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VAPOR PHASE CORROSION INHIBITION

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The present invention relates to prevention of corrosion of metal parts, which corrosion normally occurs in the presence of air (oxygen) and water vapor and/or aqueous condensates. More particularly, this invention pertains to novel methods and compositions capable of inhibiting such corrosion by providing an atmosphere containing one or more of the present novel vapor phase inhibitors. In one of its embodiments, this invention relates to packaging of metals in such a manner that corrosion thereof by moist air is prevented.

During storage, handling, transportation, etc. of objects having corrodible metal or metal-containing surfaces, more especially those of ferruginous metals, such as various steels or ferrous alloys, it is often desirable to prevent corrosion of these metals. Heretofore, the various methods used for this purpose have been unsatisfactory because of inadequate prevention of corrosion, cumbersomeness, and/or the necessity of using an excessive amount of labor and expenditure of time.

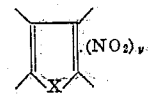
Partially or completely enclosed metal parts are usually housed, packaged, boxed, enveloped, or placed in a container under such conditions that water vapor and air are either present, or are introduced to the metal parts at the time of their being disposed therein, or water vapor with air enters through the enclosure walls after packaging.

It is an object of this invention to obviate or materially reduce the above defects of the prior art. It is an object to provide novel methods and means for inhibiting corrosion of corrodible metals. It is another object to provide certain compounds as corrosion-inhibitors which will prevent water and aix (oxygen) from corroding metals, particularly steel. A further object is to introduce certain volatile or vaporizable corrosion-inhibitors suitable for preventing water-corrosion of metals disposed in an enclosed space. A still further object is to provide novel means of enclosing a metal and inhibiting moist air corrosion of the enclosed metal. Another object is to provide materials containing or impregnated with certain corrosion-inhibitors which latter volatilize therefrom and prevent moist air corrosion of metal parts in the substantial vicinity thereof. Still another object is to provide introduction of an atmosphere containing certain corrosion-inhibitor vapors whereby metal parts in contact with this atmosphere are significantly reduced and even prevented from their otherwise normal aqueous corrosion.

It has now been discovered that the above and

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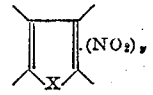
other objects may be attained, and that particularly the corrosion of the surfaces of a corrodible metal in the presence of water and oxygen may be prevented by contact of said surfaces with vapors of a compound having a nucleus of the general formula



wherein X is a sulfur, selenium or oxygen atom or an NH group and y is an integer from 1 to 4, inclusive, wherein the unsatisfied bonds (as shown in above formula) are satisfied by hydrogen atoms and/or by organic radicals substantially non-corrosive or inert under the operating conditions and so long as the compound has a vapor pressure of at least 0.00002 mm. of Hg at 21° C. Particularly useful organic substituents on said nucleus are the conventionally known non-corrosive organic radicals, preferably having up to about 20 carbon atoms. Within this general class of organic substituents, especially desirable are the commonly known non-corrosive hydrocarbon and/or oxyhydrocarbon organic radicals. Said single valence bonds may thus be satisfied by the hydrogen atom, as well as by alkyl, alkenyl, cycloalkyl, aralkyl, aralkenyl, aryl, alkaryl, alkarylalkyl, heterocyclic, or terpenic radicals, and any two or more of these single valence bonds may be joined together via an organic cycle to form a second ring which may be alicyclic, heterocyclic, terpenic, or aromatic attached to the specified nucleus. The single valence bonds may be satisfied by carbalkoxy, acyloxy, particularly carbethoxy, acetyl, etc. groups, and also by halogen atoms, particularly chlorine or bromine atoms. Other substantially neutral substituents or at least non-corrosive substituent groups may be present; this excludes corrosive substituents such as sulfonic acid, free mercaptan groups, and other known corrosively active substituents. In all cases for the present purposes, there must be present at least one nitro group attached to the above heterocyclic ring nucleus which is of the class of nitrothiophenes, nitrofurans, nitroselenophenes and nitropyrroles. It is desirable, in order to obtain fast corrosion-inhibiting action and practically complete protection, to have the organic substituents (on said nucleus) have a total of up to about ten carbon atoms, which substituents may be alkyl, cycloalkyl, aryl, and/or phenyl radicals. Preferred substituents are these described hydrocarbon radicals. In general, most

preferred are compounds having a molecular weight not exceeding about 330. The lower molecular weight compounds are generally associated with higher volatility and more effective vapor phase action, although higher molecular weight compounds are also surprisingly effective.

For purposes of clarity and simplicity, the above-described nucleus of



is referred to herein under the term of "nitro-heterophene nucleus" and compounds containing this nucleus are termed herein "nitro-heterophene compounds."

Suitable examples of the above described hydrocarbon radical substituents on the specified nitro-heterophene nucleus, are:

Alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, amyl, octyl, dodecyl, and their homologues;

Alkenyl groups such as allyl, methallyl, crotyl, octenyl, oleyl, etc.;

Cycloaliphatic or naphthenic such as cyclohexyl, alkylated cyclohexyl, methylcyclopentyl, cyclopentyl, cyclohexenyl, etc.;

Aralkyl such as benzyl, alkylated benzyl, phenylethylene, phenylalkylene radicals, etc.;

Aryl radicals such as phenyl group, a fused benzene ring, i. e. attached by two adjacent carbon atoms of the nitro-heterophene nucleus, a naphthalene ring similarly fused, etc.;

Heterocyclic radicals such as oxazine, morpholine, thiazoline, pyrazole, piperazine, pyrrolidine radicals, etc.;

Terpinyl radicals such as bornyl, fenchyl, etc.

The organic substituents forming part of the present nitroheterophene structure or which are attached thereto, may contain stable polar substituents and/or radicals, e. g. chloro, fluoro, alkoxy-ether, cycloalkoxy-ether, phenoxy-ether, thio-ether, ketone, ester, cyanate, nitrile, or nitro groups.

Of the above class of nitro-heterophene vapor phase corrosion-inhibitors, those containing a nitro-thiophene nucleus have been found to be most effective, while compounds containing a nitro-furan nucleus and compounds containing a nitro-pyrrole nucleus are of somewhat lesser effectiveness, at least in some cases.

Most preferred within any of these sub-genera are compounds in which the heterophene nucleus has a nitro group on the carbon atom alpha to the hetero atom. Examples of this are in the simplest cases, 2-nitro-thiophene, 2-nitro-furan, 2-nitro-pyrrole, and their lower alkylated and also benzo substituted homologues and analogues.

One or more of the nitro-groups may be attached to either of the two beta positions, that is, positions 3 and/or 4, or in postions 2 and 5, or in all of the four available positions. More preferred are compounds having not more than two nitro groups on the heterophene ring.

Examples of suitable compounds having a nitro-thiophene nucleus and applicable to the practice of this invention include: 2-nitro-thiophene, 3-nitro-thiophene, 2,5-dinitro-thiophene, 3-nitro-4,5-benzothiophene, and the various nitro derivatives of the substituted thiophenes and penthiophenes described in Beilstein, particularly in volume XVII, first series, pages 35–47 and pages 59, 60 and 66, and same volume of second series, pages 21 and 22.

Examples of suitable compounds having a

nitro-selenophene nucleus and applicable to the practice of this invention include: 2-nitro-selenophene and nitro derivatives of substituted selenophenes such as those e. g. of Beilstein, volume XVII, first series, page 42.

Examples of suitable compounds having a nitro-furan nucleus and applicable to the practice of this invention include: 2-nitro-furan, 3-nitro - furan, 2,5-dinitro-furan, 2-nitro-benzofuran, and the various nitro derivatives of the substituted furans described in Beilstein, particularly in volume XVII, first series, pages 27–29, 36, 38–43, 46, 54, 59 and 66, and same volume of second series, page 21.

Examples of suitable compounds having a nitro-pyrrole nucleus and applicable in the practice of this invention include: 2-nitro-pyrrole, 3-nitro-pyrrole, 2,3-dinitro-pyrrole, 2,5-dinitro-pyrrole, 3-nitro-2,4-dimethyl-pyrrole, 3,5-dicarbethoxy-4-methyl-2-nitro-pyrrole, 2,5-diethyl-3-carbethoxy - 4 - nitro - pyrrole, 4-acetyl-5-nitro-pyrrole, 2,4-dinitro-3,5-carbethoxy-pyrrole, 2-nitro-indole, and the various nitro derivatives of the hydrocarbon and other organo and atomic radical substituted pyrroles described for example in Beilstein, volume XX, first series, page 169 et. seq., and same volume, second series, page 41 et seq.

Nitro-pyrroles may be prepared by nitration of pyrroles having a carboxyl, carbalkoxy, acyl, or halogen-substituent group. Pyrrole itself is destroyed by nitric acid. Mono-nitropyrroles may be prepared by action of a mixture of ethyl nitrate and sodium on pyrrole where, in this case, the sodium salt of the nitropyrrole is treated with carbon dioxide and the free mono-nitropyrrole thus liberated. Further to the preparation of nitropyrroles suitable for this invention, nitro groups retain the capacity exhibited in the cases of thiophene and furan of displacing acetyl, formyl, or even sometimes methyl groups; thus by this means of preparation, 2,4-dimethyl-3-carbethoxy-5-nitropyrrole is formed by the action of concentrated nitric acid upon 2,4-dimethyl-3-carbethoxy-5-acetylpyrrole.

In general, preparations of nitro-thiophenes, nitro-furans, and nitro-pyrroles are well known to the art of organic preparations and are described in standard reference books on this subject.

In general, for the present vapor phase corrosion-prevention methods, the class of nitro-heterophene compounds should have a vapor pressure in excess of approximately 0.00002 mm. Hg at 21° C. Better results are obtained with nitro-heterophene compounds having a vapor pressure greater than about 0.0001 mm. Hg at 21° C. More rapid inhibition of aqueous corrosion is obtainable with nitro-heterophene compound having a vapor pressure greater than about 0.001 mm. Hg at 21° C.

Most preferably, vapor phase corrosion-inhibition with nitro-heterophene compounds is carried out in a medium or atmosphere which is nearly neutral, preferably between a pH of approximately 6 and a pH of about 8. However, practical prevention of corrosion of steel is obtainable under conditions of pH as low as about 3.

The proportion or amount of one or more of the class of nitro-heterophene compounds which is to be introduced into and/or maintained in the atmosphere contacting a metal to prevent corrosion thereof, may vary within wide limits. The amount required for different conditions varies depending upon a number of variables,

such as severity of conditions, temperature, degree of humidity, the particular nitro-heterophene compound introduced, and the manner in which it is introduced. Usually the placing of a piece of solid material, e. g. a sheet of paper or of a fibrous or like absorbent material impregnated with or coated by a nitro-heterophene compound, in the proximity of a corrodible metal enclosed in a container, or a package, or the like, provides satisfactory corrosion-inhibition when between about 0.01 gram and about 5.0 grams, preferably between about 1.0 gram and about 2.0 grams of the inhibitor(s) is present per each square foot of the inner surface of the container. Particularly satisfactory results are secured when the inhibitor is present in such an amount as to allow between about 0.01 gm. and about 15 gm. (for average conditions about 0.2 to 4 gm.) thereof for each cubic foot of enclosed vapor space.

The nitro-heterophene vapor phase inhibitors can be applied either separately or in various mixtures of members of this class, or with other discovered classes of vapor phase corrosion-inhibitors. In certain cases it is advantageous to apply a mixture containing a nitro-heterophene compound with relatively high vapor pressure (preferably above about 0.001 mm. Hg at 21° C.) and another nitro-heterophene compound having a relatively low vapor pressure (e. g. between about 0.0005 and 0.00002 mm. Hg at 21° C.).

Compositions containing the present inhibitors are effective in gaseous, liquid, or solid form so long as vapors of the inhibitor(s) may contact the metal to be protected from corrosion.

Various techniques are effective in the utilization of the present nitro-heterophene compounds as vapor phase corrosion-inhibitors. Within any enclosure means, corrosion of metal surfaces by moisture is prevented by enclosing, or making available therein, one or more of the specified nitro-heterophene compounds. The latter can be originally introduced as a solid, a liquid, or a vapor, or in solution, as an emulsion or dispersion, etc., as long as the inhibitor may vaporize and thus be present in the atmosphere around the metal. In the case of enclosed metal articles, the inhibitor(s) may be disposed in the enclosure as crystals or as a powder; or the metal article or the wrapping material thereof may be coated with material containing the inhibitor(s); or there may be introduced into the enclosure or container a piece of solid, e. g. absorbent, preferably fibrous material, coated or impregnated with a nitro-heterophene compound. Thus, paper, cloth, various textile materials, ethylcellulose, any sheet or filamentous material, which is coated or impregnated with the inhibitor(s) may be inserted near or wrapped around the metal parts. In one of the preferred embodiments of the invention it is advantageous to use paper which is impregnated with a nitro-heterophene compound. The metal parts may be enclosed within a covering or packaging material, only one side of which allows disposal of vapors of the contained inhibitor(s) to the contiguous atmosphere. Laminates of paper, parts of which are impregnated with or contain the inhibitor(s) are also useful. Asphalt papers may also be used as suitable carriers of the inhibitor(s). After providing the containers with the inhibitor(s) in any of the above, or like modes, these containers may then be closed or sealed. The resultant container or package does not have to be completely closed or impervious to vapors or gases, but only has to be closed to the extent that a corrosion-inhibiting concentration of vapors of the inhibitor(s) is retained or maintained in the package.

In cases wherein free circulation of air is prevented around metal articles or steel containers in storage, the inhibitor(s) is also effectively utilized by introducing it as fine crystals or as vapor, or by providing an atmosphere containing vapors of the nitro-heterophene compound(s) around the metal articles. Corrosion by circulation of air over metal surfaces can be prevented by partially or substantially saturating the introduced air with vapors of the inhibitor(s). Metal parts can be effectively corrosion-proofed by coating them with the inhibitor(s) by depositing the latter from a solution or a dispersion thereof, or from heated vapors contacting a metal, or by incorporating the inhibitor(s) in relatively non-volatile coating materials which remain on the metal.

The metal walls or parts enclosed within tanks, pipes, machinery, or instruments are prevented from corroding by either enclosing or making the inhibitor(s) available within the vapor spaces present therein. This is also true in hydraulically operated mechanisms. In a preferred method the inhibitor(s) is disposed in and allowed to vaporize from a hydraulic fluid introduced into such mechanisms. When disposed in a liquid, the nitro-heterophene compounds not only inhibit corrosion of metals contacting this liquid but also inhibit corrosion of metals contacting the vapor phase above the liquid.

Aerosols are also effective for distributing the inhibitor(s). In such a case, the inhibitor is dissolved in a liquefied, normally gaseous solvent which is under sufficient pressure in a vessel to maintain the solvent in its liquid state. The solution of the inhibitor thus prepared is released through an orifice in the vessel, thereby distributing the inhibitor in a state of minute subdivision.

The present inhibitors are effective agents for reducing corrosive wear of moving machined metal parts, particularly in engines, e. g. steam engines, steam turbines, internal combustion engines, etc. The inhibitors are incorporated into fueling or lubricating media for such engines or for other metal parts in machinery, such as organic lubricants and thereby the wear attendant upon corrosion is inhibited.

Stability of the present class of nitro-heterophene compounds, particularly at elevated temperatures above room temperature, is improved, and undesirable decomposition of the nitro-heterophene compounds which may sometimes occur is even practically entirely eliminated by the simultaneous presence of a basic-acting agent. The latter may be defined as an alkaline agent and/or a compound which reacts as a base in the presence of acidic-reacting materials. Preferably, it is advisable to employ organic or inorganic compounds which, when dispersed in water, yield an aqueous phase or tend to maintain a dispersion or solution having a pH value of at least approximately 6. As such stabilizers, minor amounts (with respect to the nitroheterophene compound) of amines, cyclic-nitrogen and heterocyclic organic bases, guanidine, amine carbonates, amine bicarbonates, alkali and alkaline earth metal bicarbonates and carbonates and similarly basic materials may be employed with advantage. In general, strong alkali and alkaline earth metal hydroxides are to be avoided although

they may be used in some cases depending upon circumstances which are readily determinable by a small-scale empirical or pilot test. The amount of a basic-reacting stabilizer should usually be between about 0.1% and about 25% by weight of the nitro-heterophene compound(s), depending upon the acidity of the conditions encountered, although larger or smaller amounts may be used. A few specific stabilizers which are here mentioned are: dicyclohexylamine bicarbonate, also this amine's carbonate, and sodium bicarbonate.

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 details therein.

Samples of steel strips of low carbon content, ½ inch by 2 inches, with thoroughly cleaned surfaces were dried and weighed. The steel strips were then suspended in the upper part of closed glass containers, into which various amounts of the compound to be tested, as set forth in the table below, were disposed. Distilled water was also placed separately within each of the glass containers. The steel pieces under test were not in contact with any of the unvaporized form of the compounds being tested for corrosion-inhibition. After the duration of each test, the weight changes of the steel strip samples were measured.

Inhibitor	Parts by Weight of Inhibitor	Time, Days	Temp., °F.	Gain in Weight of Steel, Milligrams	Visually Observed Protection Against Rusting (Approx.)
					Per Cent
None	None	7	150	102.2	(1)
2-Nitrothiophene	0.5	7	150	0.9	90
o-Nitrotoluene	0.5	7	150	61.4	15
o-Nitro-iso-propyl-benzene	0.5	7	150	34.2	1
p-Nitro-iso-propyl-benzene	0.5	7	150	39.6	10
2-Nitrothiophene	0.5	7	150	1.2	85
2-Nitrothiophene	0.1	14	150	0.7	90
2-Nitrothiophene	0.1	28	100	0.5	95
2-Nitrothiophene	0.5	14	100	0.2	95
2-Nitro-p-cymene	0.1	7	150	89.1	15
o-Nitrodiethyl-aniline	0.1	7	150	57.1	5
o-Nitrodiphenyl-ether	0.1	7	150	29.4	(2)
p-Nitrofluoro-benzene	0.1	7	150	52.7	15
2-Nitro-3-methoxy-toluene	0.1	7	150	125.7	0

[1] Completely covered with rust.
[2] Covered with black rust scales.

It will be noted from the data in the above table that a wide variety of nitro-aromatic nuclei not containing the nitro-heterophene nucleus (two double bonds in a five-membered ring conjugate with the hetero atom therein) were tested under comparative conditions and found to give weight increases due to rusting varying from approximately 30 to 125 times that found from the use of a compound containing a nitro-heterophene nucleus. In view of the above tests, the presence of a nitro group in an aromatic compound or even in a hetero-atomic aromatic compound is not sufficient to significantly inhibit rusting. On the other hand, the results from employment of a nitro-heterophene compound show practically negligible weight increases due to rusting, and the steel was substantially protected by the vapors of such a compound. The above significant differences in corrosion-inhibition were not due to differences in volatility or lack of vaporization since the non-heterophene compounds are of comparable volatility to nitro-heterophene compounds which give good protection under similar conditions.

We claim as our invention:

1. In a method for inhibiting corrosion of a ferruginous metal occurring by contact with water vapor and air, the step of providing, in the proximity of a ferruginous metal, a vaporous atmosphere containing a corrosion-inhibiting amount of 2-nitro-thiophene.

2. In a method for inhibiting corrosion of a ferruginous metal occurring by contact with water vapor and air, the step of providing, in the proximity of a ferruginous metal, a vaporous atmosphere containing a corrosion-inhibiting amount of 3-nitro-thiophene.

3. A method for inhibiting corrosion of a ferruginous metal surface by contact with water vapor and air comprising placing said metal surface and 2,5-di-nitro-thiophene in a condensed state in locations relative to each other such that the metal surface is contacted by a corrosion-inhibiting concentration of vapors given off by the condensed 2,5-di-nitro-thiophene.

4. The combination of a ferruginous metal object normally corrodible by contact with water vapor and air, an atmosphere containing a corrosion-inhibiting amount of 2-nitro-thiophene, and a container enclosing said atmosphere and metal object.

5. In a method for inhibiting corrosion of a ferruginous metal object by contact with water vapor in air, the steps comprising enclosing said metal in a container containing a corrosion-inhibiting amount of 2-nitro-thiophene.

6. In a method for inhibiting corrosion of a ferruginous metal occurring by contact with water vapor and air, the step of providing in the proximity of a ferruginous metal, a vaporous atmosphere containing a corrosion-inhibiting amount of an unsubstituted nitro-thiophene containing from one to two nitro groups, said nitro-thiophene having a vapor pressure of at least 0.001 mm. Hg at 21° C.

7. In a method for inhibiting corrosion of a ferruginous metal occurring by contact with water vapor and air, the step of providing, in the proximity of a ferruginous metal, a vaporous atmosphere containing a corrosion-inhibiting amount of a nitro-substituted thiophene containing from one to two nitro groups in substitution for thiophene-hydrogen atoms, and in which the only other substituents are hydrocarbon radicals ranging in total carbon content from one to ten carbon atoms, said nitro-thiophene having

a vapor pressure of at least 0.0002 mm. Hg at 21° C.

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