being preferred, 3 to 30% being more preferred, and 5 to 20% being most preferred. The total amount of corrosion inhibition ingredients, whether added individually or as a premixed concentrate, is at least a minimum corrosion-inhibitive effective amount, the exact measurement for which will necessarily depend upon the acid being used. Where an aqueous corrosion inhibitor concentrate is used, it will be added to the aqueous acid cleaner in 0.1 to 4% v/v, preferably 0.5 to 2% v/v, most preferably 0.75 to 1.5% v/v. The corrosion inhibition ingredients, whether added individually or as a premixed concentrate, may be added to the acid cleaning bath and mixed thoroughly. As is known in the art, measurement of acid and corrosion inhibitor levels in an acid cleaning or pickling bath is performed periodically and any loss of acid and/or corrosion inhibitor replenished. Alternatively, the acid cleaner and the corrosion inhibitor concentrate may be introduced separately in metered amounts in situ; this practice being best suited to spray cleaner applications. After cleaning with acid cleaner solutions according to the invention, the surfaces are desirably rinsed at least once with water. Tap water or deionized water is generally acceptable; for units holding, delivering or otherwise coming into contact with, food or potable water, a tap or other potable water rinse is used.

II. Corrosion Inhibitor Aqueous Solution Concentrate

[0049] The above-identified ingredients should be present in the following amounts, all in % w/w.

[0050] (A) 1 to 50%, preferably 8 to 20%, most preferably 10 to 15%.

[0051] (B) 0.1 to 10%, preferably 1 to 8%, most preferably 2 to 5%.

[0052] (C) 0 to 20%, preferably 1 to 18%, most preferably 2 to 16%.

[0053] (D) 0 to 12.5%, preferably 5 to 10%, most preferably 6 to 9%.

[0054] (E) 0.5 to 5%, preferably 0.8 to 3%, most preferably 1.0 to 2.5%.

[0055] (F) 0.1 to 5%, preferably 0.3 to 3%, most preferably 0.5 to 1.5%.

[0056] All the above are ingredients mixed with water in a quantity sufficient (q.s.) to 100%, a preferred amount of water being 50 to 70%. The water should be relatively pure and free of interfering electrolytes, although tap water is acceptable.

EXAMPLES

[0057] The following illustrate various embodiments of this invention and are not intended as limiting. An aqueous acid inhibitor concentrate according to the invention (Example 1) and an aqueous acid inhibitor concentrate according to the prior art (Comparative Example 1) were formulated as shown in Table 1:

TABLE 1

Formulations of aqueous acid inhibitor concentrates			
		Amount (parts by weight)	
Ingredient Category	Ingredient	Comparative Example 1	Example 1
A	Protein hydrolysate (Rousselot 92B, a product of Rousselot Inc. of Dubuque, IA)	12.00	12.00
B	Nonylphenoxypolyethyleneoxy ethanol - iodine complex providing at least 20% available iodine (Biosurf I-20, a product of Lonza Group Ltd. Switzerland)	1.40	0
B	Ethylene diamine dihydriodide	3.27	3.27
C	Polyoxyethylene (20) sorbitan monooleate ("Tween 80", a product of ICI Americas, Inc., Wilmington DE)	4.0	4.0
C	Nonylphenoxypolyethyleneoxy ethanol (Igepal CO-660, a product of Stepan Company, Northfield, IL)	9.83	0
D	Propylene Glycol	7.5	7.5
E	Phosphoric Acid, 75% aq. Sol.	2.0	2.0
—	Water	q.s.	q.s.
TOTAL		100	100

[0058] Test solutions were prepared to compare the acid inhibitory action of the above formulations in an aqueous acid cleaner to an uninhibited aqueous acid cleaner. Three types of 2-liter test solutions were prepared to an acid concentration in deionized water of a 5.0 wt %/volume HCl: Unaltered acidic cleaner test solution was reserved as an uninhibited control; a comparative 2 liter test solution had 0.5% vol/vol of Comparative Example 1 added; and for a test solution according to the invention 0.5% vol/vol of Example 1 was added. 2 inch by 4 inch test coupons of the following materials were exposed to the test solutions for six hours with agitation: 1008 Cold Rolled Steel (1008 CRS), copper and stainless steel (304SS and 316SS). Each test coupon of 1008 CRS and of copper was run separately, using fresh solution for each material. The stainless steel coupons were run simultaneously in the same test solutions. Test

solutions were covered with a vented cold-water condenser and heated to 50 deg. C. with agitation. After six hours of exposure to their respective acid cleaner test solutions, the coupons were removed and weight loss of the coupons (in g), as well as percent inhibition were calculated. The results are shown in Table 2. Percent inhibition is calculated according to Formula I:

$$1 - \frac{(\text{average weight loss in the inhibited bath})}{(\text{average weight loss in the uninhibited bath})} \times 100 = \text{Percent inhibition} \quad (I)$$

TABLE 2

Etching of metal substrates by inhibited and uninhibited aqueous HCl acid cleaner			
Substrate	Uninhibited aqueous acid cleaner (Comparative)	Inhibited with 0.5% vol/vol Comparative Example 1	Inhibited with 0.5% vol/vol Example 1
1008 CRS	Cleaner Solution 1	Cleaner Solution 4	Cleaner Solution 7
Coupon 1	4.1689	0.2143	0.1473
Coupon 2	4.1875	0.2124	0.1460
Average	4.1782	0.2134	0.1467
Lb/ft ² /day		0.0169	0.0116
Percent Inhibition	0	94.89%	96.49%
Copper	Cleaner Solution 2	Cleaner Solution 5	Cleaner Solution 8
Coupon 1	0.1058	0.0968	0.0610
Coupon 2	0.1044	0.0946	0.0656
Average	0.1051	0.0957	0.0633
Lb/ft ² /day		0.0076	0.0050
Percent Inhibition	0	9.82%	39.77%
Stainless Steel	Cleaner Solution 3	Cleaner Solution 6	Cleaner Solution 9
(304SS) Lb/ft ² /day	0.0128	0.0041	0.0038
(316SS) Lb/ft ² /day	0.0407	0.0040	0.0038

[0059] A comparison of the metal etching resulting from Example 1 inhibited acid cleaners to the etching of both the uninhibited acid cleaner and that of Comparative Example 1 shows improved protection against etching of metal in cleaners inhibited by the formulation of Example 1. The improved etch inhibition by Example 1 is found in cold rolled steel, copper and stainless steel, the improvement being most marked for copper substrates.

[0060] Additional comparisons were made with different cleaning solutions, specifically a glycolic acid (hydroxyacetic acid) cleaning solution and a sodium bisulfite acid salt cleaning solution. Test aqueous acid cleaning solutions were inhibited with the aqueous acid inhibitor concentrates from Table 1 and compared to uninhibited cleaning solutions.

[0061] For Examples 2-7, 1-liter test solutions of glycolic acid were prepared by adding 268 grams of a 70 wt % glycolic acid solution to deionized water to reach an acid concentration in deionized water of a 20.0 wt %/volume glycolic acid. One 1-liter test solution was reserved as an uninhibited control and the remaining test solutions were inhibited as shown in Table 3. The test solutions were covered with a watch glass and heated to 100 deg. F with agitation. 2-inch by 4-inch test coupons of 1008 Cold Rolled Steel (1008 CRS) were exposed to their respective test

solutions for two hours with agitation. After two hours of exposure to the acid cleaner test solutions, the coupons were removed and weight loss of the coupons (in g), as well as percent inhibition were calculated. The results are shown in Table 3.

[0064] The results in Table 4 show that the aqueous acid inhibitor concentrate of the invention provides improved protection against etching on CRS 1020, which is readily etched by sodium bisulfate, and no additional protection against etching of 316 stainless steel, which is relatively

TABLE 3

Etching of metal substrates by inhibited and uninhibited aqueous glycolic acid cleaner								
Example	Inhibitor	Inhibitor Conc.	Acid Conc.	Temp Deg. F.	Time Hours	% Inh.	Lb/Ft ² /day	Gross Loss
2 (Control)	None	0		100	2.00	0	0.0152	0.0640
3	Example 1	0.20 vol/vol	20% wt/vol	100	2.00	74.4	0.0039	0.0164
4	Example 1	0.50 vol/vol	20% wt/vol	100	2.00	81.8	0.0028	0.0116
5	Example 1	1.00 vol/vol	20% wt/vol	100	2.00	89.8	0.0015	0.0065
6	Comparative	0.50 vol/vol	20% wt/vol	100	2.00	80.5	0.0030	0.0125
(Comp.)	Example 1							
7	Comparative	1.00 vol/vol	20% wt/vol	100	2.00	85.5	0.0022	0.0093
(Comp.)	Example 1							

[0062] As shown by a comparison of Example 4 to Example 6 and of Example 5 to Example 7, at like concentrations, the aqueous acid inhibitor concentrate of the invention provides improved protection against etching of CRS 1008 by glycolic acid.

[0063] For Examples 8-15, 2-liter test solutions of a 6.0 wt %/vol sodium bisulfate solution in deionized water were prepared. One 2-liter test solution was reserved as an uninhibited control and the remaining test solutions were inhibited as shown in Table 4. 2-inch by 4-inch test coupons of 1020 Cold Rolled Steel (1020 CRS) and of 316 stainless steel (316SS) were exposed to the test solutions as recited in Table 4, with agitation. Each test coupon of 1020 CRS and of 316SS was run separately, using fresh solution for each material. The test solutions were covered with a watch glass and heated to 190 deg. F. with agitation. After exposure to the acid cleaner test solutions, the coupons were removed and weight loss of the coupons (in g), as well as percent inhibition were calculated.

impervious to etch by sodium bisulfate as shown by Example 9.

Shelf-Life Testing

[0065] The aqueous acid inhibitor concentrate formulation of Example 1 showed adequate high temperature stability at 120 deg. F. for 2 weeks. The Example 1 formulation showed some color change and haziness after 10 weeks storage at room temperature. Generally, the concentrates can be re-mixed prior to addition to the acid cleaner, as necessary, provided there is no sediment formed which cannot be re-dispersed homogeneously. Color changes are generally interpreted as indicating a change in the concentrate, which has the potential for affecting performance. It is preferred that the aqueous acid inhibitor concentrate exhibit little or no separation or color change after months of storage and/or exposure to temperatures lower than or higher than room temperature and/or one or more freeze/thaw cycles.

TABLE 4

Etching of metal substrates by inhibited and uninhibited aqueous sodium bisulfate cleaner								
Example	Inhibitor	Inhibitor Conc.	Metal	Temp Deg. F.	Time Hours	% Inh.	Lb/Ft ² /day	Gross Loss
8 (Control)	None	0	CRS 1020	190	0.50	0	1.3937	1.4647
9 (Control)	None	0	316SS	190	24.00	0	<0.00001	<0.0005
10	Example 1	0.50% wt/vol	CRS 1020	190	3.00	95.1	0.0677	0.4270
11	Example 1	0.50% wt/vol	316SS	190	3.00	Neg.	0.0012	0.0077
12	Comp.	0.25% wt/vol	CRS 1020	190	3.00	93.4	0.0925	0.5834
(Comp.)	Example 1							
13	Comp.	0.25% wt/vol	316SS	190	3.00	NA	<0.000016	<0.0001
(Comp.)	Example 1							
14	Comp.	0.50% wt/vol	CRS 1020	190	3.00	96.8	0.0446	0.2809
(Comp.)	Example 1							
15	Comp.	0.50% wt/vol	316SS	190	3.00	NA	<0.000016	<0.0001
(Comp.)	Example 1							

[0066] Experimentation was performed relating to shelf life of various embodiments of the invention including aqueous concentrates containing additional surfactant. Shelf life was assessed by examining changes in color, phase separation and gellation apparent to the unaided human eye. Example 16 was made according to the formulation for Example 1 set forth in TABLE 1, but was more concentrated in that less water was used to make the concentrate. In Example 16, the total parts by weight is 90 for the concentrate, with all component amounts kept constant except the amount of water added to achieve a total of 90 parts concentrate.

[0067] For each concentrate of Examples 17-25, a 90-gram sample of the concentrate formulation of Example 16 was mixed with the additional ingredients listed in TABLE 5, below. Rhodasurf BC-720 is an alkoxypoly(ethyleneoxy)ethanol, which the manufacturer identifies as an ethoxylated tridecyl alcohol, available from Rhodia Inc., Cranbury, N.J. The pH was tested in the control and in test concentrates that included a pH adjuster comprising an alkaline source. Low temperature, freeze/thaw and storage stability at 21 and 49 deg. C. were then evaluated.

TABLE 5

Stability testing of various formulations aqueous acid inhibitor concentrates With changes in time and temperature										
Ingredient (g)	Control	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23	Ex. 24	Ex. 25
Example 16 Concentrate	90	90	90	90	90	90	90	90	90	90
NaOH	—	2.5	5.0	10.0	—	—	—	—	—	5.0
6.12% wt/wt Rhodasurf BC-720	—	—	—	—	5.0	2.5	1.0	—	5.0	5.0
Propylene Glycol	—	—	—	—	—	—	—	5.0	5.0	—
Tap water	10.0	7.5	5.0	—	5.0	7.5	9.0	5.0	—	—
TOTAL (g)	100	100	100	100	100	100	100	100	100	100

[0068] Stability performance of the test concentrates according to the invention varied with the presence of surfactant and alkaline source. General trends for shelf stability at 21 and 49 deg. C. showed that the addition of adequate amounts of surfactant and/or alkaline source allows the aqueous concentrate to maintain a longer shelf life in these temperatures. Low temperature, freeze/thaw and separation stability appeared to vary with the presence of surfactant, but did not parallel shelf stability trends.

1. An aqueous, storage stable, corrosion inhibitor concentrate, comprising:

- (A) at least one polymer, which may be protein-derived or synthetic;
- (B) at least one iodine ion providing compound;
- (C) optionally, at least one anionic, nonionic or amphoteric surfactant;
- (D) optionally, at least one coupling agent;
- (E) an acidifier; and
- (F) a pH adjuster comprising at least one alkaline source;

wherein the aqueous corrosion inhibitor concentrate is storage stable.

2. The aqueous corrosion inhibitor concentrate of claim 1 wherein the acidifier comprises a polyprotic acid.

3. The aqueous corrosion inhibitor concentrate of claim 2 wherein the acidifier comprises a phosphoric acid.

4. The aqueous corrosion inhibitor concentrate of claim 1 wherein the acidifier and pH adjuster form a buffer system in the concentrate.

5. The aqueous corrosion inhibitor concentrate of claim 1 wherein (A) is a protein-derived polymer and (B) is a salt containing iodide anion.

6. The aqueous corrosion inhibitor concentrate of claim 1 comprising:

- (A) about 1 to about 50% by weight of a gelatin hydrolysate;
- (B) about 0.1 to about 15% by weight of ethylene diamine dihydroiodide;
- (C) optionally, about 1 to about 20% by weight of at least one surfactant selected from the group consisting of anionic, nonionic, and amphoteric surfactants;

(D) optionally, at least one coupling agent;

(E) from about 0.5 to about 5% by weight of an acidifier; and

(F) an amount of pH adjuster comprising an alkaline source sufficient to give the concentrate a pH in the range of about 6.5 to about 3.

7. The aqueous corrosion inhibitor concentrate according to claim 6, wherein the amount of gelatin hydrolysate is between about 10 to about 15% by weight; the amount of ethylene diamine dihydroiodide is between about 2 and about 8% by weight; the amount of surfactant is between about 2 to about 16% by weight; the amount of acidifier is between about 1.5 and 2.5% by weight and the pH adjuster comprising an alkaline source is present in an amount sufficient to give the concentrate a pH in the range of about 6.0 to about 3.5.

8. The aqueous corrosion inhibitor concentrate of claim 1 comprising less than 1.0 wt % nonylphenol derivatives and less than 0.1 wt % of compounds containing elemental iodine.

9. An aqueous, nonylphenol-free, storage stable, corrosion inhibitor concentrate, comprising:

- (A) at least one polymer, which may be protein-derived or synthetic;
- (B) at least one iodine ion providing compound;
- (C) at least one anionic, nonionic or amphoteric surfactant and/or a pH adjuster comprising at least one alkaline source;
- (D) optionally, at least one coupling agent; and
- (E) an acidifier;

said concentrate being substantially free of nonylphenol and nonyl phenol derivatives, wherein component (C) is present in an amount effective to render the aqueous corrosion inhibitor concentrate more storage stable, than a similar concentrate in the absence of component (C).

10. The aqueous corrosion inhibitor concentrate of claim 9 wherein (E) is a phosphoric acid.

11. The aqueous corrosion inhibitor concentrate of claim 9 having a pH of 2.7 to 6.

12. The aqueous corrosion inhibitor concentrate of claim 9 wherein (C) is a pH adjuster comprising at least one alkaline source.

13. The aqueous corrosion inhibitor concentrate of claim 12 comprising:

- (A) about 1 to about 50% by weight of a gelatin hydrolysate;
- (B) about 0.1 to about 15% by weight of ethylene diamine dihydroiodide;
- (C) optionally, in addition to said pH adjuster, about 1 to about 20% by weight of at least one surfactant selected from the group consisting of anionic, nonionic, and amphoteric surfactants;
- (D) optionally, at least one coupling agent; and
- (E) from about 0.5 to about 5% by weight of an acidifier.

14. An aqueous, corrosion inhibitor concentrate, comprising:

- (A) at least one polymer, which may be protein-derived or synthetic;
- (B) at least one iodine ion providing compound;
- (C) optionally, at least one anionic, nonionic or amphoteric surfactant;
- (D) optionally, at least one coupling agent; and
- (E) an acidifier;

said concentrate comprising less than 1.0 wt % nonylphenol derivatives and less than 0.1 wt % of compounds containing elemental iodine, wherein said concentrate provides greater metal corrosion protection in acid cleaner solutions than a substantially identical concentrate containing nonylphenol derivatives and elemental iodine in greater amounts.

15. The aqueous corrosion inhibitor concentrate of claim 14 wherein (A) is a protein-derived polymer and (B) is a salt containing iodide anion.

16. The aqueous corrosion inhibitor concentrate of claim 15 comprising:

- (A) about 1 to about 50% by weight of a gelatin hydrolysate;
- (B) about 0.1 to about 15% by weight of ethylene diamine dihydroiodide;
- (C) optionally, about 1 to about 20% by weight of at least one surfactant selected from the group consisting of anionic, nonionic, and amphoteric surfactants;
- (D) optionally, at least one coupling agent; and
- (E) from about 0.5 to about 5% by weight of an acidifier.

17. The aqueous corrosion inhibitor concentrate of claim 15 further comprising a pH adjuster comprising at least one alkaline source, said aqueous corrosion inhibitor concentrate having improved shelf life as compared to a substantially identical concentrate prepared in the absence of said alkaline source.

18. An aqueous corrosion inhibited acid cleaning composition comprising:

- (1) from about 1 to about 50% by weight of an acid;
- (2) a corrosion inhibiting effective amount of an aqueous concentrate comprising:
 - (A) at least one polymer, which may be protein-derived or synthetic;
 - (B) at least one iodine ion providing compound;
 - (C) optionally, at least one anionic, nonionic or amphoteric surfactant;
 - (D) optionally, at least one coupling agent; and
 - (E) an acidifier;

in the absence of: nonylphenol derivatives and compounds containing elemental iodine

and having a lower metal etch rate than similar compositions comprising nonylphenol derivatives and elemental iodine.

19. The aqueous corrosion inhibitor concentrate of claim 18 further comprising a pH adjuster comprising at least one alkaline source.

20. The aqueous corrosion inhibited acid cleaning composition of claim 18, comprising a corrosion inhibiting effective amount of an aqueous concentrate comprising:

- (i) about 1 to about 50% by weight of a gelatin hydrolysate;
- (ii) about 0.1 to about 15% by weight of ethylene diamine dihydroiodide;
- (iii) about 1 to about 20% by weight of at least one surfactant selected from the group consisting of anionic, nonionic, and amphoteric surfactants;
- (iv) optionally, a coupling agent; and
- (v) about 0.5 to about 5% by weight of an acidifier.

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