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(54) Title: CORROSION INHIBITING COMPOSITIONS FOR HEAT TRANSFER FLUIDS

(54) Titre: COMPOSITIONS INHIBITRICES DE LA CORROSION POUR FLUIDES DE TRANSFERT DE CHALEUR

(57) Abstract: The invention concerns compositions for inhibiting corrosion of various metals by heat transfer fluids consisting of a combination of an unsaturated monocarboxylic acid, a saturated monocarboxylic or dicarboxylic acid, a 1,3,5-triazine tricarboxylic derivative and an azole compound derivative. Said compositions inhibit corrosion by cavitation in particular.

(57) Abrégé: On décrit des compositions inhibitrices multimétaux de la corrosion par les fluides de transfert de chaleur qui sont constituées par l'association d'un acide monocarboxylique insaturé, d'un acide mono- ou dicarboxylique saturé, d'un dérivé tricarboxylique de la 1, 3, 5-triazine et d'un dérivé azole. Ces compositions inhibent en particulier la corrosion par cavitation.

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CORROSION-INHIBITING COMPOSITIONS FOR HEAT TRANSFERFLUIDS

The field of the invention is that of aqueous
5 liquids which can be used as heat transfer fluids for
cooling circuits, for example cooling circuits of
internal combustion engines, the corrosiveness of which
is to be overcome.

Water and aqueous solutions are very widely
10 used as cooling fluids in circuits constructed of
various metals, copper, steel, aluminium, cast iron and
their alloys, which they attack as soon as the
corrosion conditions are achieved. There are many
corrosion factors: presence of ions, high temperatures,
15 pressure, flow of fluids (cavitation corrosion),
coupling to welds. Very particular attention must be
paid to cavitation corrosion phenomena.

The first consequence of corrosion is the
loss of material from the walls of the circuits and
20 their perforation. In addition, corrosion products are
formed, the deposits of which disrupt transfer of heat
between the fluid and the walls of the circuit and
bring about superheating on the hot walls, with high
risks of failure of sensitive mechanical components.

25 The products used to lower the freezing point
of water are a factor having a particularly serious
effect on worsening the corrosiveness of cooling

fluids. The use of saline brines, for the aggressiveness of which, in particular towards welds and aluminium, a satisfactory solution has never really been found, has virtually been abandoned. Industry has
5 been won over to organic antifreezes of the class of the alcohols, methanol, ethanol, 2-propanol, glycerol, ethylene glycol, diethylene glycol, propylene glycol, ethylene glycol methyl, ethyl, propyl or butyl ether, and 1-methoxy-2-propanol. Ethylene glycol is by far the
10 most widely used antifreeze today. Nevertheless, the problem is still posed of protecting from corrosion cooling circuits fed with aqueous fluids comprising or not comprising organic antifreezes, of developing compositions which inhibit corrosion in such media and,
15 if possible, of formulating antifreeze compositions which are themselves corrosion inhibiting.

These compositions are burdened by specific constraints relating to environmental protection. It is forbidden, or in any case highly inadvisable, to
20 include phosphates, nitrites, borates, molybdates and amines in combination with nitrites, which, in the prior art, had all the same been recommended and some of which had been widely used. Phosphates precipitate on contact with hard water and, for this reason, their
25 concentration and activity decreases (depletion). It is possible to combat this, but at the price of an

increase in the cost of the protection, by the use of certain additives (JP-A-62205183). In addition, these phosphates are harmful to the environment (eutrophication of water). Amines, when they are used
5 in combination with nitrites, lead to the risk of formation of nitrosamines, which are highly toxic products. Discharges of fluids to which boron derivatives or molybdates have been added are also harmful and require treatment before they are returned
10 to the environment. Attention has therefore been firmly directed towards other organic inhibitors, which has given rise to a great many publications and a great many patents, including, for example:

- US Application No. 819,321, cited in
15 US 4,759,864, concerning an antifreeze based on the combination of an alkylbenzoic acid (or alkylbenzoate) with a C₈-C₁₂ monocarboxylic acid (or carboxylate) and triazol, with an aminophosphonic acid derivative as precipitation inhibitor and polyacrylic acid
20 (polyacrylate) as stabilizer;

- US 4,647,392, for an antifreeze with C₅-C₁₆ monocarboxylic acid (monocarboxylate), C₅-C₁₆ diacid (salt) and triazol derivative;

- US 4,657,689, for an antifreeze
25 comprising a C₅-C₁₆ carboxylic acid (carboxylate), a

C₅-C₁₆ dicarboxylic acid (or salt), a triazol derivative and an alkaline C₁₀-C₂₀ sulphonate;

- US 4,588,513, for antifreeze with dicarboxylic acid (or a salt), an alkaline silicate and
5 a triazol derivative;

- US 2,832,742, for an inhibitor comprising a C₇-C₁₈ carboxylic acid and p-tert-butylbenzoic acid;

- US 4,759,864, for an antifreeze
10 comprising a C₆-C₁₂ acid or a salt, an alkaline derivative of boron and a triazol derivative.

The article by G.T. Hefter et al., "Organic Corrosion Inhibitor in Neutral Solutions", published in "Corrosion, Vol. 53, No. 8, 1997, NACE International",
15 pages 657-667, reviews the problems encountered in multimetal corrosion.

However, in any case, these compositions do not provide a satisfactory solution to the problem of cavitation corrosion, which remains a major
20 preoccupation, in particular for manufacturers of automobile engines. The compositions of the present invention provide an answer to this problem, which is expressed in practice in their conformity to the requirements of the so-called "cavitation" test, at the
25 same time as those of the standard tests for evaluating the inhibiting effectiveness under hot conditions with

respect to various metals in an antifreeze liquid. The CEC C-05X-95 "cavitation" test is that which provides an evaluation of the performance of an inhibiting combination with regard to the corrosion of steel and
5 of aluminium by cavitation of a possibly antifreeze fluid circulating in a loop under standard flow rate, temperature and pressure conditions. These tests are described in the examples.

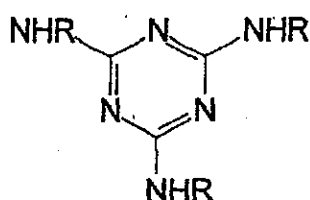
The present invention is that of a process
10 for inhibiting multimetal corrosion by heat transfer fluids, whether or not these fluids comprise an organic compound which lowers the freezing point, which consists in introducing, into the said fluids, 3 to 6% by weight and preferably 3.8 to 5% of a system of
15 organic inhibitors composed of:

- (I) 5 to 15% by weight of at least one unsaturated monocarboxylic acid comprising 10-18 carbon atoms or of one of its alkali metal salts, amine salts, the amine being from the group of monoethylamine,
20 diethylamine or triethylamine, or alkanolamine salts, the alkanolamine being from the group of monoethanolamine, diethanolamine, triethanolamine or methyldiethanolamine;

- (II) 40 to 70% by weight of at least one
25 saturated carboxylic acid taken from the group consisting of saturated monocarboxylic acids comprising

5-16 carbon atoms and saturated dicarboxylic acids comprising 4-12 carbon atoms, or an alkali metal or amine or alkanolamine salt of these acids;

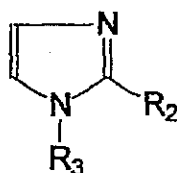
- (III) 20 to 40% by weight of a tricarboxylic derivative of 1,3,5-triazine corresponding to the formula:



in which formula R is a carboxyalkyl group comprising 2-6 carbon atoms, or an alkali metal or amine or alkanolamine salt of this derivative;

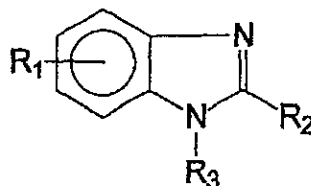
- (IV) 1 to 5% by weight of an azole derivative taken from the group consisting of:

(a) imidazoles of formula



15

(b) benzimidazoles of formula



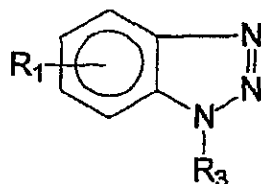
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(c) triazoles of formula



or

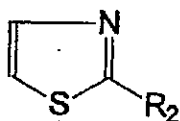
(d) benzotriazoles of formula



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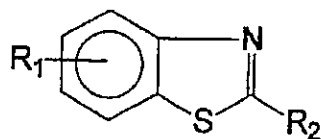
(e) tetrahydrobenzotriazole

(f) thiazoles of formula



10

(g) benzothiazoles of formula



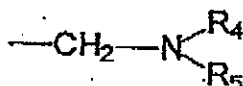
15 (h) and the alkali metal salts of these
azole derivatives,

in which formulae

R_1 is a hydrogen atom or a methyl radical

R_2 is a hydrogen atom or a mercapto radical

R_3 is a hydrogen atom or a radical of formula



with R_4 and R_5 , which are identical or different, representing a 2-ethylhexyl or hydroxyalkyl radical, in particular a hydroxyethyl residue.

10 In a preferred embodiment of the process of the invention, the ratio by weight of the constituents I and II (I/II) will be between 5 and 15 and preferably between 8 and 12 and the ratio by weight of the constituents I and II, on the one hand, and III ((I + II)/III) will be
15 between 1.5 and 3 and preferably between 1.9 and 2.2.

For the salts of the organic acids, the percentages by weight relate to the acid fraction of the salt concerned.

Preference is given, among saturated C_5 - C_{16}
20 monocarboxylic acids, to C_5 - C_{10} acids, in particular n-hexanoic acid, heptanoic acid, n-octanoic acid and nonanoic acid.

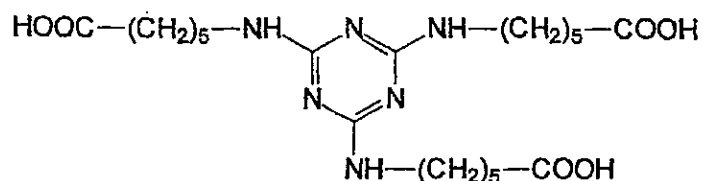
Preference is given, among aliphatic
25 dicarboxylic acids comprising saturated C_4 - C_{12} chains,

to C₄-C₁₀ acids, in particular suberic acid, azelaic acid and sebacic acid.

Preference is given, among unsaturated C₁₀-C₂₂ monocarboxylic acids, to undecylenic acid.

5 When a saturated monocarboxylic acid and a saturated dicarboxylic acid are used together, it is advantageous to combine them in a diacid/monoacid ratio by mass of 0.1:1 to 10:1, preferably 0.6:1 to 5:1.

 The preferred tricarboxylic derivative of
10 1,3,5-triazine is the compound of formula:



RN = 80584-91-4

or its triethanolamine salt.

 The inhibitor system according to the
15 invention can be used in aqueous fluids, with or without antifreeze, for cooling circuits and in particular for cooling circuits of internal combustion engines.

 It can be employed by directly introducing
20 the various components of the inhibitor system into the transfer fluid. It is more convenient to employ mother solutions, which are aqueous solutions comprising from 10 to 60% by weight of the inhibitor system composed of the components (I), (II), (III) and (IV) as described

above, the pH of which will be adjusted by
neutralization, for example with sodium hydroxide, in
order to dissolve all the components and so that the pH
of the transfer fluid will be in the range 7-9,
5 preferably 7.5-8.5.

These aqueous mother solutions are compositions of
the invention.

The system of inhibitors according to the
invention provides protection against multimetal
10 corrosion under cavitation corrosion conditions (high

temperature, high pressure), a fortiori under milder conditions of aggressiveness.

The system of inhibitors of the invention can be used in wide ranges of applications employing media
5 of ferrous iron, cast iron, cuprous copper and aluminium type, in particular. Mention may be made of surface treatment, the working of metals, paint stripping or lubrication.

EXAMPLES

10 The examples which follow will make the invention better understood. They require the results of tests regularly carried out in the automobile industry, which tests are restated here:

- a) The corrosion test in glassware (ASTM
15 Standard D 1384: "Corrosion test for Engine Coolants in Glassware"), which makes it possible to monitor the variations in weight of different metals (copper, solder, brass, steel, cast steel, cast aluminium) after immersion for 336 hours (15 days) at 88°C in a
20 corrosive aqueous medium to which antifreeze has been added;

- b) Hot plate test (ASTM Standard D 4340: "Corrosion of cast aluminium alloys in Engine Coolants under Heat-rejecting Conditions"), by which the
25 variations in weight are monitored of a sample made of cast aluminium, simulating a piston, heated at 135°C

for 168 hours (7 days) and subjected to a pressure of 193 kPa in a corrosive solution (0.165 g/l of NaCl) comprising 25% of antifreeze;

- c) Cavitation test (CEC Standard C-05X-95),
5 by which the variation in mass is measured of test bodies composed of discs made of cast steel and cast aluminium subjected to the action of the circulating flow of a corrosive solution according to ASTM Standard D 1384 (Na_2SO_4 : 148 mg/l, NaCl: 165 mg/l, NaHCO_3 :
10 138 mg/l) under test conditions generating differences in local speed and local pressure and in temperature likely to induce cavitation and corrosion phenomena. The temperature of the test is 115°C, the flow rate of the fluid 300 l/h and the pressure 150 kPa. The
15 duration of the test is 72 hours.

The tests take into consideration three types of inhibitors:

- i) conventional inorganic compositions based on nitrites, on borax or on sodium molybdate,
20 ii) organic or mixed compositions of the prior art comprising sebacic acid,
iii) compositions according to the invention.

For all the test compositions, the inhibitor components were dissolved in ethylene glycol. The pH of
25 the concentrated solution was adjusted to between 7 and 8 by addition of sodium hydroxide. The alkaline reserve

(AR) of these compositions, expressed in millilitres of 0.1N hydrochloric acid, is determined according to ASTM Standard D 1121-93. These concentrated solutions constitute the antifreezes. The cooling liquids are
5 obtained by dilution to 50% with deionized water. The test solution is composed of a corrosive solution to which this cooling liquid has been added in a proportion of 33% by volume, if ASTM Standard D 1384 is applied, 25% by volume for ASTM Standard D 4340 or 20%
10 by volume for CEC Standard C-05X-95.

Use was made, in preparing the compositions given in the examples, of:

- heptanoic acid (C_7) as monocarboxylic acid of type (I),
- 15 - undecylenic acid ($C_{11:1}$) as monocarboxylic acid of type (II),
- the compound Irgacor® L190, sold by Ciba (L190; RN=80584-91-4), as tricarboxylic derivative of triazine,
- 20 - tolyltriazole (TTZ) as triazole derivative.

EXAMPLE 1:

The following compositions were prepared as % by weight with respect to the composition in ethylene glycol, the compositions V9 and V10 being preferred
25 compositions according to the invention; the compositions V_2 , V_3 and V_6 being outside the invention.

Component	COMPOSITION					
	V2	V3	V6	V8	V9	V10
C ₇	-	3	3	2	2.5	2.5
C _{11:1}	-	-	-	0.2	0.3	0.3
L190	2	-	1	1	1	1.5
TTZ	0.1	0.2	0.2	0.1	0.1	0.1

The results in the various tests according to the standards referred to below are given in Table 1.

5 - For ASTM D1384 (corrosion in glassware), the test is successfully passed if the loss in weight is less than 5 mg with respect to copper, 5 mg with respect to brass, 5 mg with respect to solder, 2.5 mg with respect to steel, 4 mg with respect to cast iron
10 and 10 mg with respect to aluminium.

- The ASTM D4340 test (hot plate) is passed if the loss in weight is less than 1 mg/cm²/week.

- The CEC C-05X-95 test is regarded as accepted if the variation in weight is between -50 and
15 +10 mg for aluminium and between -10 and +5 mg for cast iron.

TABLE 1

Test	Speci- fications	COMPOSITION					
		V2	V3	V6	V8	V9	V10
ASTM D 1384							
Copper	- 5 mg	-2.1	-0.1	-0.2	-0.4	-0.4	-0.2
Brass	- 5 mg	-2.0	-0.1	-0.7	-0.5	-0.5	-0.4
Solder	- 5 mg	-6.0	-4.0	-9.3		-5.0	-5.0
Steel	- 2 mg	-3.5	-2.0	-1.0	-0.2	-0.2	-0.1
Cast steel	- 4 mg	-4.7	-2.8	-1.0	-0.5	-0.5	-0.4
Cast Al.	- 10 mg	-9.0	-8.0	-1.5	-0.3	-0.4	-0.3
ASTM D 4340							
Cast Al.	-1 mg/cm ² /wk	-2.5	-1.1	-0.2	-0.4	-0.3	-0.1
CEC C-05X-95							
Cast Al.	-50 +10 mg	-275	-240	-140	-55	-49.2	-45.0
Cast steel	-10 +5 mg	+65	-14	+12	+8	+0.9	+0.5

5 It may be observed that only the systems possessing four inhibitor components and possessing these components within the limits of the claimed compositions pass all the tests. In particular, it is seen how difficult it is to pass the cavitation test.

10 EXAMPLE 2 (Comparative): compositions of the prior art

These are organic (O) or organic/inorganic (I) compositions, with diacids (adipic (H₂C₆) and sebacic (H₂C₁₀)), octanoic acid (C₈), sodium molybdate (Molyb.), sodium nitrite (Nitrite) and tolyltriazole (TTZ), comprising (as % by weight):

Component	COMPOSITION			
	O1	O2	O3	I1
C ₈	2	-	-	-
H ₂ C ₆	-	1	-	-
H ₂ C ₁₀	1.5	3.5	4.25	4.5
Molyb.	-	-	-	0.25
Nitrite	-	-	-	0.25
TTZ	0.1	0.1	0.25	0.1

The results of the tests are given in Table 2 below.

5

TABLE 2

			COMPOSITION		
Test	Speci- fications	O1	O2	O3	I1
ASTM D 1384					
Copper	-5 mg	-1.5	-2.2	-2.2	-2.0
Brass	-5 mg	-1.7	-2.0	-1.8	-1.5
Solder	-5 mg	-10.2	-15	-2.1	-4.2
Steel	-2 mg	-0.5	-0.4	-0.2	-0.1
Cast steel	-4 mg	-0.9	-0.7	+0.5	-0.5
Cast Al.	-10 mg	-5.0	-7.1	-3.2	-3.0
ASTM D 4340					
Cast Al.	-1 mg/cm ² /wk	-0.5	-1.0	-0.1	-0.2
CEC C-05X-95					
Cast Al.	+50 +10 mg	-150	-275	-44	-48.0
Cast steel	-10 +5 mg	+4	-20	+2.6	+2.0

10

Of all these formulae according to the prior art, only the entirely inorganic composition passes all the tests, but with banned or highly inadvisable components. It may also be observed that the composition O3 has an advantageous performance except,

however, in the ASTM D 1384 test for cast steel, where it leads to an increase in weight (instead of a loss). This increase in weight is contraindicated with respect to a potential blockage of the circuits.

5 It is well known to persons skilled in the art that some additional additives can be incorporated in this type of formulation in order to introduce specific properties. The commonest products include antifoaming agents, sequestering agents and colorants.

10 Among commercial antifoaming agents, the following products are particularly suited to the claimed composition:

- Wacker SE47 (silicone-based surfactant)
- Pluronic PE6100 from BASF (nonionic
- 15 surfactant)
- Ultra MS 455-3A (mixture of a silicone
- surfactant and of a PO-EO nonionic
- [lacuna])

 The dose for use of these products is

20 generally between 0.01 and 0.03% by weight with respect to the total of the mother-solutions formulation.

 Among sequestering agents, a product well suited to the formulations is 1-hydroxyethane-1,1-diphosphonic acid and in particular the commercial

product Dequest 2010 from Solutia. This product can exhibit a degree of activity with respect to corrosion tests which may require an adjustment of the overall composition according to the invention.

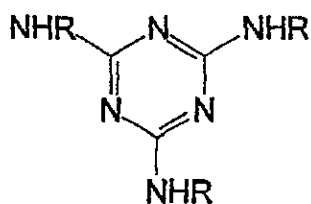
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CLAIMS

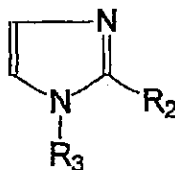
1. Process for inhibiting multimetal corrosion by heat transfer fluids, whether or not these fluids comprise an organic compound which lowers the freezing point, which consists in introducing, into the said fluids, 3 to 6% by weight and preferably 3.8 to 5% of a system of organic inhibitors composed of:
- (I) 5 to 15% by weight of at least one unsaturated monocarboxylic acid comprising 10-18 carbon atoms or of one of its alkali metal salts, amine salts, the amine being from the group of monoethylamine, diethylamine or triethylamine, or alkanolamine salts, the alkanolamine being from the group of monoethanolamine, diethanolamine, triethanolamine or methyldiethanolamine;
 - (II) 40 to 70% by weight of at least one saturated carboxylic acid taken from the group consisting of saturated monocarboxylic acids comprising 5-16 carbon atoms and saturated dicarboxylic acids comprising 4-12 carbon atoms, or an alkali metal or amine or alkanolamine salt of these acids;
 - (III) 20 to 40% by weight of a tricarboxylic derivative of 1,3,5-triazine corresponding to the formula



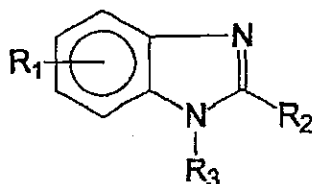
in which formula R is a carboxyalkyl group comprising 2-6 carbon atoms, or an alkali metal or amine or alkanolamine salt of this derivative;

- 5 - (IV) 1 to 5% by weight of an azole derivative taken from the group consisting of:

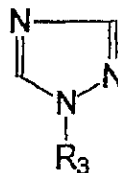
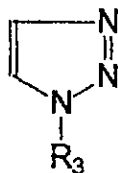
(h) imidazoles of formula



- 10 (i) benzimidazoles of formula

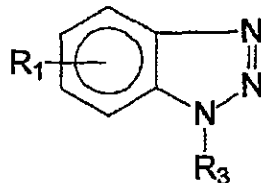


(j) triazoles of formula



or

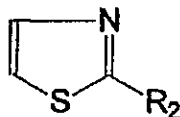
(k) benzotriazoles of formula



(l) tetrahydrobenzotriazole

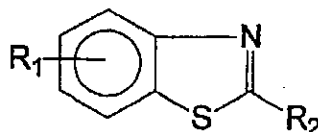
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(m) thiazoles of formula



(n) benzothiazoles of formula

10



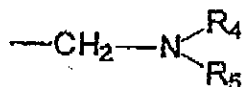
(h) and the alkali metal salts of these
azole derivatives,

15 in which formulae

R_1 is a hydrogen atom or a methyl radical

R_2 is a hydrogen atom or a mercapto radical

R_3 is a hydrogen atom or a radical of formula



with R_4 and R_5 , which are identical or different,
 representing a 2-ethylhexyl or hydroxyalkyl radical, in
 5 particular a hydroxyethyl residue.

2. Process according to Claim 1,
 characterized in that the I/II ratio by weight is between
 5 and 15, and preferably between 8 and 12, and the (I +
 II)/III ratio by weight is between 1.5 and 3 and
 10 preferably between 1.9 and 2.2.

3. Process according to either of Claims 1
 and 2, in which the system of organic inhibitors is
 composed of:

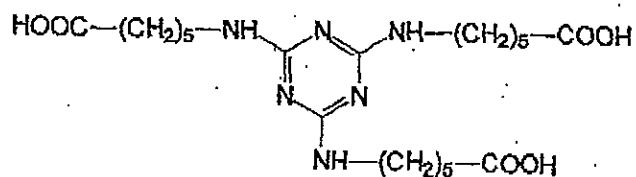
- 6 to 8% by weight of the constituent (I);
- 15 - 55 to 65% by weight of the constituent
 (II);
- 25 to 35% by weight of the constituent
 (III);
- 2 to 3% of the constituent (IV).

20 4. Process according to one of Claims 1 to 3,
 in which the saturated carboxylic acid is n-hexanoic
 acid, heptanoic acid, n-octanoic acid or nonanoic acid.

5. Process according to one of Claims 1 to 3,
 in which the dicarboxylic acid is suberic acid, azelaic
 25 acid or sebacic acid.

6. Process according to one of Claims 1 to 3, characterized in that the unsaturated monocarboxylic acid is undecylenic acid.

7. Process according to one of Claims 1 to 3,
5 in which the tricarboxylic derivative of 1,3,5-triazine is
the compound of formula:



8. Composition which inhibits multimetal corrosion, composed of an aqueous solution assaying from 10 to 60% by weight of an inhibitor system as described in Claims 1 to 5.