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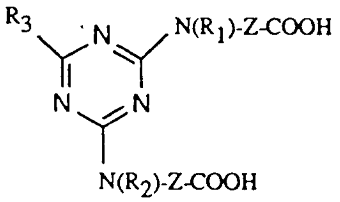
(54) Corrosion inhibiting compositions.

(57) A corrosion inhibiting composition comprising :

A) 40-90% by weight of a carboxylic acid corrosion inhibitor, or a water-soluble salt thereof, comprising one or more of :

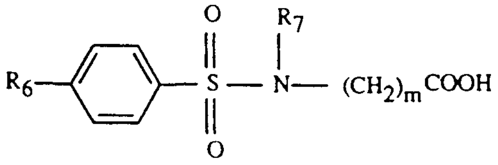
A1) a triazine-carboxylic acid of formula I :



I

in which Z is a C_1-C_{11} alkylene group, R_1 and R_2, independently, are hydrogen or methyl, and R_3 is a group $-NR_4R_5$ in which R_4 is C_1-C_{12} alkyl or -Z-COOH in which Z has its previous significance, and R_5 is hydrogen or C_1-C_{12} alkyl, or a water-soluble salt thereof ;

A2) a sulphonamidocarboxylic acid of formula II :



II

in which R_6 and R_7, independently, are hydrogen or C_1-C_4 alkyl, and m is an integer ranging from 1 to 10 or a water-soluble salt thereof ; and

A3) a dicarboxylic acid, or mixture thereof, having the formula III :

$$HOOC-(CH_2)_n-COOH \qquad III$$

in which n is an integer ranging from 4 to 12, or a water-soluble salt thereof ;

B) 10-60% by weight of one or more aminobenzoic acids having the formula IV :

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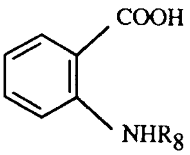
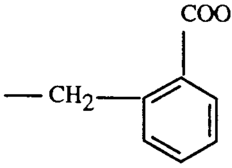
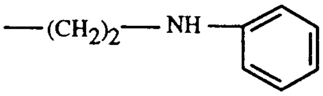


IV

in which R_8 is hydrogen or a group of formula V or VI :



V



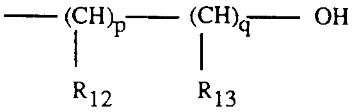
VI

or one or more water-soluble salts thereof ;

C) 0-10% by weight of an alkanolamine of formula VII :

$$NR_9R_{10}R_{11} \qquad VII$$

in which R_9,R_{10} and R_{11}, independently, are hydrogen, a linear or branched C_1-C_{12} alkyl group which is optionally interrupted by an oxygen atom, or R_9,R_{10} and R_{11} are a group of formula VIII :



$$—(\underset{R_{12}}{\underset{|}{CH}})_p—(\underset{R_{13}}{\underset{|}{CH}})_q—OH \qquad VIII$$

where R_{12} and R_{13}, independently, are hydrogen or C_1-C_{12} alkyl and p and q, independently, are 0 or an integer ranging from 1 to 10, provided that p and q are not simultaneously 0 and provided that at least one of R_9,R_{10} and R_{11} is a group of formula VIII ; and

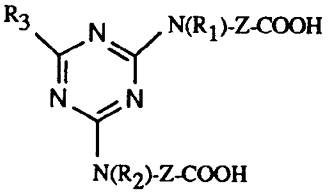
D) 0-10% by weight of an alkali metal borate ;

the percentages by weight being based on the total weight of the corrosion inhibitor composition.

The present invention relates to corrosion inhibiting compositions.

A wide variety of different chemical structures have found use as corrosion inhibitors for metals which come into operational contact with corrosive media.

One such group of chemical compounds is carboxylic acid compounds. One example of a group of carboxylic acid compounds, which are very effective corrosion inhibitors for ferrous metal in contact with aqueous systems, is that described in US 4402907 and comprising compounds of formula:



I

in which Z is e.g. a C_1-C_{11} alkylene group, R_1 and R_2, independently, are e.g. hydrogen or methyl; and R_3 is e.g. a group $-NR_4R_5$ in which R_4 is C_1-C_{12} alkyl or -Z-COOH in which Z has its previous significance, and R_5 is hydrogen or C_1-C_{12} alkyl; or water-soluble salts thereof.

Also known, as a corrosion inhibitor for, e.g. ferrous metal in aqueous systems is o-aminobenzoic acid (anthranilic acid) as well as derivatives thereof, c.f. e.g. Kriss et al. Zh. Prikl. Chem., 1989, 62(8), 1844-9.

These known carboxylic acid corrosion inhibitors have the disadvantage that they tend to be less effective when used in hard water systems.

EP 341 536 describes an attempt to improve the corrosion protection and hard water sensitivity of anthranilic acid derivatives by combining them with an alkenylsuccinic acid and an alkanolamine.

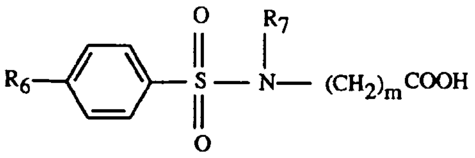
We have now found that by constructing a different combination of carboxylic acid corrosion inhibitors, the resulting combination has outstanding corrosion inhibiting properties which are much less sensitive to hard water environments.

Accordingly, the present invention provides a corrosion inhibiting composition comprising:

A) 40-90% by weight of a carboxylic acid corrosion inhibitor or a water-soluble, salt thereof, comprising one or more of:

A1) a triazino- carboxylic acid of formula I as hereinbefore defined;

A2) a sulphonamidocarboxylic acid formula II:



II

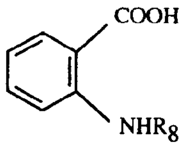
in which R_6 and R_7, independently, are hydrogen or C_1-C_4 alkyl, and m is an integer ranging from 1 to 10; and

A3) a dicarboxylic acid, or mixture thereof, having the formula III:

$$HOOC\text{-}(CH_2)_n\text{-}COOH \qquad III$$

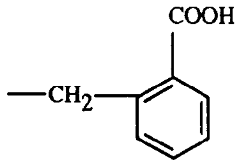
in which n is an integer ranging from 4 to 12;

B) 10 to 60% by weight of one or more aminobenzoic acids or water-soluble salts thereof having the formula IV:

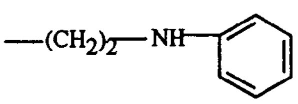


IV

in which R_5 is hydrogen or a group of formula V or VI:



V

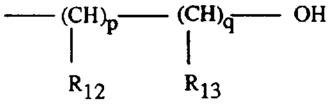


VI ;

optionally, C) 0 to 10% by weight of an alkanolamine of formula VII:

$NR_9R_{10}R_{11}$ VII

in which R_9, R_{10} and R_{11}, independently, are hydrogen, a linear or branched C_1-C_{12} alkyl group which is optionally interrupted by an oxygen atom, or R_9, R_{10} and R_{11} are a group of formula VIII:



$$-\underset{R_{12}}{(CH)_p}-\underset{R_{13}}{(CH)_q}-OH$$

VIII

in which R_{12} and R_{13}, independently, are hydrogen or linear or branched C_1-C_{12} alkyl and p and q, independently, are 0 or an integer ranging from 1 to 10, provided that p and q are not simultaneously 0; and provided that at least one of R_9, R_{10} and R_{11} is a group of formula VIII; and, optionally, D) 0 to 10% by weight of an alkali metal borate; the percentages by weight being based on the total weight of the corrosion inhibitor composition.

C_1-C_{11} Alkylene groups Z are, e.g., methylene, ethylene, n-propylene, n-butylene, n-pentylene, n-hexylene, n-heptylene, n-octylene, n-decylene and n-undecylene. Preferred such groups are C_1-C_5 alkylene groups, especially n-pentylene.

C_1-C_4 Alkyl groups R_6 and/or R_7 are, e.g., methyl, ethyl, n-propyl, isopropyl or n-butyl. Preferably, R_6 and R_7 are independently hydrogen or methyl, R^6 being methyl and R^7 being hydrogen in especially preferred embodiments.

C_1-C_{12} Alkyl groups R_4, R_6, R_9, R_{10}, R_{11}, R_{12} and R_{13} are e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, n-hexyl, n-octyl, n-decyl or n-dodecyl.

C_1-C_{12} Alkyl groups R_9, R_{10} and R_{11} interrupted by an oxygen atom are, e.g., methoxymethyl, ethoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 3-methoxypropyl, 1-or 2-methoxybutyl, 1-methoxyoctyl, 1-methoxydecyl or 1-methoxydodecyl.

In formula III n is preferably 11 and/or 12.

Preferably, R_4 is C_1-C_8 alkyl or -Z-COOH where Z is a C_1-C_5 alkylene group; R_5 is hydrogen or C_1-C_4 alkyl; R_9 and R_{10} are independently hydrogen, C_1-C_4 alkyl or a group of formula VIII where R_{12} and R_{13} are independently hydrogen or C_1-C_4 alkyl, while R_{11} is a group of formula VIII where R_{12} and R_{13} are independently hydrogen or C_1-C_4 alkyl.

Thus, preferred compounds A1) are of formula I where R_1 and R_2 are independently hydrogen or methyl, R_3 is $-NR_4R_5$ where R_4 is C_1-C_8 alkyl or -Z-COOH, R_6 is hydrogen or C_1-C_4 alkyl, and Z is C_1-C_5 alkylene and their water soluble salts; preferred compounds A2) are of formula II where R_6 and R_7 are independently hydrogen or methyl and their water-soluble salts; and preferred compounds A3) are of formula III where n is 11 or 12, mixtures of an acid where n is 11 with an acid where n is 12, and water-soluble salts of such acids and mixtures of acids.

Examples of specific compounds of formula I are as follows:

2,4,6-Tris(5'-carboxypentylamino)-1,3,5-triazine,
2,4,6-Tris(carboxymethylamino)-1,3,5-triazine,
2,4,6-Tris(3'-carboxypropylamino)-1,3,5-triazine,
2,4,6-Tris(4'-carboxybutylamino)-1,3,5-triazine,
2,4,6-Tris(11'-carboxyundecylamino)-1,3,5-triazine,
2,4,6-Tris(5'-carboxypentyl-N-methylamino)-1,3,5-triazine,
2,4,6-Tris(carboxymethyl-N-methylamino)-1,3,5-triazine,
2,4,6-Tris(3'-carboxypropyl-N-methylamino)-1,3,5-triazine,
2,4-Bis(5'-carboxypentylamino)-6-n-octylamino)-1,3,5-triazine,
2,4-Bis(2'-carboxyethylamino)-6-n-octylamino)-1,3,5-triazine,
2,4-Bis(2'-carboxyethylamino)-6-diethylamino)-1,3,5-triazine,
2,4-Bis(2'-carboxyethylamino)-6-butylamino)-1,3,5-triazine,
2,4-Bis(2'-carboxyethylamino)-6-ethylamino)-1,3,5-triazine,
2,4-Bis(3'-carboxypropylamino)-6-ethylamino)-1,3,5-triazine,

2,4-Bis(3'-carboxypropylamino)-6-n-octylamino)-1,3,5-triazine
2,4-Bis(3'-carboxypropylamino)-6-n-propylamino)-1,3,5-triazine
2,4-Bis(carboxymethylamino)-6-n-octylamino)-1,3,5-triazine,
2,4,-Bis(carboxymethylamino)-6-dodecylamino)-1,3,5-triazine,
2,4-Bis(3'-carboxypropyl-N-methylamino)-6-n-octylamino)-1,3,5-triazine,
2,4-Bis(carboxymethyl-N-methylamino)-6-n-octylamino)-1,3,5-triazine,
2,4-Bis(2'-carboxyethyl-N-methylamino)-6-n-octylamino)-1,3,5-triazine,
2,4-Bis(5'-carboxypentylamino)-6-(2"-carboxyethylamino)-1,3,5-triazine,
2,4-Bis(5'-carboxypentylamino)-6-(carboxymethylamino)-1,3,5-triazine,
2,4-Bis(3'-carboxypropylamino)-6-(2"-carboxyethylamino)-1,3,5-triazine,
2,4-Bis(2'-carboxyethylamino)-6-(5"-carboxypentylamino)-1,3,5-triazine,
2,4-Bis(3'-carboxypropylamino)-6-(5"-carboxypentylamino)-1,3,5-triazine,

The compounds of formula I are not new. These compounds and their production are described e.g. in Zhurnal Analiticheskoi Khimii 15, 419-423 (1960), in DE-OS 1935010, in DE-OS 2819796, in US Patent Specification 3697520 and in J. Prakt Chemie 23 173-85 (1963). Especially preferred compounds are
2,4,6-tris(5-carboxypentylamino)-1,3,5-triazine and water-soluble salts thereof.

Examples of compounds of formula II include benzenesulphonamidoacetic acid, benzenesulphonamido-2-propionic acid, benzenesulphonamido-4-butyric acid, benzenesulphonamido-6-n-hexanoic acid, benzenesulphonamido-8-n-octanoic acid, benzenesulphonamido-10-n-decanoic acid, N-methylbenzenesulphonamido acetic acid, 4-toluene sulphonamidoacetic acid and N-methyl-4-toluene sulphonamidoacetic acid. Especially preferred compounds are p-toluenesulphonamidocaproic acid and water-soluble salts thereof.

Compounds of formula III include, e.g. adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, nonane-1,9-dioic acid, decane-1,10-dioic acid, undecane-1,11-dioic acid and dodecane-1,12-dioic acid, as well as mixtures of these e.g. the commercially - available mixture of undecane-1,11-dioic acid and dodecane-1,12-dioic acid sold as "Alox 232", the last-named being especially preferred.

Specific examples of aminobenzoic acids of formula IV include anthranilic acid and N-(2-carboxy benzyl)-2-aminobenzoic acid.

The optional alkanolamine of formula VII may be, e.g., ethanolamine, diethanolamine, triethanolamine, methylelthanolamine, dimethylethanolamine, diethylethanolamine, butylethanolamine, dibutylethanolamine, di-isopropylethanolamine, methyldiethanolamine, ethyldiethanolamine, isopropanolamine, di-isopropanolamine, tri-isopropanolamine, sec.butanolamine, di-sec.butanolamine, tri-sec.butanolamine, or dimethylisopropanolamine. An especially preferred alkanolamine is triethanolamine.

The alkali metal borate may be e.g. sodium borate or potassium borate.

The water-soluble salts of carboxylic acid compounds of formula I and/or II may be alkali metal salts such as sodium or potassium salts; alkaline earth metal salts such as calcium or magnesium salts; or C_1-C_{12} alkyl amine salts such as methylamine, ethylamine, isopropylamine, dibutylamine, tributylamine, octylamine or dodecylamine salts. The C_1-C_{12} amine salt may be hydroxy-substituted and may be, e.g., a mono-, di- or tri-ethanolamine salt.

As already indicated, the corrosion inhibiting composition according to the present invention provide excellent inhibition against corrosion of ferrous metals in contact with an aqueous medium.

Accordingly, the present invention also provides a method of inhibiting the corrosion of a ferrous metal in contact with an aqueous system, comprising incorporating into the aqueous system an effective, corrosion-inhibiting amount, preferably 0.001 to 5% by weight, based on the weight of the aqueous system, of a corrosion inhibiting composition as hereinbefore defined.

The aqueous system which is treated according to the method of the present invention may be a totally aqueous or a partly aqueous medium.

Aqueous systems which may be effectively treated according to the present invention include e.g. cooling water systems, steam generating systems, sea-water evaporators, reverse osmosis equipment, bottle washing plants, paper manufacturing equipment, sugar evaporator equipment, soil irrigation systems, hydrostatic cookers, gas scrubbing systems, closed circuit heating systems, aqueous - based refrigeration systems, down-well systems, aqueous machining fluid formations (e.g. for use in boring, milling, reaming, broaching, drawing, turning, cutting, sawing, grinding, and in thread-cutting operations, or in non-cutting shaping, spinning, drawing or rolling operations), aqueous scouring systems, aqueous glycol anti-freeze systems, water/glycol hydraulic fluids; and aqueous - based polymer surface coating systems.

The corrosion-inhibiting composition of the present invention may be used in the method of the present invention either alone or in conjunction with other materials known to be useful in water treatment.

In the treatment of systems which are completely aqueous, e.g. cooling water systems, steam-generating systems, sea water evaporator systems, hydrostatic cookers and closed circuit heating systems, examples of further water treatment additives include one or more of further corrosion inhibitors; metal deactivators; further scale inhibitors/dispersing agents; threshold agents; precipitating agents; oxygen scavengers; sequestering agents; antifoaming agents; and biocides.

Further corrosion inhibitors which may be used include water-soluble zinc salts; phosphates; polyphosphates; phosphonic acids or their salts, e.g. hydroxyethyl diphosphonic acid (HEDP), nitrilotris methylene phosphonic acid, methylamino dimethylene phosphonocarboxylic acids and their salts (e.g. those described in DE-OS 2632774), hydroxyphosphonoacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid and those described in GB-PS 1572406; nitrates e.g. sodium nitrate; nitrites e.g. sodium nitrite; tungstates and molybdates e.g. sodium tungstate or molybdate; silicates e.g. sodium silicate; N-acylsarcosines; N-acylimino diacetic acids; ethanolamines; fatty amines; and polycarboxylic acids, e.g. polymaleic acid and polyacrylic acid (and their respective alkali metal salts), copolymers of maleic anhydride e.g. with sulphonated styrene, copolymers of acrylic acid e.g. with hydroxyalkylated acrylic acid, and substituted derivatives of polymaleic and polyacrylic acids and their copolymers.

Metal deactivators especially for copper, include benzotriazole, 5,5'-methylene bis-benzotriazole or copper - deactivating derivatives of benzotriazole or tolutriazole, or their Mannich base derivatives, or mercaptobenzothiazole.

Scale inhibitors/dispersing agents include polymerized acrylic acid (or its salts), phosphino-polycarboxylic acids (e.g. those described in GB-PS 1458235), the cotelomers described in EP-PS 0150706, hydrolyzed polyacrylonitrile, polymerized methacrylic acid and its salts, polyacrylamide and copolymers of acrylamide with acrylic and methacrylic acids, lignin sulphonic acid and its salts , tannin naphthalene sulphonic acid/formaldehyde condensation products, starch and its derivatives, cellulose, acrylic acid / lower alkyl hydroxy-acrylate copolymers (e.g. those described in US-PS 4029577) styrene/maleic anhydride copolymers and sulphonated styrene homopolymers (e.g. those described in US-PS 4374733, and combinations of these).

Specific threshold agents, include 2-phosphonobutane-1,2,4-tri-carboxylic acid, HEDP, hydrolyzed polymaleic anhydride and its salts, alkyl phosphonic acids, hydroxyphosphonoacetic acid, 1-aminoalkyl-1,1-diphosphonic acids and their salts, and alkali metal polyphosphates.

It will be clear from the above lists that certain additive compounds, e.g. phosphonocarboxylic acids, function both as scale inhibitors and as corrosion inhibitors.

Precipitating agent co-additives which may be used are alkali metal orthophosphates or carbonates; oxygen scavengers include alkali metal sulphites and hydrazines; sequestering agents are nitrilotriacetic acid and its salts; antifoaming agents are silicones, e.g. polydimethylsiloxanes, distearyl sebacimide, distearyl adipamide, and related products derived from ethylene oxide and/or propylene oxide condensations, in addition to fatty alcohols such as capryl alcohol and its ethylene oxide condensates. Biocides which may be used are, e.g. amines, quaternary ammonium compounds, m-chlorophenols, sulphur-containing compounds such as sulphones, methylene bis thiocyanates and carbonates, isothiazolines, brominated propionamides, triazines, phosphonium compounds, chlorine and chlorine-release agents, bromine and bromine release agents, and organometailic compounds such as tributyl tin oxide.

If the system to be treated according to the invention is not completely aqueous e.g. an aqueous machining fluid formulation, it may be e.g. a water dilutable cutting or grinding fluid.

The aqueous machining fluid formulations of the invention may be e.g. metal working formulations. By "metal working" we mean "reaming, broaching, drawing, spinning, cutting, grinding, boring, milling, turning, sawing, non-cutting shaping or rolling". Examples of water-dilutable cutting or grinding fluids into which the corrosion inhibiting compound of formula I may be incorporated include:

a) Aqueous concentrates of one or more corrosion inhibitors, and optionally one or more anti-wear additives, used at dilutions of 1:50 to 1:100, which are usually employed as grinding fluids;

b) Polyglycols containing biocides, corrosion inhibitors and anti-wear additives which are used at dilutions of 1:20 to 1:40 for cutting operations and 1:60 to 1:80 for grinding;

c) Semi-synthetic cutting fluids similar to b) but containing in addition 10 to 25% oil with sufficient emulsifier to render the water diluted product translucent;

d) An emulsifiable mineral oil concentrate containing, for example, emulsifiers, corrosion inhibitors, extreme pressure/anti-wear additives, biocides, antifoaming agents, coupling agents etc; they are generally diluted from 1:10 to 1:50 with water to a white opaque emulsion;

e) A product similar to d) containing less oil and more emulsifier which, on dilution to the range 1:50 to 1:100, gives a translucent emulsion for cutting or grinding operations.

Mixtures of sodium nitrite and triethanolamine have been used to inhibit corrosion in metal working but, because of related toxicity problems, due e.g. to the danger of forming N-nitrosamines, and because of legal regulations in some countries relating to effluents, alternatives to the use of sodium nitrite are being sought.

For those partly-aqueous systems in which the aqueous system component is an aqueous machining fluid formulation, the corrosion inhibitor composition of the present invention may be used singly, or in admixture with other additives e.g. known further corrosion inhibitors and/or extreme pressure additives.

Examples of other corrosion inhibitors which may be used in these aqueous systems, in addition to the corrosion inhibitor composition of the present invention include the following groups:

a) Further organic acids, their esters or ammonium, amine, alkanolamine and metal salts, for example, benzoic acid, p-tert-butyl benzoic acid, triethanolamine laurate, iso-nonanoic acid, sodium N-lauroyl sarcosinate or nonyl phenoxy acetic acid;

b) Nitrogen containing materials such as the following types: fatty acid alkanolamides; imidazolines, for example, 1-hydroxyethyl-2-oleyl-imidazolines; oxazolines; triazoles, for example, benzotriazoles, triethanolamines; fatty amines; and inorganic salts, for example sodium nitrate;

c) Phosphorus containing materials such as the following types: amine phosphates, phosphonic acids or inorganic salts, for example, sodium dihydrogen phosphate or zinc phosphate;

d) Sulphur containing compounds such as the following types: sodium, calcium or barium petroleum sulphonates, or heterocyclics, for example, sodium mercaptobenzothiazole.

Nitrogen containing materials, particularly triethanolamine, are preferred.

Examples of extreme pressure additives which may be present in the systems of the present invention include sulphur and/or phosphorus and/or halogen containing materials, for instance, sulphurised sperm oil, sulphurised fats, tritolyl phosphate, chlorinated paraffins or ethoxylated phosphate esters.

When triethanolamine is present in the aqueous systems treated according to the present invention, it is preferably present in an amount such that the ratio of the corrosion inhibitor composition of the present invention to triethanolamine is from 2:1 to 1:20.

The partly-aqueous systems treated by the method of the present invention may also be aqueous surface-coating compositions e.g. primer emulsion paints and aqueous powder coatings for metallic substrates.

The aqueous surface-coating composition may be e.g. a paint such as styrene-acrylic copolymer emulsion paint, a resin, latex, or other aqueous based polymer surface-coating systems.

Sodium nitrite and sodium benzoate have been used to inhibit flash rusting of aqueous based primer paints but, because of related toxicity problems and problems of emulsion stability at the high ionic concentrations used, industry is moving away from sodium nitrite and sodium benzoate.

In aqueous surface-coating compositions treated according to the invention the corrosion inhibitor composition of the present invention may be used singly, or in admixture with other additives e.g. known corrosion inhibitors, biocides, emulsifiers and/or pigments.

The further known corrosion inhibitors which may be used are e.g. those of classes a), b), c) and d) hereinbefore defined.

Examples of biocides which may be used in these aqueous systems, in addition to the corrosion inhibitor composition of the present invention, include the following:

Phenols and alkyl- and halogenated phenols, for example pentachlorophenol, o-phenyl phenol, o-phenoxyphenol and chlorinated o-phenoxyphenol, and salicylanilides, diamines, triazines and organometailic compounds such as organomercury compounds and organotin compounds.

Examples of pigments which may be used in these aqueous systems, in addition to the corrosion inhibitor composition of the present invention, include titanium dioxide, zinc chromate, iron oxide and organic pigments such as the phthalocyanines.

The following Examples further illustrate the present invention.

Examples 1 and 2

A) A corrosion inhibitor composition is formed by mixing 30 parts by weight of 2,4,6-tris(5-carboxypentylamino)-1,3,5-triazine and 20 parts by weight of anthranilic acid.

B) The corrosion-inhibiting performance of this composition A) is then evaluated in the DIN 51 360 test ("Filter Chip Test"). The composition A) is dissolved in DIN 51 360 water, with triethanolamine and/or borax added, to adjust the resulting solution to a pH of 8.0 or 8.5. The concentration of the corrosion inhibitor A) in the solution is 1.0% or 1.5% by weight, respectively.

Staining by cast iron "chips", that lie on a filter paper and which are wetted by a small volume of the test solution, is evaluated according to the following rating scale:

0	no staining
1	traces of staining
2	slight staining
3	moderate staining
4	heavy staining

The results obtained, as well as the corresponding results obtained with each of 2,4,6-tris(5-carboxypentylamino)-1,3,5-triazine or anthranilic acid, respectively used alone, are set out in the following Tables 1 and 2:

Table 1

Example	Formulation	Concentration % by weight	Rating at pH 8.5
-	2,4,6-tris(5-carboxypentylamino)-1,3,5-triazine	1.0	2
-	anthranilic acid	1.0	3
1	Product of Example 1(A)	1.0	0

Table 2

Example	Formulation	Concentration % by weight	Rating at pH 8.0
-	2,4,6-tris(5-carboxypentylamino)-1,3,5-triazine	1.5	3
-	anthranilic acid	1.5	2
2	Product of Example 1(A)	1.5	0

Example 3

A) A corrosion inhibitor composition is made up by mixing 10 parts by weight of p-toluene sulphonamido-caproic acid and 10 parts by weight of anthranilic acid.
B) Using the procedure described in Example 1(B), at pH 8.5, the following results are obtained.

Table 3

Example	Formulation	Concentration % by weight	Rating
-	p-toluene sulphonamido-caproic acid	0.9	3
-	anthranilic acid	0.9	3
3	Product of Example 2(B)	0.9	0

Example 4

A) A corrosion inhibitor composition comprising 10 parts by weight of Alox 232 (a commerically - available mixture of C_{11}/C_{12} dicarboxylic acids) and 10 parts by weight of anthranilic acid is prepared.
B) Using the procedure described in Example 1(B), at pH 8.5, the following results:

Table 4

Example	Formulation	Concentration % by weight	Rating
-	Alox 232	1.2	3
-	anthranilic acid	1.2	2
4	Product of Example 3(A)	1.2	0

Example 5

A) A corrosion inhibitor composition is prepared comprising 30 parts by weight of 2,4,6-tris(5-carboxypentylamino)-1,3,5-triazine and 10 parts by weight of N'-(2-carboxybenzyl)-2-aminobenzoic acid.
B) Using the procedure described in Example 1(B), at pH 9.0, the following results are obtained:

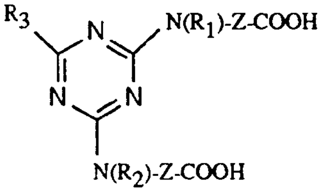
Table 5

Example	Formulation	Concentration % by weight	Rating
-	2,4,6-tris(5-carboxypentylamino)-1,3,5-triazine	0.6	4
-	N'-(2-carboxybenzyl)-2-aminobenzoic acid	0.6	1
5	Product of Example 4(A)	0.6	0

The results in Tables 1, 2, 3, 4 and 5 demonstrate the striking improvement in corrosion inhibitor performance of the compositions of the invention, in alkaline pH ranges.

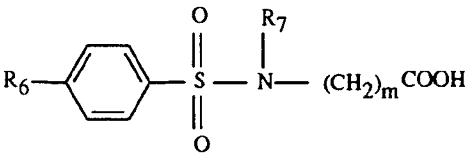
Claims

1. A corrosion inhibiting composition comprising:
A) 40-90% by weight of a carboxylic acid corrosion inhibitor, or a water-soluble salt thereof, comprising one or more of:
A1) a triazine-carboxylic acid of formula I:



I

in which Z is a C_1-C_{11} alkylene group, R_1 and R_2, independently, are, hydrogen or methyl, and R_3 is a group $-NR_4R_5$ in which R_4 is C_1-C_{12} alkyl or -Z-COOH in which Z has its previous significance, and R_5 is hydrogen or C_1-C_{12} alkyl, or a water-soluble salt thereof;
A2) a sulphonamidocarboxylic acid of formula II:



II

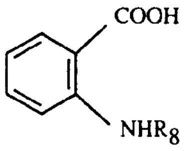
in which R_6 and R_7, independently, are hydrogen or C_1-C_4 alkyl, and m is an integer ranging from 1 to 10 or a water-soluble salt thereof; and

A3) a dicarboxylic acid, or mixture thereof, having the formula III:

$$HOOC\text{-}(CH_2)_n\text{-}COOH \qquad III$$

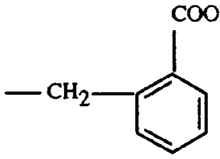
in which n is an integer ranging from 4 to 12, or a water-soluble salt thereof;

B) 10-60% by weight of one or more aminobenzoic acids having the formula IV:

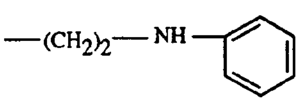


IV

in which R_8 is hydrogen or a group of formula V or VI:



V



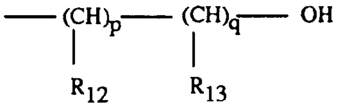
VI

or one or more water-soluble salts thereof;

C) 0-10% by weight of an alkanolamine of formula VII:

$$NR_9R_{10}R_{11} \qquad VII$$

in which R_9,R_{10} and R_{11}, independently, are hydrogen, a linear or branched C_1-C_{12} alkyl group which is optionally interrupted by an oxygen atom, or R_9,R_{10} and R_{11} are a group of formula VIII:



$$-(\underset{R_{12}}{\underset{|}{CH}})_p-(\underset{R_{13}}{\underset{|}{CH}})_q-OH$$

VIII

where R_{12} and R_{13}, independently, are hydrogen or C_1-C_{12} alkyl and p and q, independently, are 0 or an integer ranging from 1 to 10, provided that p and q are not simultaneously 0 and provided that at least one of R_9,R_{10} and R_{11} is a group of formula VIII; and

D) 0-10% by weight of an alkali metal borate; the percentages by weight being based on the total weight of the corrosion inhibitor composition.

2. A composition according to claim 1, in which

A1) is of formula I where R_1 and R_2 are independently hydogen or methyl, R_3 is $-NR_4R_8$ where R_4 is C_1-C_8 alkyl or -Z-COOH, R_5 is hydrogen or C_1-C_4 alkyl and Z is C_1-C_5 alkylene, or a water-soluble salt thereof;

A2) is of formula II where R_6 and R_7 are independently hydrogen or methyl, or a water-soluble salt thereof; and

A3) is an acid of formula III where n is 11 or 12, a mixture of an acid of formula III where n is 11 with an acid of formula III where n is 12, or a water-soluble salt thereof.

3. A composition according to claim 1, in which A1) is 2,4,6-tris(5-carboxypentylamino)-1,3,5-triazine or a water-soluble salt thereof;

A2) is p-toluenesulphonamidocaproic acid or a water-soluble salt thereof; and

A3) is a mixture of an acid of formula III where n is 11 with an acid of formula III where n is 12, or a water-soluble salt thereof.

4. A composition according to any of claims 1 to 3, in which A) is A1).

5. A composition according to any of claims 1 to 3, in which A) is A2).

6. A composition according to any of claims 1 to 3, in which A) is A3).

7. A composition according to any of claims 1 to 6, in which B) is anthranilic acid, N-(2-carboxybenzyl)-2^1aminobenzoic acid, or a water-soluble salt thereof.

8. A composition according to any of claims 1 to 7, in which the alkanolamine C) is present and is triethanolamine.

9. A composition according to any of claims 1 to 8, in which the borate D) is present and is sodium borate or potassium borate.

10. A method of inhibiting corrosion of a ferrous metal in contact with an aqueous system, comprising incorporating into the aqueous system an effective, corrosion inhibiting amount of a composition according to any of claims 1 to 9.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 93 30 0175

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 511 163 (CIBA-GEIGY AG) 28 October 1992 * claims 1,5,10,11 *	1-4,6,7,10	C23F11/10 C23F11/08
X	PATENT ABSTRACTS OF JAPAN vol. 7, no. 108 (C-165)(1253) 13 May 1983 & JP-A-58 031 086 (OTSUKA KAGAKU YAKUHIN) 23 February 1983 * abstract *	1,6,7	
X	PATENT ABSTRACTS OF JAPAN vol. 8, no. 77 (C-218)(1514) 10 April 1984 & JP-A-59 001 686 (KAWASAKI SEITETSU) 7 January 1984 * abstract *	1,6,7	
A	GB-A-2 194 782 (CIBA-GEIGY) * page 3, line 4-31; claims 1,10 *	8,9	
A	GB-A-2 004 911 (HOECHST AG)		
A	GB-A-2 204 864 (CIBA-GEIGY AG)		**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
A	EP-A-0 116 348 (HOECHST AG)		C23F
A,D	EP-A-0 046 139 (CIBA-GEIGY AG)		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 APRIL 1993	TORFS F.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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