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[54] **CORROSION INHIBITING COMPOSITION CONTAINING AN AMINOALKYL-PHOSPHONIC ACID AND AN INORGANIC NITRITE**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.**..... **252/389 A**; 21/2.5 A; 21/2.7 A; 106/14; 252/8.55 E; 210/58; 252/181; 252/387; 252/390

[51] **Int. Cl.²**..... **C23F 11/10**; C23F 11/16

[58] **Field of Search**..... 252/389 A, 387, 8.55 E, 252/181, 390; 21/2.7 A, 2.5 A; 106/14; 210/58

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[57] **ABSTRACT**

The present invention relates to a synergistic composition for inhibiting the corrosion of metal surfaces, particularly ferrous metals, in contact with aqueous systems comprising a combination of an inorganic nitrite and an aminoalkyl-phosphonic acid.

22 Claims, 6 Drawing Figures

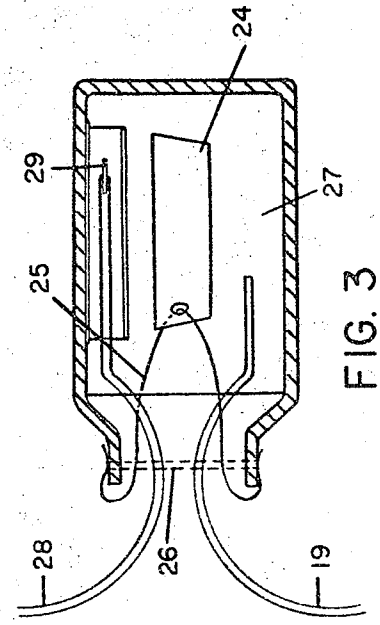


FIG. 3

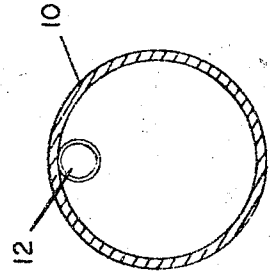


FIG. 2

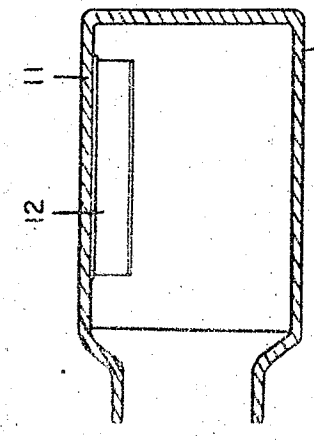


FIG. 1

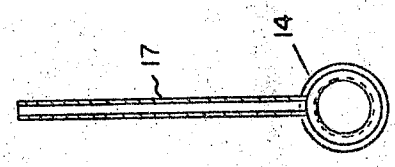
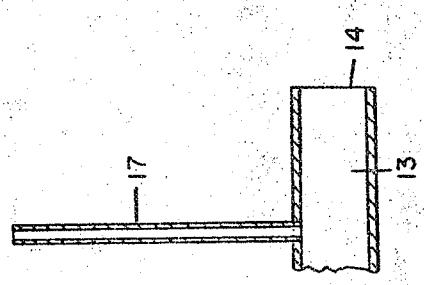


FIG. 5



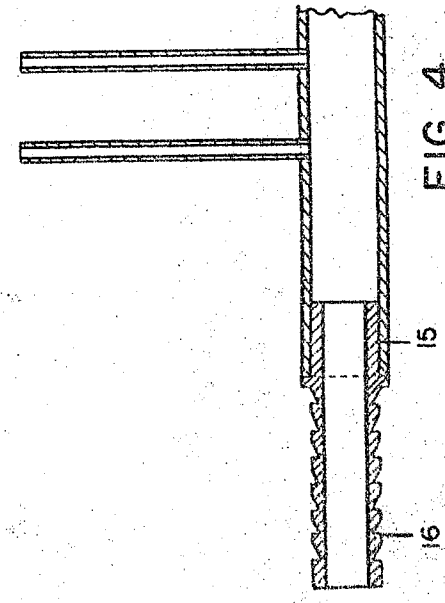


FIG. 4

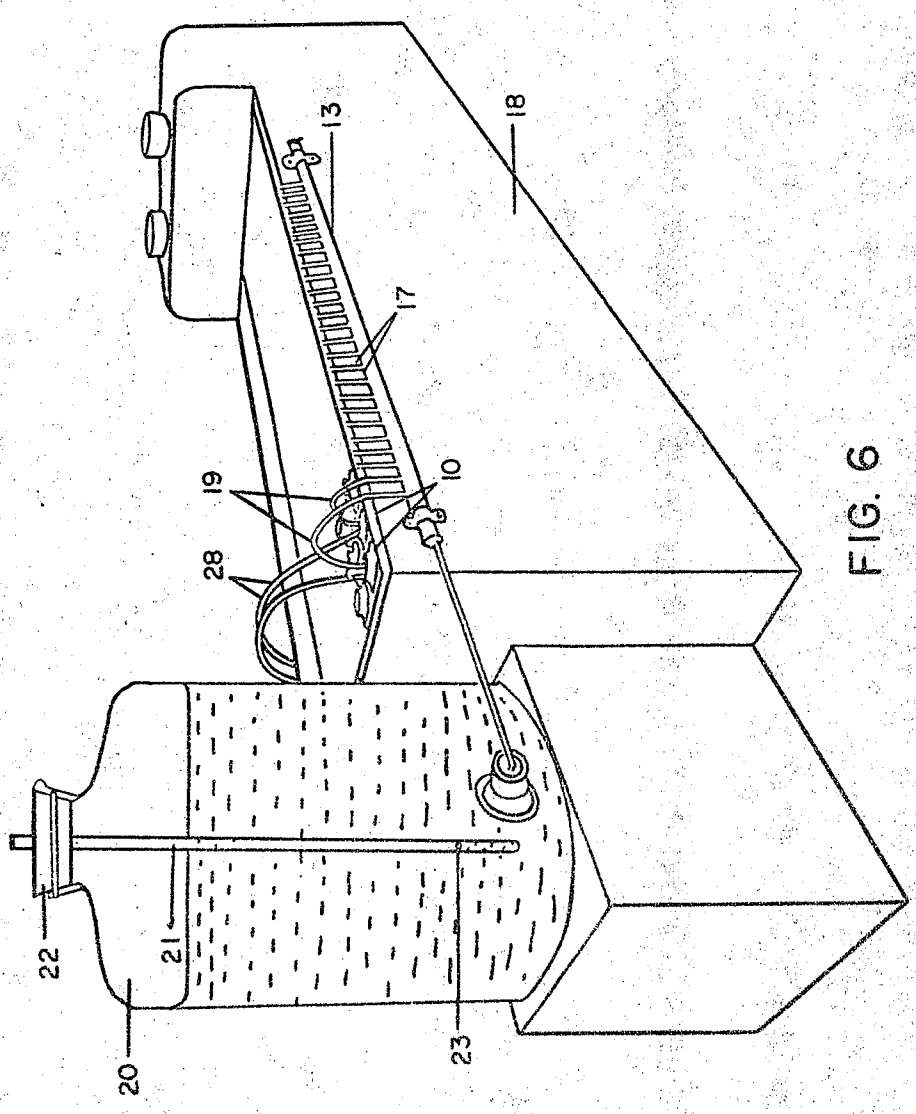


FIG. 6

CORROSION INHIBITING COMPOSITION CONTAINING AN AMINOALKYL-PHOSPHONIC ACID AND AN INORGANIC NITRITE

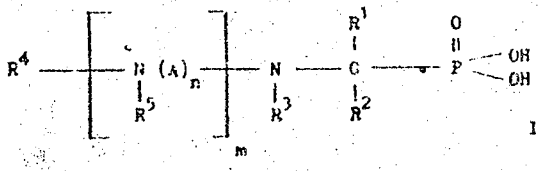
The present invention relates to a composition for inhibiting the corrosion of metal surfaces, particularly ferrous metals, in contact with aqueous systems.

In the past, water-soluble chromates and dichromates have been widely used for inhibiting the corrosion of metals in contact with aqueous systems. However, chromate and dichromate ions are toxic and pollute any stream of river into which water containing them is discharged and are therefore ecologically unacceptable. Inorganic nitrites have been used as corrosion inhibitors, but it is usually necessary to use them at high dosage levels, often as much as 650 parts per million. Amino phosphonic acids have also been proposed as corrosion inhibitors, usually in conjunction with zinc or chromate ions or tannins since when used alone some amino phosphonic acids have the disadvantage that, being sequestering agents, they promote dissolution of the metal with formation of complexed ions.

A major advantage of inorganic nitrites is their cheapness, but this is offset by the fact that it is necessary to use them at high dosage levels. Clearly it would be most advantageous if a corrosion inhibitor combination could be devised, based on nitrite for cheapness, which had at least the same efficiency at much lower dose rates, that is if a suitable compromise could be reached between efficiency, dose rate and cost of use at that dose rate.

Surprisingly we have found that the combination of an inorganic nitrite and a member of certain classes of aminoalkyl phosphonic acids can result in a corrosion inhibitor which is better than could be foreseen from a knowledge of the properties of each, that is to say these compounds can form synergistic combinations. The mechanism of synergism is not simple; in chemical synergism, cases are well known of two or more materials which demonstrate significant synergy when combined in certain ranges of proportions, but whose combined effect is only additive (or even worse than additive) at other proportions, and this is the situation in the present case. All combinations we shall describe show synergism as we shall define it when combined in some proportions; in other proportions, the combined effect may merely be additive, or can be antagonistic.

According to this invention, there is provided a synergistic combination (as hereinafter defined) comprising a combination of an inorganic nitrite and a compound having the formula:



I

wherein R^1 and R^2 may be the same or different and each represents hydrogen or a hydrocarbyl or hydroxy-substituted hydrocarbyl radical containing up to 8 carbon atoms, R^3 and R^4 may be the same or different and each represents hydrogen or a hydrocarbyl or hydroxy-substituted hydrocarbyl radical containing up to 8 carbon atoms, a carboxyalkyl or alkoxy radical containing up to 3 carbon atoms, a phosphonic acid, an alkylene phosphonic acid grouping containing up to 4 carbon atoms or an aralkylene phosphonic acid such that not more than two phosphonic acid groupings separated by less than two carbon atoms may be attached to any nitrogen atom, R^5 is hydrogen or an alkylene phosphonic acid containing up to 4 carbon atoms, A is a saturated divalent hydrocarbyl radical containing up to 6 carbon atoms, m is 0 or an integer from 1 to 60, n is 0 or 1; when m is 0, R^4 may be a hydroxy grouping or R^3 and R^4 together with the nitrogen atom may form a six membered ring, when m is 1, the grouping $R^3N—A—NR^5$ may form a hetercyclic ring. and when m is greater than 1, the constituent R^5 groupings may be the same or diferent; and the water-soluble salts thereof.

If desired, the radicals R^1, R^2, R^3, R^4 and R^5 of the compound of formula I may contain substituents which do not increase the water solubility or react in aqueous solutions, for example, chlorine.

The water-soluble salts of the compounds of formula I may be the alkali metal and ammonium salts or the salts of organic bases, for example, the mono-, di- and tri-ethanolamines, alkyl and arylamines, and guanidine.

In this specification, we define synergism in terms of the graphical interpretation of the results derived from a simple test for corrosion inhibition properties of materials. In this test, the effectiveness of an additive as a corrosion inhibitor in aqueous solution is measured in terms of the loss of metal from a test specimen immersed in the aqueous solution under standard conditions. A result is obtained to show the efficiency of inorganic nitrite by itself as a corrosion inhibitor, and a result is obtained to show the efficiency of the aminoalkyl phosphonic acid under test by itself as a corrosion inhibitor; these are plotted on a graph as the figures for 100% inorganic nitrite and 100% aminoalkyl phosphonic acid. Combinations such as 80% nitrite/20% aminoalkyl phosphonic acid, 60% nitrite/40% aminoalkyl phosphonic acid, 40% nitrite/60% aminoalkyl phosphonic acid and 20% nitrite/80% aminoalkyl phosphonic acid are then tested until a clear graph can be plotted to show the effectiveness as a corrosion inhibitor of all combinations of the nitrite and aminoalkyl phosphonic acid under test. This graph is plotted, and at the same time the linear interpolation between the values for 100% inorganic nitrite and 100% aminoalkyl phosphonic acid is drawn. We define a combination of inorganic nitrite and aminoalkyl phosphonic acid as a synergistic combination if the value of corrosive weight loss observed in practice by means of this test is 90% of or less than 90% of the value of the corrosive weight loss for that combination on the linear interpolation between the values for 100% inorganic nitrite and 100% aminoalkyl phosphonic acid.

The test method we use will be preferred to as the Aerated-Solution Bottle Test and is described in detail as follows:

The apparatus itself is described with reference to the accompanying drawings. FIG. 1 is a longitudinal section of the bottle used for the test to show a length of glass tubing cemented to the inside of the bottle using "Araldite" resin AY103 in conjunction with hardener HY965. About 2 grams of the mixture for each bottle is usually required.

FIG. 2 is a transverse cross-section of the bottle used for the test.

FIG. 3 is a longitudinal section of the bottle in use during the test showing the connections and contents.

FIG. 4 is a contracted longitudinal section of a water distributor with T-pieces

FIG. 5 is a cross-section of a water distributor with a T-piece.

FIG. 6 is a perspective view of the whole apparatus.

Referring to FIGS. 1 and 2, the bottle, 10, having a volume of approximately 130 millilitres has attached to the inside wall by means of cement, 11, a glass chimney, 12, which is 2 inches in length and positioned so that there is a ¼ inch gap between the bottom of the tube and the bottom of the bottle.

In FIG. 3 the bottle, 10, is shown with a mild steel test coupon, 24, suspended from the neck of the bottle by a nylon thread, 25, which is held in position round the neck by a rubber band, 26. A piece of polythene tubing, 19, dips below the surface of the water, 27, in the bottle, 10, and another piece of polythene tubing, 28, having an internal diameter of 0.030 inches fitted with a jet, 29, passes into the glass chimney, 12, and terminates near the bottom of the glass chimney.

Referring to FIGS. 4 and 5, a distributor, 13, made from copper tubing 17 inches in length and having an outside diameter of ⅝ inch, is sealed at one end, 14. The other end, 15, is threaded to take a nozzle 16 and polythene tubing, of ¼ inch internal diameter is fitted over this nozzle. Into the copper tube are welded 30 pieces of copper tubing, 17, each of which are 2 inches long, have an internal diameter 1/16 inch and are spaced ½ inch apart to form effectively 30 T-pieces.

In FIG. 6, the bottles, 10, are placed in a thermostatted water-bath, 18. Pushed over the ends of the T-pieces, 17, are lengths of polythene tubing, 19, approximately 12 to 15 inches in length and ⅛ inch internal diameter. A 20-litre water reservoir, 20, is connected to each of the bottles via the distributor, 13, and polythene tubing, 19, dipping below the surface of the liquid in each of the bottles, 10. The reservoir is tightly stoppered with a long glass tube, 21, passing through a rubber bung, 22, to the bottom of the reservoir. A small hole, 23, is made in the wall of the tube near the bottom.

In the test itself a sample of the mixture to be tested is added to a 100 millilitre sample of a synthetic corrosive water having the following composition

20 grams $CaSO_4.2H_2O$
15 grams $MgSO_4.7H_2O$
4.6 grams $NaHCO_3$
7.7 grams $CaCl_2.6H_2O$
45 gallons of distilled water.

The concentration of the mixture to be tested is 100 parts of mixture per million parts of synthetic corrosive water.

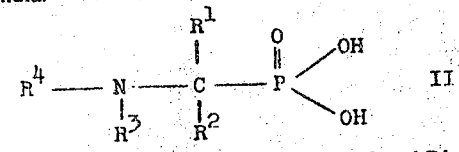
A mild steel test coupon (5 × 2.5 centimetres), which has been scrubbed with pumice, dipped for one minute in hydrochloric acid, dried and weighed, is suspended below the surface of the solution. The solution is then stored at 40°C in the thermostatted water bath.

During the storage period the bottle is continuously aerated by passing air (500 millilitres/minute) through the tube, 28, screened from the metal surface by the glass chimney, 12. The aeration of the bottle is controlled by a rotameter calibrated in litres per minute which is connected to an air supply. The outlet of the rotameter is connected to a distributor, constructed similarly to that already described, by polythene tubing. Control of the air bubble size and individual aeration rates in each bottle is achieved by using the polythene tubing, 28, with the jet, 29. Water losses caused by evaporation are replenished with deionised water dispensed from a constant head device, this being the 20-litre water reservoir which is connected to the distributor, 13 by polythene tubing and then to the bottle containing the sample by more polythene tubing. The position of the glass tube, 21, in the reservoir is adjusted so that the level of the hole, 23, coincides with the required water level in the bottle under test.

After 48 hours the mild steel coupon is removed, scrubbed with pumice, dipped in hydrochloric acid inhibited with 1% by weight of hexamine for one minute and reweighed.

The corrosion rate is recorded as the weight loss in terms of milligrams per square decimetre per day (m.d.d.). Each test is carried out on duplicate specimens.

The following particular classes of compounds may be selected from the general formula I. Class I having the formula:

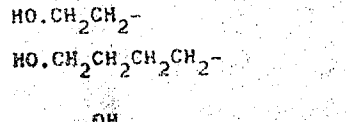


II

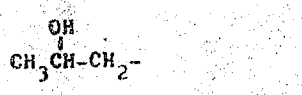
derived from the general formula I where n=0 and R^1, R^2, R^3 and R^4 may represent hydrogen, hydrocarbyl or hydroxyl substituted hydrocarbyl, R^3 and R^4 may represent carboxyalkyl, or R^3 and R^4 together with the nitrogen atom may form a 6-membered ring, and the total number of carbon atoms in the groups R^3 and R^4 together does not exceed 10.

The hydrocarbyl or hydroxy substituted hydrocarbyl group may be:

a. alkyl, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-hexyl, n-octyl or t-octyl group but preferably a methyl group.
b. aryl, for example phenyl
c. alkaryl, for example o,m,p-tolyl
d. aralkyl, for example benzyl
e. alkenyl, for example allyl, α-methallyl, crotonyl
f. cycloalkyl, for example cyclohexyl
g. hydroxyalkyl, for example:

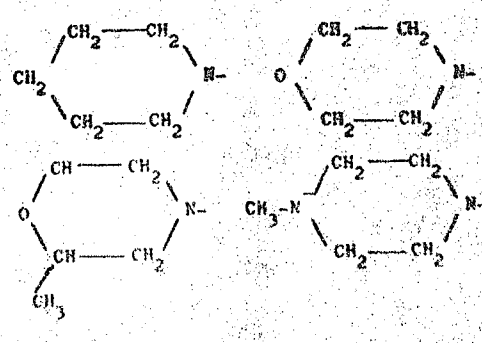


or

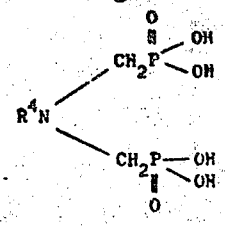


The carboxyalkyl group may be for example carboxymethyl or β-carboxymethyl groups.

The six-membered ring may be for example:

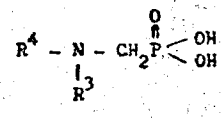


Class II having the formula:



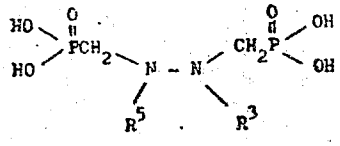
III

derived from the formula I where m=0, R^1 and R^2 are both hydrogen, R^3 is a methylene phosphonic acid grouping and R^4 is a hydrocarbyl or hydroxy substituted hydrocarbyl radical. Class III having the formula:



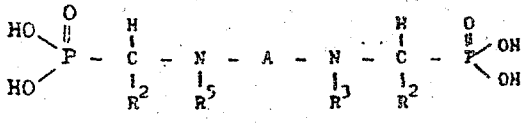
IV

derived from formula I wherein $m = 0$, R^3 is hydrogen or a methylene phosphonic acid grouping and R^4 is a hydroxy, $-CH_2COOH$ or a $-CH_2CH_2COOH$ grouping. Class IV having the formula:

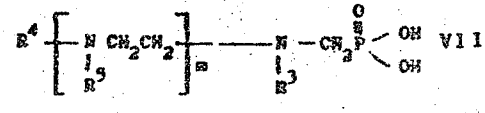


V

derived from formula I wherein R^1 and R^2 are hydrogen, R^3 is hydrogen or a methylene phosphonic acid grouping, $m = 1$, $n = 0$, R^5 is hydrogen or a methylene phosphonic acid grouping and R^4 is a methylene phosphonic acid grouping. Class V having the formula:



derived from the fromula I where $m = 1$, $n = 1$, R^1 is hydrogen R^2 may be hydrogen or a hydroxy phenyl grouping, R^3 and R^5 are the same and are hydrogen or methylene phosphonic acid groupings and A is a saturated divalent hydrocarbyl, which may be linear or branched, containing from 1 to 6 carbon atoms and may be for instance a methylene, ethylene, n-propylene, isopropylene, n-butylene, m-phenylene or p-phenylene grouping; or the grouping $R^5N—A—NR^5$ may form a ring for instance to give a piperazinyl grouping; and R^4 is a methylene phosphonic acid grouping. Class VI having the formula



VII

derived from formula I where m is a positive integer from 2 to 60, $n = 1$, A is an ethylene grouping, R^3, R^4 and R^5 may each be hydrogen or a methylene phosphonic acid grouping, provided that at least 50% of these groups are methylene phosphonic acid groups, and that not all the R^5 groupings need be identical.

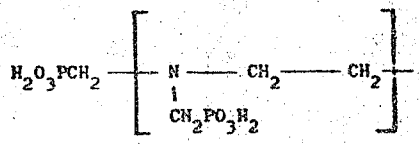
Examples of compounds of class I are α(2-acetoxy anilino) benzyl phosphonic acid, α-anilino orthohydroxy benzyl phosphonic acid, piperidino methylene phosphonic acid and amino methane phosphonic acid.

Examples of compounds of Class II are methyl amino di(methylene phosphonic acid), ethyl amino di(methylene phosphonic acid), n-pentylamino di(methylene phosphonic acid), n-hexylamino di(methylene phosphonic acid), p-toluidino di(methylene phosphonic acid), hydroxy ethyl amino di(methylene phosphonic acid), n-propylamino di(methylene phosphonic acid), allylamino di(methylene phosphonic acid) and cyclohexylamino di(methylene phosphonic acid).

An example of a compound of Class III is hydroxy amino methylene phosphonic acid and carboxy methyl amino di(methylene phosphonic acid) and hydroxy amino di(methylene phosphonic acid). An example of a compound of Class IV is hydrazine tetra(methylene phosphonic acid).

An example of a compound of Class V is ethylene diamine tetra(methylene phosphonic acid).

An example of a compound of Class VI is a compound having the formula:



VIII

$—N(CH_2PO_3H_2)_2$

41.5(average)

The compositions of the present invention contain from 10% to 99% by weight of an inorganic nitrite and from 90% to 1% by weight of an aminoalkylphosphonic acid having the formula I. Preferred synergistic combinations are compositions containing a compound of Class I, II, V or VI in combination with from 10% to 95% by weight of sodium nitrite; compositions containing a compound of Class III in combination with from 10% to 90% by weight of sodium nitrite and compositions containing a compound of Class IV in combination with from 10% to 80% by weight of sodium nitrite.

In order to illustrate the synergism obtained more clearly, FIGS. 7 to 12 in the accompanying drawings were plotted to show the efficiency as corrosion inhibitors of mixtures of sodium nitrite and a compound of each of the classes 1 to 6. FIGS. 7 to 12 show the variation of the corrosion ratio against the percentage of sodium nitrite in the mixture. The corrosion ratio is defined as the corrosion rate in the presence of the mixture divided by the corrosion rate in the presence of 100% sodium nitrite. The value for 100% sodium nitrite is, therefore, 1 in all examples.

FIG. 7 shows the synergism obtained for a mixture containing methylamino di(methylene phosphonic acid), a compound of Class II;

FIG. 8 shows the synergism obtained for a mixture containing hydrazine tetra(methylene phosphonic acid) a compound of Class IV;

FIG. 10 shows the synergism obtained for a mixture containing α-anilino orthohydroxy benzyl phosphonic acid a compound of Class I. Graph 9 shows the syner-

gism obtained for carboxy methylamino di(methylene phosphonic acid), a compound of Class III;

FIG. 11 shows the synergism obtained for ethylene diamine tetra (methylene phosphonic acid), a compound of Class V; and FIG. 12 shows the synergism of a compound of Class VI wherein m has an average value of 41.5.

From these graphs, it can easily be seen that excellent results are obtained when the compounds of formula I present in the mixtures are hydrazine tetra(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), methylamino di(methylene phosphonic acid) and α-anilino ortho hydroxy benzyl phosphonic acid.

Particularly preferred synergistic combinations of the present invention are those where the value of corrosion observed in practice by means of this test is 50% or less than 50% of the value of the corrosion for that combination on the linear interpolation between the values for 100% inorganic nitrite and 100% aminoalkylphosphonic acid. As can be seen from the graphs, mixtures which give such a corrosion value are:

1. Mixtures of methylaminodi(methylene phosphonic acid and sodium nitrite containing from 30% to 85% sodium nitrite.
2. Mixtures of hydrazine tetra(methylene phosphonic acid) and sodium nitrite containing from 22% to 30% of sodium nitrite.
3. Mixtures of α-anilino ortho hydroxy benzyl phosphonic acid and sodium nitrite containing from 30% to 85% of sodium nitrite.
4. Mixtures of ethylene diamine tetra(methylene phosphonic acid) and sodium nitrite containing from 25% to 85% sodium nitrite.

Mixtures of the compound of Class VI where the average value of *m* is 41.5 and sodium nitrite containing from 20% to 80% sodium nitrite.

The nitrite that is used may be an alkali metal nitrite, for example, potassium nitrite, but is preferably sodium nitrite.

The present invention also provides an aqueous system containing a synergistic combination as hereinbefore defined.

Furthermore there is provided a method of forming or replenishing an inhibited aqueous solution which comprises adding to the system inorganic nitrite or a compound of formula I or both in such quantities that the effect of their addition is to cause synergism as hereinbefore defined. Conveniently, the corrosion inhibiting mixture is present in an amount of from 50 to 10,000 parts per million of the aqueous solution. However amounts greater than 200 parts per million are usually unnecessary except when added in initial 'shock' doses.

If desired there may be added to the mixture, specific corrosion inhibitors for non-ferrous metals such as a silicate to control attack on aluminum, or a specific inhibitor to control attack on (or induced by) copper. There may also be added other corrosion inhibitors for ferrous metals known per se, e.g., zinc, polyphosphate or chromium ions or amines.

The following Examples further illustrate the present invention. Parts and percentages are expressed by weight.

EXAMPLES 1 to 8

In each of the following Examples, four mixtures were made up from sodium nitrite and a compound of formula I as illustrated in Table 1, each mixture containing 20%, 40%, 60% and 80% by weight of the compound of formula I respectively. Samples of each of these mixtures were added to 100 millilitre samples of the agressive as hereinbefore defined water so that four solutions were prepared each containing 100 parts per million of the mixture. The aerated bottle test was carried out on these solutions.

In order to demonstrate the synergistic effect of the mixtures of the present invention when compared with the individual constituents of the mixture, samples containing sodium nitrite and the respective compound of formula I were tested separately in a similar manner at concentrations of 100 parts per million. The corrosion ratio was calculated as hereinbefore defined and the results are shown in Table 1.

The results obtained clearly show the synergism of mixtures of the present invention.

EXAMPLES 9 to 20

The same procedure described in Examples 1 to 8 was followed except that instead of four mixtures, three mixtures were made up containing 25%, 50% and 75% by weight of various other compounds of formula I. The results are shown in Table 2.

TABLE 1

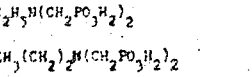
Example	Compound of Formula 1	Corrosion Ratio of mixtures containing varying percentages of compound of formula 1					
		100%	80%	60%	40%	20%	0%
1	$CH_3N(CH_2PO_3H_2)_2$	0.68	0.59	0.16	0.03	0.19	1.00
2	$C_2H_5N(CH_2PO_3H_2)_2$	1.19	0.69	0.51	0.14	0.33	1.00
3	$CH_3(CH_2)_2N(CH_2PO_3H_2)_2$	1.79	1.09	0.25	0.42	0.39	1.00
4	$CH_2{=}CHCH_2N(CH_2PO_3H_2)_2$	0.37	0.19	0.05	0.31	0.24	1.00
5	$C_6H_{13}N(CH_2PO_3H_2)_2$	2.25	0.96	0.37	0.01	0.20	1.00
6		1.28	0.95	0.81	0.33	0.47	1.00

Table I—Continued

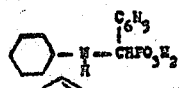
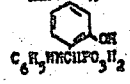
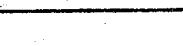
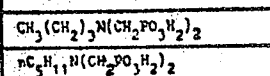
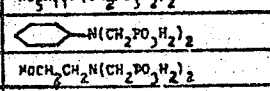
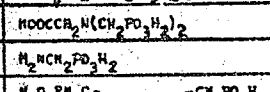
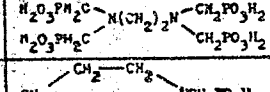
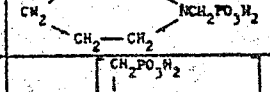
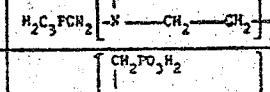
Example	Compound of Formula 1	Corrosion Ratio of mixtures containing varying percentages of compound of formula 1					
		100%	80%	60%	40%	20%	0%
7		1.20	0.89	0.72	0.08	0.68	1.00
8		1.08	0.58	0.09	0.02	0.78	1.00

TABLE 2

Example	Compound of Formula I	Corrosion Rate of Mixtures Containing varying Percentages of Compound of Formula I				
		100%	75%	50%	25%	0%
9	$CH_3(CH_2)_3N(CH_2PO_3H_2)_2$	0.63	0.36	0.34	0.62	1.00
10	$nC_5H_{11}N(CH_2PO_3H_2)_2$	1.04	0.32	0.57	0.80	1.00
11		0.41	0.33	0.04	0.33	1.00
12	$HOCH_2CH_2N(CH_2PO_3H_2)_2$	0.62	0.46	0.55	0.55	1.00
13	$HOOCCH_2N(CH_2PO_3H_2)_2$	0.73	0.61	0.52	0.80	1.00
14	$H_2NCH_2PO_3H_2$	0.67	0.36	0.54	0.54	1.00
15		0.62	0.28	0.06	0.03	1.00
16		0.21	0.24	0.45	0.49	1.00
17		0.48	0.55	0.51	0.80	1.00
18	 13.5 (average)	0.09	0.07	0.08	0.48	1.00
19	 41.5 (average)	0.11	0.13	0.17	0.27	1.00
20		1.07	0.44	0.74	0.86	1.00

Some further laboratory tests were carried out using a Laboratory Heat Exchanger Rig, a form of laboratory testing intended to simulate practical use conditions more closely than does the Aerated Solution Bottle Test just described. In this rig, corrosive water is aerated and circulated over a number of metal coupons, and is heated by being passed through a heated steel heat exchanger tube. After a suitable test period, the metal coupons and the heat exchanger tube are examined, and their state assessed.

In detail, the rig consists of a closed water circuit, made up of the following items in order;

2 litre reservoir
1 litre reservoir
flow meter
coupon chamber
heat exchanger
cooling condenser

Corrosive water in the 2 litre reservoir is aerated with compressed air introduced through a sintered disc at about 5 litres per minute, and is then pumped to the 1 litre reservoir. From this reservoir it is pumped through the flow meter to the glass coupon chamber in which are a number of rectangular metal coupons each 2.5 by 5.0 cms. mounted on a perspex jig. The water then flows through the heat exchanger which is made up of a ⅝ inch internal diameter steel tube with copper end pieces around which is wound a 960 watt heater coil; from the heat exchanger the water flows through the cooling condenser back to the 2 litre reservoir.

A flow rate in the circuit of about 1.0 gallon per minute provides a velocity of about 1.25 feet per second and a Reynolds number of approx. 6,000 in the heat exchanger. The heater coil gives the heat exchanger tube a skin temperature of about 60°C. and the water leaves at about 45°C., a difference across the heat transfer surface of some 15°C. The cooling condenser is so operated as to cool the water to about 35°C. before it begins a fresh circuit.

Metal coupons are scrubbed with pumice and then immersed in acid as follows

metal	acid
mild steel	Conc. HCl diluted 1:1 with water at room temperature for 1 minute
copper	do.
brass	do.
aluminium	5% phosphoric acid/2% chromic acid, at 75°C. for 5 minutes

The results obtained are illustrated in Table 3 and show quite clearly that synergistic mixtures of the present invention are at least as good as, if not better than, corrosion inhibiting mixtures containing zinc and/or chromate ions.

Run	CORROSION RATE OF METAL COUPONS mg. per sq. decimetre per day				Condition of Heat Exchange Tube
	Mild Steel	Copper	Brass	Aluminium	
1	69	42	15.6	5.5	SEVERELY CORRODED
2	42.5	1	5	25	WHOLE SURFACE ENCRUSTED WITH HEAVY CORROSION PRODUCTS
3	4.4	0.3	0.5	2.6	SMALL PATCHES OF CORROSION. REST OF TUBE SURFACE COVERED BY A PROTECTIVE GREEN FILM
4	1.8	1.6	1.0	1.3	do.
5	2.6	1.5	1.1	1.1	SURFACE PROTECTED APART FROM SOME SMALL PITS
6	19.4	0.8	2.4	6.7	CORROSION UNDER SCALE DEPOSIT

After such immersion, the coupons are rinsed with water, dried and weighed; they are then mounted on a perspex jig, care being taken to ensure that none of the coupons touch each other, and that they are insulated from the bolt holding the jig together. The heat exchanger tube is cleaned with pumice, dipped in conc. hydrochloric acid diluted 1:1 with water, and then rinsed in water and dried.

The rig is assembled, and cleaned thoroughly by circulating conc. hydrochloric acid diluted 1:1 with water, then flushing with tap water for about half an hour (about 30 gallons in all) and draining. The necessary quantity of additives to produce the desired concentrations is put into one of the reservoirs and the rig is filled with 4.5 litres of a standardised corrosive test water, which is characterised as follows:

Phenol Alkalinity	0	
Total Alkalinity	20	as p.p.m. of $CaCO_3$
Total Hardness	80	
Chloride	10	p.p.m.
Conductance	180	

The pump is primed and started, and the heater switched on.

The concentration of inhibitor and the water level in the rig are checked daily and any losses made good.

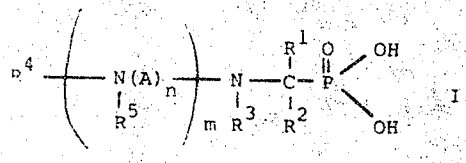
After a standard period of 10 days, the heat exchanger tube is removed, sectioned and examined; the test coupons are removed, cleaned as before except that the acid is in each case inhibited with 1% hexamine, rinsed, dried and reweighed. The results observed enable an assessment to be made of the anti-scaling and anti-corrosive action of the inhibitor under test.

The following additives were tested, all parts and percentages being by weight:

Run	Additives and Concentration	
1		None
2	200 ppm	Sodium nitrite
3	200 ppm	20% methylammo dimethylene diphosphonic acid 80% sodium nitrite
4	Initial level of 400 ppm	20% methylammo dimethylene diphosphonic acid 80% sodium nitrite followed by maintenance as for Run 3
5	50 ppm	Synergised Zinc/chromate, 8% Zn^{++}, 44% CrO_4^{--}
6	100 ppm	Zinc/Polyphosphate, 10.7% ZnO, 57% P_2O_5, 32.3% Na_2O

We claim:

1. A synergistic combination consisting essentially of a combination of from 10% to 99% by weight of an alkali metal nitrite and from 90% to 1% by weight of a compound having the formula



I

wherein

R^1 and R^2 may be the same or different and each represents hydrogen or a hyrocarbyl or hydroxy-substituted hydrocarbyl radical containing up to 8 carbon atoms,

R^3 and R^4 may be the same or different and each represents hydrogen or a hydrocarbyl or hydroxy-substituted hydrocarbyl radical containing up to 8 carbon atoms, a carboxy-alkyl or alkoxy radical containing up to 3 carbon atoms, a phosphonic acid, an alkylene phosphonic acid grouping containing up to 4 carbon atoms or an aralkylene phosphonic acid such that not more than two phosphonic acid groupings separated by less than two carbon atoms may be attached to any nitrogen atoms,

R^5 is hydrogen or an alkylene phosphonic acid containing up to 4 carbon atoms,

A is a saturated divalent hydrocarbyl radical containing up to 6 carbon atoms.

m is 0 or an integer from 1 to 60,

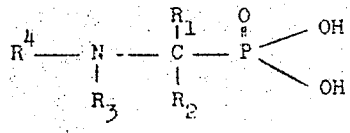
n is 0 or 1; when m is 0, R^4 may be a hydroxy grouping or R^3 and R^4 together with the nitrogen atom may form a six membered ring; when m is 1, the grouping $R^3N—A—NR^5$ may form a heterocyclic ring, and when m is greater than 1, the constituent R^5 groupings may be the same or different; and the water-soluble salts thereof.

2. A synergistic combination as claimed in claim 1 in which the water-soluble salt of the compound of formula I is the alkali metal or ammonium salt.

3. A synergistic combination as claimed in claim 1 in which the alkali metal nitrite is sodium nitrite.

4. A synergistic combination as claimed in claim 1, comprising a mixture containing from 10% to 99% of sodium nitrite and from 90% to 1% of a compound having the formula I, wherein R^1 and R^2 may be the same or different and each represents hydrogen or alkyl, alkenyl or cycloalkyl containing up to 8 carbon atoms, R^3 and R^4 may be the same or different and each represents hydrogen or alkyl, alkenyl or cycloalkyl radical containing up to 8 carbon atoms, an alkylene phosphonic acid grouping containing up to 4 carbon atoms such that not more than two phosphonic acid groupings separated by less than two carbon atoms may be attached to any nitrogen atom, R^5 is hydrogen or an alkylene phosphonic acid containing up to 4 carbon atoms, A is an alkylene radical containing up to 6 carbon atoms, m is 0 or an integer from 1 to 60, n is 0 or 1, and when m is greater than 1, the constituent R^5 groupings may be the same or different, and the water-soluble salts thereof.

5. A synergistic combination as claimed in claim 1 in which the compound of formula I has the formula

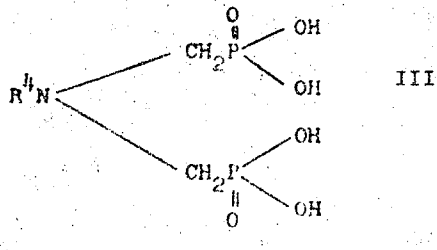


II

where R^1, R^2, R^3 and R^4 may represent hydrogen, hydrocarbyl or hydroxy substituted hydrocarbyl, R^3 and R^4 may represent carboxyalkyl, or R^3 and R^4 together with the nitrogen atom may form a 6-membered ring, and the total number of carbon atoms in the groups R^3 and R_4 together does not exceed 10.

6. A synergistic combination as claimed in claim 5 in which the compound of formula II is α(2-acetoxy anilino) benzyl phosphonic acid, α-anilino ortho-hydroxy benzyl phosphonic acid, piperidino methylene phosphonic acid or amino methane phosphonic acid.

7. A synergistic combination as claimed in claim 1 in which the compound of formula I has the formula

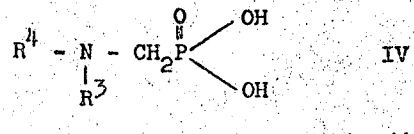


III

where R^1 and R^2 are both hydrogen, R^3 is a methylene phosphonic acid grouping and R^4 is a hydrocarbyl or hydroxysubstituted hydrocarbyl radical.

8. A synergistic combination as claimed in claim 7 in which the compound of formula III is methyl amino di(methylene phosphonic acid), ethyl amino di(methylene phosphonic acid), n-hexylamino di(methylene phosphonic acid), p-toluidino di(methylene phosphonic acid) or hydroxy ethyl amino di(methylene phosphonic acid), n-pentylamino di(methylene phosphonic acid), n-propylamino di(methylene phosphonic acid), allylamino di(methylene phosphonic acid), or cyclohexylamino di(methylene phosphonic acid).

9. A synergistic combination as claimed in claim 1 in which the compound of formula I has the formula

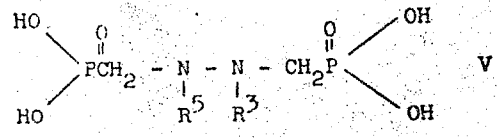


IV

wherein R^3 is hydrogen or a methylene phosphonic acid grouping and R^4 is a hydroxy, $—CH_2COOH$ or a $—CH_2CH_2COOH$ grouping.

10. A synergistic combination as claimed in claim 9 in which the compound of formula IV is hydroxy amino methylene phosphonic acid, carboxymethylamino di(methylene phosphonic acid) or hydroxy amino di(methylene phosphonic acid).

11. A synergistic combination as claimed in claim 1 in which the compound of formula I has the formula

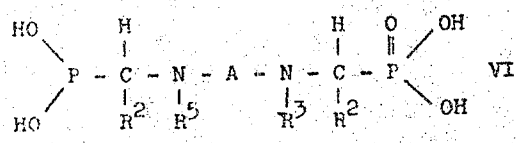


V

wherein each of the groupings R^3 and R^5 is hydrogen or a methylene phosphonic acid grouping.

12. A synergistic combination as claimed in claim 11 in which the compound of formula V is hydrazine tetra(methylene phosphonic acid).

13. A synergistic combination as claimed in claim 1 in which the compound of formula I has the formula



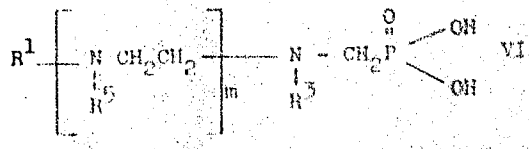
VI

where R^2 is hydrogen or a hydroxy phenyl grouping, R^3 and R^5 are the same and are hydrogen or methylene phosphonic acid groupings and A is a linear or branched saturated divalent hydrocarbyl, containing from 1 to 6 carbon atoms; or the grouping $R^3N—A—NR^5$ may form a ring.

14. A synergistic combination as claimed in claim 13 wherein A, in the compound of formula VI, is a methylene, ethylene, n-propylene, isopropylene, n-butylene, m-phenylene or p-Phenylene grouping.

15. A synergistic combination as claimed in claim 13 wherein the compound of formula VI is ethylene diamine tetra(methylene phosphonic acid).

16. A synergistic combination as claimed in claim 1 in which the compound of formula I has the formula

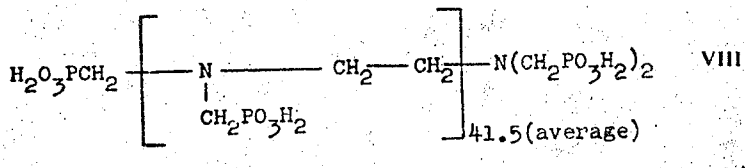


VII

where m is a positive integer from 2 to 60, R^3, R^4 and R^5 may each be hydrogen or a methylene phosphonic

acid grouping, provided that at least 50% of these groups are methylene phosphonic acid groups, and that not all the R^5 groupings need by identical.

17. A synergistic combination as claimed in claim 16 in which the compound of formula VII is:



VIII

18. A synergistic combination as claimed in claim 1 consisting essentially of a mixture containing methylamino di(methylene phosphonic acid) and from 30 to 85% by weight of sodium nitrite.

19. A synergistic combination as claimed in claim 1 consisting essentially of a mixture containing hydrazine tetra(methylene phosphonic acid) and from 22% to 30% by weight of sodium nitrite.

20. A synergistic combination as claimed in claim 1 consisting essentially of a mixture containing α-anilino ortho hydroxy benzyl phosphonic acid and from 30% to 85% of sodium nitrite.

21. A synergistic combination as claimed in claim 1 consisting essentially of a mixture containing ethylene diamine tetra (methylene phosphonic acid) and from 25% to 85% sodium nitrite.

22. A synergistic combination as claimed in claim 17 consisting essentially of a mixture containing a compound of formula VIII and from 20% to 80% sodium nitrite.

* * * * *