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CORROSION INHIBITION WITH A MIXTURE OF INHIBITORS OF DIFFERING VOLATILITY

Aaron Wachter and Nathan Stillman, Berkeley, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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The present invention relates to a method of preventing or inhibiting corrosion of metal surfaces, which corrosion normally occurs in the presence of water, and to the novel compositions of matter employed in such a method. More specifically, this invention relates to employing two or more vapor phase inhibitors in the presence of each other under conditions in which at least two of them are complementary to each other.

A vapor phase inhibitor may be defined as comprising a compound which inhibits corrosion of metal parts in the presence of water and air (oxygen) because said compound possesses corrosion-inhibiting properties and is capable of vaporization under conditions of use with the resultant presence of these vapors in the vicinity of the metal.

During storage, handling, transportation, operation, and use of objects having metalliferous surfaces, as for example various metal articles, particularly those of ferrous metals, various steels, aluminum, and alloys of these metals, it is often necessary to prevent the corrosion of these metals that occurs in the presence of water vapor. Heretofore, the various methods tried to prevent such corrosion have been unsatisfactory because they did not adequately prevent the corrosion, were cumbersome, and/or required an excessive amount of labor and expenditure of time. For example, it has been common to smear grease over engines, exposed metal surfaces, and military ordnance equipment subject to common rusting, in an attempt to provide a physical barrier to water and air and thereby prevent corrosion. As a result of the necessary liberal use of grease, the job of preparing an inactive naval ship for return to active duty was a long and costly one, involving many thousands of man-hours spent mostly in removing the grease, and also in replacing deteriorated equipment that had not been protected sufficiently from corrosion by the grease. A serious defect of previous corrosion-preventive means was that they were particularly inadequate or ineffective in preventing initial corrosion due to the presence of high concentrations of water in the atmosphere (usually air) contiguous to the metal.

It is, therefore, an object of the present invention to provide novel methods and means for overcoming the above and other defects of the prior art. It is a primary object of the invention to provide mixtures of complementary vapor phase inhibitors (and methods and means of utilizing such mixtures) for both initial and subsequent corrosion-prevention of metal surfaces. Another object of this invention is to provide mixtures of vapor phase corrosion-inhibitors capable of maintaining an effective corrosion-preventive atmosphere around a metal object normally subject to corrosion when in the presence of air (oxygen) and moisture. Another object is to provide a composition which is capable of rapid immediate vapor phase corrosion inhibition combined with effective corrosion inhibition over prolonged periods of time.

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It has now been discovered that the above and other objects are attained by introducing into the proximity of a corrodible metal, vapors of at least two organic vapor phase corrosion-inhibitors at least, one of which has a relatively higher vapor pressure with respect to that of the other or others, each vapor phase inhibitor having a vapor pressure of at least about 0.00002 mm. Hg at 21° C., and preferably a vapor pressure of at least about 0.0001 mm. Hg at 21° C.

Preferred vapor phase corrosion-inhibitors employed in accordance with the present invention are salts of organic bases with nitrous acid, i. e., organic base nitrites, more preferably, organic nitrogen-base nitrites.

It has been discovered that the relatively higher vapor pressure component of the mixture preferably should have a vapor pressure higher than about 0.001 mm. Hg at 21° C. The introduction of the as yet unvaporized form of a mixture of at least two organic vapor phase inhibitors at least, one with a high vapor pressure and at least one with a low vapor pressure, in the vicinity of a corrodible metal within an enclosure prevents corrosion of the metal from the outset and for prolonged periods of time. A composition comprising an organic inhibitor having a relatively high vapor pressure and a second organic inhibitor having a relatively low vapor pressure, as for example a mixture of diisopropylamine nitrite and dicyclohexylamine nitrite, is particularly advantageous for the practice of the invention and may be used per se or together with a carrier. Rapid and immediate protection of metals from corrosion is attained by the use of such and similar combinations. For example, for certain types of packaging problems wherein relatively large quantities of moisture are present at the time the package is sealed, it has been found to be particularly advantageous to enclose, or form as part of the package, one of the present mixtures of complementary organic vapor phase corrosion-inhibitors. In this manner the inhibitor having the higher vapor pressure provides immediate

protection against corrosion, while the inhibitor with the relatively lower vapor pressure provides long term corrosion-inhibition.

The present combinations of vapor phase organic corrosion-inhibitors have also been found to provide a gradual building up of a sufficient concentration of the less volatile inhibitor in the atmosphere around an enclosed metal such that corrosion is prevented at a later date. Preferably, the enclosure of the metal is composed of a substantially solid enclosure-material which allows escape therethrough of not more than about 1.7 gm. of the vapor phase inhibitor having the higher vapor pressure per square foot of the surface of the enclosure-material per month. Also, the enclosure means should be such that in cases where protection against corrosion for about ten months and longer is desired, the inhibitor with the lower vapor pressure may not escape at a rate of more than about 0.05 gm. per square foot of the surface of the enclosure-material per month when about 0.5 gm. of this inhibitor is present per square foot of the interior surface of the enclosure-material. In some cases it has been found that the inhibitor with the lower vapor pressure may escape at a rate of not more than about 0.20 gm. per square foot of the surface of the enclosure-material per month to still obtain about ten months of corrosion-inhibition when about 2 gm. of this inhibitor in the combination is present per square foot of the interior surface of the enclosure-material.

The corrosion of a metal is effectively prevented by the presence of the vapors of a sufficient quantity of a mixture of two or more vapor phase inhibitors at least, one of which preferably has a vapor pressure of below about 0.0015 mm. Hg at 21° C., and another of which preferably has a vapor pressure of above about 0.0030 mm. Hg at 21° C. Also in cases where the swiftness of action occasioned by such a combination is found to be unnecessary, a combination of, for example, one or more vapor phase inhibitors preferably having a vapor pressure between about 0.001 mm. and about 0.0025 mm. Hg at 21° C., employed in the immediate vicinity of one or more inhibitors preferably having a vapor pressure of between about 0.0005 mm. and about 0.00002 mm. Hg at 21° C. is highly useful and satisfactory for preventing corrosion of the metals.

Usually it is preferable to employ a combination of at least two vapor phase inhibitors, one of which has more than about twice the vapor pressure of one of the other inhibitors in the combination.

The vapor phase inhibitors preferably should have sufficient solubility in water so that they may transfer readily from the vapor phase either into any water vapor which may condense upon a metal part or into liquid water present upon a metal part. In some cases a true solution may not result; the vapor phase inhibitor may become incorporated sufficiently with either water vapor or liquid water present, and thus may form a colloidal sol or a solvate. In most cases vapor phase inhibitors having a solubility in water of at least approximately 1.0% by weight are preferable.

The vapor phase inhibitors should either be sufficiently stable at the temperatures of their normal usage, such as temperatures ranging from atmospheric temperature to about 100° F., or higher, or the inhibitors should respond to stabilization by the presence of a basic-acting agent or alkaline agent.

The vapor phase inhibitors of the present invention, whether as such or disposed on or in inert substances, upon contact with, or dispersion in water, should yield an aqueous phase having a pH value of at least about 5, and preferably above a pH of about 6. Basic-acting agents or alkaline agents, either volatile or non-volatile, and either organic or inorganic, may be used with the present inhibitors to maintain the desired pH. The described inhibitors are more effective in preventing aqueous corrosion of metal parts occurring in the presence of water having a pH value of approximately 7, or higher, for example, pH ranges up to a pH of 12, or higher.

The present vapor phase inhibitors are more effective in preventing aqueous corrosion (above a pH value of about 6) of various ferrous metals, e. g., steels, and also aluminum, nickel, chromium, and alloys of these metals. Satisfactory corrosion-inhibition of couples of steel with aluminum, copper, brass, bronze, or with solder (tin-lead alloy) are also obtained.

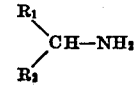
The organic vapor phase inhibitors which may be employed in accordance with the present invention include: Organic base nitrites, for example, organic nitrogen-base nitrites, organic amine nitrites, guanidine nitrites, alkylated imidazoline nitrites, nitrosamines, nitro-phenolic substances, nitro - aliphatic substances, and others. Respresentative classes of organic nitrogen-bases which are suitable for preparing the constituent nitrite salts to be employed in the present mixtures as vapor phase inhibitors according to the present invention, include: primary amines, secondary amines, tertiary amines, cyclic secondary amines of the type of piperidine, oxazines, morpholine, thiazolines, thiaoxazines, diazoles, basic diazole derivatives, imidazolines, diazines, basic diazine derivatives, pyrrolidine, and basic pyrrolidine derivatives; and various nitrogenous bases such as urea, thiourea, hydrazines, hydroxylamines, amidines, guanamines, guanidine, and the basic derivatives of these and other organic nitrogenous base nuclei. In any of the above nuclei, alkyl, cycloalkyl, terpinyl, bornyl, aralkyl, benzyl, phenyl, aryl, and various substituent groups or atomic radicals may be present so long as the sum total basicity of the organic nitrogenous compound is approximately equal to or greater than the acidity of nitrous acid with which it forms salt. Among the substituent groups the alkyl and cycloalkyl groups are preferred.

The basicity of various basic organic compounds which react with nitrous acid to form the nitrite salts disclosed herein is described, for example, in "The Organic Chemistry of Nitrogen," by N. V. Sidgwick, 1937 edition, and in "Organic Chemistry," by Paul Karrer, 1938 edition.

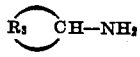
More specifically and preferably, types of organic nitrogen base salts of nitrous acid, from which may be selected salts having suitable high vapor pressures and those with low vapor pressures for combinations in accordance with the present invention, include the following nitrite salts of:

1. Primary amines, such as—

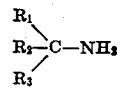
(a) Primary amines in which the amine group is attached to a secondary or a tertiary aliphatic carbon atom as in the following structural formulas:



or



or



wherein R_1, R_2 and R_3 are hydrocarbon radicals which are aliphatic, alicyclic, heterocyclic, aromatic, or alkylated cyclic radicals, and may, if desired, contain preferably not more than one olefinic double bond, or R_1 and R_2 are joined in the form of a cyclo-aliphatic or heterocyclic-aliphatic ring radical R_3;

(*b*) Primary amines in which the amine group is attached to an aralkyl group as in the following structural formula:

$$R_4-(CH_2)_n-NH_2$$

wherein R_4 is an aromatic hydrocarbon radical, preferably a phenyl or alkylated phenyl radical and n is an integer which is preferably 1 or 2;

(*c*) Primary aliphatic amines, such as methyl amine, which react with nitrous acid in the presence of an excess of the amine to give a primary amine nitrite salt (as distinguished from a primary aliphatic amine which reacts with nitrous acid to yield nitrogen, an alcohol, or other reaction products).

2. Secondary amines, such as secondary amines in which the amine group is attached to an aliphatic carbon atom, more preferably to a secondary or tertiary carbon atom, as represented by the following structural formulas—



or



wherein R_1 and R_2 are hydrocarbon radicals as in 1 (*a*) and wherein R_1 and R_2 may be joined in the form of a ring forming



which is either N-alicyclic or contains in the R_3 portion of the organic ring atoms of the type of oxygen and/or sulfur.

3. Tertiary amines.

4. Quaternary ammonium bases including pyridinium bases.

Specific examples of organic nitrogen bases suitable for preparation of the organic nitrogen-base nitrite salt vapor phase corrosion inhibitors of the present invention include:

Primary amines: methylamine, isopropyl amine, 2-amino-butane, tertiary butyl amine, 2-amino-4-methyl-pentane, various amyl, hexyl, heptyl, octyl and higher homologous primary amines where the amine group is attached to a secondary or tertiary carbon atom; cyclopentyl amine, alkylated cyclopentyl amines, cyclohexylamine, mono-methyl cyclohexylamines, dimethyl cyclohexylamines, trimethyl cyclohexylamines, other alkylated cyclohexylamines, bornyl amine, fenchyl amine, cycloterpenyl amines, pinyl amine, benzylamine, betaphenylethylamine, alkylated benzylamines, tetrahydro betanaphthylamine, allyl amine, beta-methyl allylamine, beta-chloro allylamine, and their homologs and analogs.

Secondary amines: di-methyl-, di-ethyl-, di-n-propyl-, di-isopropyl-, di-butyl-amines; various secondary amines derived from amyl, hexyl, heptyl, octyl, and higher homologous alkyl groups; methyl isobutyl amine, N-methyl N-tertiary-butyl amine, N-alkyl N-cyclohexyl amine, N-alkyl N-bornyl amine, di-bornyl amine, N-methyl N-cycloterpenyl amine, N-isopropyl N-(1)-methyl amine, N-alkyl N-benzyl amines and their homologs and analogs; dicyclopentyl amine, dicyclohexyl amine, alkylated dicyclohexyl amines; dibenzylamine, di-(beta phenyl ethyl) amine; piperidine, piperazine, alkylated piperidines or piperazines; alkylated and unalkylated oxazines such as morpholine and 2,4,4,6-tetramethyl tetrahydro-1,3-oxazine; alkylated-1,3-thiazolines such as 2,4,4,6-tetramethyl tetrahydro-3-thiazoline.

Secondary amine type derivatives of alkylene diamines, such as:

$$R_1-NH-R_2-NH-R_3$$

wherein R_1 and R_3 may be like or different aliphatic, alicyclic, aralkyl, alkarylalkyl, heterocyclic, terpenic radicals, and wherein R_2 is an alkylene or cycloalkylene radical. These R_1 and R_3 radicals for instance, may be isopropyl, butyl, cyclohexyl, benzyl, and/or bornyl radicals? The R_2 radical is preferably an ethylene, propylene or tetramethylene radical.

Tertiary amines: trimethyl amine, triethylamine, tri-n-propyl-amine, tri-isopropylamine, tributylamine, higher homologous and isomeric trialkylamines, variously N-substituted tertiary amines having different organic radicals on the amino nitrogen atom, e. g., alkyl, alicyclic, bornyl, fenchyl, aralkyl, and like homologs and analogs; and tertiary amine type derivatives of alkylene diamines.

Quaternary ammonium bases: tetramethyl and higher tetraalkyl ammonium bases; trimethyl benzyl-, trimethyl cyclohexyl-, tributyl decyl ammonium bases; various quaternary N-substituted ammonium bases having various organic radicals (of the type described above) on the quaternary nitrogen atom; pyridinium and alkylated pyridinium or quinolinium quaternary ammonium bases having an alkyl, cycloalkyl, or aralkyl group on the quaternary nitrogen atom, including methyl, butyl, cyclohexyl, benzyl groups and like homologs and analogs.

Various organic nitrogenous bases, particularly guanidine, alkylated guanidines, alkylated thioureas, and also diazoles, imidazolines, diazines, pyrimidines, and the basic derivatives of these and other organic nitrogenous-base nuclei.

The various hydrocarbon radicals contained within the above organic nitrogen-base nuclei may also contain stable and inert polar substituent atoms or radicals, such as chlorine, ether, thio-ether, alcohol, free amino, or nitro groups. Neutral ketone, ester, and nitrile groups and aliphatic unsaturation may also be present, particularly in the case of allyl and chlorallyl groups.

The salts of nitrous acid and the various organic nitrogen bases described herein may usually be prepared by a stoichiometric reaction of an organic nitrogen base with nitrous acid carried out under preferably at least slightly alkaline conditions above a pH value of 7.

In the following examples and in the specification the abbreviation, V. P., means vapor pressure in millimeters of mercury at 21° C.

Examples of suitable combinations of organic base nitrites applicable to the practice

of the present invention include compositions comprising:

	A Mixture of—	With a V. P. of	Factor of high V. P. divided by low V. P.
A	betaphenylethylamine nitrite and piperidine nitrite	0.0019 / 0.00057	3.0
B	3,3,5-trimethylcyclohexylamine nitrite and trimethylbenzyl-ammonium nitrite	0.0018 / 0.00035	5.3
C	di-isopropylamine nitrite and 3,3,5-trimethylcyclohexylamine nitrite	0.0047 / 0.0018	2.6
D	Di-isopropylamine nitrite and 2,4,4,6-tetramethyl-tetrahydro-3-oxazine nitrite	0.0047 / 0.0017	2.7
E	cyclohexylamine nitrite and piperidine nitrite	0.0027 / 0.00057	4.7
F	2-amino-butane nitrite and 3,3,5-trimethylcycohexyl amine nitrite	0.0038 / 0.0018	2.1
G	cyclohexylamine nitrite and di-cyclohexylamine nitrite	0.0027 / 0.00012	22.5
H	di-isopropylamine nitrite and di-cyclohexylamine nitrite	0.0047 / 0.00012	39.2
I	2-amino-butane nitrite and di-cyclohexylamine nitrite	0.0038 / 0.00012	31.7
J	morpholine nitrite and di-cyclohexylamine nitrite	0.0030 / 0.00012	25.0
K	morpholine nitrite and dibenzylamine nitrite	0.0030 / 0.00087	3.5
L	trimethylbenzylammoniumnitrite and di-cyclohexylamine nitrite	0.00035 / 0.00012	2.9
M	dibenzylamine nitrite and di-cyclohexylamine nitrite	0.00037 / 0.00012	7.2
N	piperidine nitrite and di-cyclohexylamine nitrite	0.00057 / 0.00012	4.7
O	di-isopropylamine nitrite and piperidine nitrite	0.0047 / 0.00057	8.2

Among the above examples, the invention is most preferably practiced by the introduction of combination (G) and/or combination (H), combination (I), and/or combination (J). The most preferred example at present known is that of combination (H). A practical example of this combination is preferably one in which a mixture of between about 0.05 gm. and 1.5 gm. of di-isopropylamine nitrite and between about 0.05 gm. and 1.5 gm. of di-cyclohexylamine nitrite are present per square foot of surface of the enclosure material. In most cases it is preferred to have the sum of the amounts of the two vapor phase inhibitors approximately about 2.0 gm. per square foot of the interior surface of the enclosure material, although lesser or higher concentrations may be used depending upon the severity of corrosive conditions. Usually a mixture of about 1.0 gm. each of these organic amine nitrites, or of any like combination of organic nitrites having similar characteristics of volatility, is preferred. Larger amounts of such combinations up to any practically operable amount may be used.

It will be understood that the required amounts of the respective vapor phase inhibitors will vary depending upon a number of factors, e. g., the severity of conditions of use, the particular vapor phase inhibitors employed, and the mode in which they are applied. In general, the placing of a sheet of paper, of an absorbent material or of another solid carrier, impregnated with or coated by a minor amount of a combination of vapor phase inhibitors, in the proximity of a corrodible metal enclosed in a package or the like, provides satisfactory corrosion inhibition when between about 0.1 gm. to about 5.0 gm., and preferably about 0.5 gm. to about 2.0 gm., of the inhibitor mixture is present per square foot of the container inner surface. Particularly satisfactory results are attained when the inhibitor mixture is present in such an amount as to allow between about 1 gm. and about 15 gm. (for average conditions about 6 gm.), of the mixture for each cubic foot of enclosed vapor space.

Stability of the present vapor phase inhibitors, and particularly the stability of organic nitrogen base nitrite salts, is adversely affected by an environment which, on contact with or dispersion in water, yields a solution having a pH value of less than approximately 6. In some instances the stability is also adversely affected by elevated temperatures, such as 120° F. to 150° F., or higher. The effect of such and like factors are greatly lessened or entirely obviated by introducing an alkaline agent either into the inhibitor per se, or into the vapor space containing the vapors thereof. Such addition of the alkaline agent is particularly applicable in cases where the inhibitor has a tendency to decompose. Suitable stabilizing agents include organic or inorganic compounds which, dispersed in water, have a pH in excess of approximately 7. Also the stabilizing agents include alkaline materials having dissociation constants greater than, approximately equal to, or slightly less than the dissociation constant of the organic base which was combined to form the nitrite salt which it is desired to stabilize. Various alkaline stabilizing agents which were found to be particularly effective were: di-isopropyl amine, dicyclohexyl amine, aliphatic primary amines containing from 16 to 18 carbon atoms, various high molecular weight amines, di-ethanol amine, tri-ethanol amine, di-isopropyl ammonium bicarbonate, dicyclohexyl ammonium bicarbonate, sodium carbonate, sodium chromate, sodium phosphate, isopropyl urea, or piperazine.

The particular stabilizing agent, and the optimum quantity thereof required to be effective depends on a number of variables. In general, between about 0.1% and about 25% of the stabilizer (by weight of the vapor phase inhibitor) are effective.

The vapors of amine nitrite salts may contain vapors of nitrosamines formed therefrom. Usually the conversion of an amine nitrite to a corresponding nitrosamine is readily prevented by the presence of an alkaline agent or basic acting agent of the nature described above.

The equilibrium of an amine nitrite salt with the corresponding nitrosamine and water (which are formed from the nitrite) usually shifts toward higher concentrations of the nitrosamine at increasingly higher temperatures. This equilibrium may be stated as follows:

$$(R)_2\overset{\frown}{N}H\cdot HNO_2 \overset{\text{heat}}{\rightleftarrows} (R)_2\overset{\frown}{N}-N=O + H_2O$$

wherein R represents an organic radical. According to the usual laws of chemical equilibrium, an excess of either water or nitrosamine or both above the chemically equivalent amounts present in a given equilibrium tends to force the equilibrium reaction toward increasing the concentration of the amine nitrite. The presence of the nitrosamine is not detrimental to vapor phase corrosion inhibition; in fact, vapors of the nitrosamine itself were found to inhibit corrosion of metal where in the presence of water vapor. However, in a number of cases, they did not appear as effective as vapors of the corresponding amine nitrite salts when the latter were substantially free of nitrosamine.

Other organic salts of nitrous acid which are suitable vapor phase inhibitors according to the present invention are the sulfonium, phosphonium, or iodonium organic nitrite salts. Among these onium nitrites, the sulfonium nitrites are preferred. In general, nitrite salts of the isologs

of the ammonium compounds, commonly termed "onium" compounds, and which have the general formula RXH_y wherein R is an organic radical which may be alkyl, cycloakyl, aryl, alkaryl, or heterocyclic; X is an element selected from the group consisting of phosphorus, arsensic, antimony, carbon, oxygen, sulfur, selenium, tin and iodine; and y is an integer which varies from 2 to 4 depending upon the valence of X, may suitably be applied as vapor phase inhibitors.

Various techniques have been practiced in the utilization of the vapor phase inhibitors disclosed herein. The process of the present invention may be applied in a number of ways which may differ in detail but not in the essentialities of the invention. It was found, for example, that corrosion of metal parts is inhibited by enclosing them in containers which are provided with vapors from the present mixtures of vapor phase inhibitors as described herein. Also, these combinations of inhibitors may be effectively applied: by placing the mixture in the form of a powder or crystals per se, or mixed with inert carriers, in a container in which the metal part(s) to be protected are disposed; by introducing into the container or enclosure a piece of solid, and preferably an absorbent material coated or impregnated with one of the present combinations of vapor phase inhibitors; by covering the corrodible metal parts with a covering material, such as paper, cloth, cellophane, ethylcellulose, polyvinyl chloride, polyvinylbutyral, polyamides, nylon-material, sheet material, or the like, which are coated or impregnated with the present combinations of vapor phase inhibitors, and/or by enclosing the metal parts within a covering or packaging material, only one side of which allows disposal of vapors of the contained mixture of inhibitors to the contiguous atmosphere, as in the case of waxed paper coated on one side with a combination of inhibitors, or of certain types of laminated papers suitably associated with the present combinations. A composite of paper laminates in which certain of the laminates, or as asphaltized paper, are carriers of the present vapor phase inhibitors, have been found particularly effective.

In general, corrosion of metal surfaces by moisture is completely prevented by enclosing, or making available therein, sufficient vapors of the presently described combinations of volatile organic corrosion-inhibitors. These combinations can originally be introduced as a solid mixture, a liquid mixture, or a vaporous mixture, or as a mixture of the inhibitors in solution, in an emulsion, or in a dispersion, etc., so long as the inhibitors may vaporize and thus be present in the atmosphere around the metal. Various absorbent materials, such as paper, cotton, wool, polyamides, certain types of synthetic resins, cloth, silica gel, alumina gel, fuller's earth, activated carbon, and charcoal may be impregnated with the present combinations of vapor phase inhibitors, or used as carriers therefor. When desired, metal parts can also be coated with the present combination of vapor phase inhibitors by depositing them from a solution, dispersion, conventional coating vehicle, or the like. Use of the present combinations of inhibitors is especially desirable, as in an ethyl cellulose or an alkyd resin coating of a metal, where fast diffusion of the inhibitor through the resin to the initial moisture on the surface of the metal is needed to prevent incipient as well as later corrosion.

For purposes of further illustration, reference will now be made to the following examples, it being understood that there is no intention of being limited to the specific conditions disclosed therein. All parts in the following examples are parts by weight.

Example I

Onto the bottom of a clean all-glass container was introduced a mixture of vapor phase inhibitors composed of one part of di-isopropylammonium nitrite and one part of di-cyclohexylammonium nitrite. The inhibitors had been powdered and thoroughly incorporated with each other. A separate receptacle containing one part of liquid water was placed within the all-glass container, and thus provided a highly moisture-laden vapor atmosphere in contact with the inhibitors and in the vapor space of the container. Freshly cleaned and polished steel strips were suspended in the vapor space of the thus-prepared all-glass container. The vapor space therein also contained air from the laboratory. The thus-prepared system was then maintained at a temperature of 100° F. during 50 hours of operation. The steel strips subjected to the mixture of vapors from the di-isopropylammonium nitrite and di-cyclohexylammonium nitrite had been practically protected from rusting over their entire surface area. Over 99% of the surface areas of these steel strips was free from all rust; less than 1% of the surface area had tiny almost imperceptible rust spots, and substantially the original polish and sheen of the metal had been maintained. In contrast a steel strip in a parallel control test which was similar in all respects except for the absence of any corrosion inhibitor was heavily rusted over about 50% of its area and the remaining surface area was covered all over with a sprinkling of tiny rust spots.

Example II

A test was run in the same manner as described in Example I above, except that a mixture of one part of piperidine nitrite and one part of di-isopropylammonium nitrite was employed as the combination of vapor phase inhibitors. The steel strip protected by the vapors from these inhibitors had retained its original appearance and was substantially completely free from rust.

Example III

A test was run in the same manner as described in Example I above, except that a mixture of one part of di-cyclohexylammonium nitrite and one part of piperidine nitrite was employed as the combination of vapor phase inhibitors. The steel strips subjected to the vapors from this combination were completely protected from rusting during the 50-hour period of operation in marked contrast to the results with the control, the latter being as specified in Example I.

Example IV

A test was run in the same manner as described in Example I above, except that one part of di-isopropylnitrosamine and one part of di-isopropyl-ammonium nitrite was employed as the combination of vapor phase inhibitors. Under these conditions about 10% of the surface area of the steel strip was rusted, about 90% of the steel having been preserved in its original uncorroded condition. These results were in marked contrast to those obtained in a control test, the latter being as specified in Example I.

The present application is a continuation-in-part of the copending application Serial No. 557,358, filed October 5, 1944, and now abandoned.

The use of various individual vapor phase corrosion inhibitors utilized in the present inhibitor combinations is described and claimed in our copending applications Serial No. 663,608, filed April 19, 1946; Serial No. 668,015, filed May 7, 1946; Serial No. 673 886, filed June 1, 1946; Serial No. 706,098, filed October 28, 1946, and Serial No. 191,330, filed October 20, 1950.

We claim as our invention:

1. In the method for inhibiting corrosion of a metal normally corrodible by contact with water vapor and air, the step of subjecting said metal in a substantially enclosed space to the vapors of di-isoproply amine nitrite and dicyclohexyl amine nitrite, the weight ratio of the two nitrites being between about 0.1 and about 10.

2. In a method for inhibiting corrosion of a metal normally corrodible by contact with water vapor and air, the steps of placing said metal in a substantially enclosed space and disposing in said space a combination comprising an effective corrosion-inhibiting amount each of diisopropyl amine nitrite and di-cyclohexyl amine nitrite.

3. In a method for inhibiting corrosion of a metal normally corrodible by contact with water vapor and air, the steps of placing said metal in a substantially enclosed space and disposing in said space a combination comprising di-isopropyl amine nitrite and piperidine nitrite, the weight ratio of the two nitrites being between about 0.1 and about 10.

4. In a method for inhibiting corrosion of a metal normally corrodible by contact with water vapor and air, the steps of placing said metal in a substantially enclosed space and disposing in said space a combination comprising morpholine nitrite and di-cyclohexyl amine nitrite, the weight ratio of the two nitrites being between about 0.1 and about 10.

5. In a method for inhibiting corrosion of a metal normally corrodible by contact with water vapor and air, the steps of placing said metal in a substantially enclosed space and disposing in said space a combination comprising two secondary amine nitrite vapor-phase corrosion inhibitors, one having a vapor pressure greater than about 0.001 mm. Hg at 21° C., and the other having a vapor pressure between about 0.0005 and about 0.00002 mm. Hg at 21° C., the weight ratio of the two inhibitors being between about 0.1 and about 10.

6. In a method for inhibiting corrosion of a metal normally corrodible by contact with water vapor and air, the steps of placing said metal in a substantially enclosed space and disposing in said space a combination comprising two organic amine nitrite vapor-phase corrosion inhibitors, one having a vapor pressure greater than about 0.001 mm. Hg at 21° C. and the other having a vapor pressure between about 0.0005 and about 0.00002 mm. Hg at 21° C., the weight ratio of the two inhibitors being between about 0.1 and about 10.

7. In a method for inhibiting corrosion of a metal normally corrodible by contact with water vapor and air, the steps of placing said metal

in a substantially enclosed space and disposing in said space a combination comprising at least two organic base nitrite salt vapor-phase corrosion inhibitors, the vapor pressure of the most volatile salt being at least about 0.001 mm. Hg and at least twice the vapor pressure of the least volatile salt at 21° C., the vapor pressure of the least volatile salt being greater than about 0.00002 mm. Hg at 21° C., the weight ratio of any two of the said salts being between about 0.1 and about 10.

8. In a method for inhibiting corrosion of a metal normally corrodible by contact with water vapor and air, the steps of placing said metal in a substantially enclosed space and disposing in said space a combination comprising at least two organic vapor-phase corrosion inhibitors, the vapor pressure of the most volatile inhibitor being at least about 0.001 mm. Hg and at least twice the vapor pressure of the least volatile inhibitor at 21° C., the vapor pressure of the least volatile inhibitor being greater than about 0.00002 mm. Hg at 21° C., the weight ratio of any two of the said inhibitors being between about 0.1 and about 10.

9. A composition of matter comprising diisopropyl amine nitrite and di-cyclohexyl amine nitrite, the weight ratios of the two nitrites being between about 0.1 and about 10.

10. A composition of matter comprising a combination of two secondary amine nitrites, one having a vapor pressure greater than 0.001 mm. Hg at 21° C. and the other having a vapor pressure between about 0.0005 and about 0.00002 mm. Hg at 21° C., the weight ratio of the two nitrites being between about 0.1 and about 10.

11. A corrosion-inhibiting composition of matter comprising at least two organic vapor-phase corrosion inhibitors, the vapor pressure of the most volatile inhibitor being at least about 0.001 mm. Hg and at least twice the vapor pressure of the least volatile inhibitor at 21° C., the vapor pressure of the least volatile inhibitor being greater than about 0.00002 mm. Hg at 21° C., the weight ratio of any two of the said inhibitors being between about 0.1 and about 10.

12. The method of claim 2 in which the metal is a ferrous metal.

13. The method of claim 5 in which the metal is a steel.

14. The method of claim 8 in which the metal is a ferrous metal.

15. The composition of claim 11 in which the organic vapor-phase corrosion inhibitors are organic base nitrite salts.

AARON WACHTER.
NATHAN STILLMAN.

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