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COMPOSITIONS FOR PROTECTION OF METALS AGAINST CORROSION

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The present invention relates to novel compositions comprising a substantially solid material which contains, or is impregnated or coated with a vapor phase inhibitor which inhibits the corrosion of metals. More particularly stated, the present invention is concerned with various absorbent materials, e. g., cellulosic substances and their derivatives (modified papers, card-board, fibreboard, wood, cotton, cloth and the like) which are coated, impregnated, or otherwise contain one or more of the vapor phase inhibitors described below.

Our copending applications Serial No. 663,608, filed April 1, 1946, Serial No. 668,015, filed May 7, 1946, and Serial No. 675,886, filed June 1, 1946, disclose and claim various methods of inhibiting corrosion by the introduction of certain types of vapor phase inhibitors; the present invention covers various substantially solid materials containing these vapor phase inhibitors, said materials being suitable for packaging or enclosing metals.

During storage, handling, transportation, etc. of objects having metal or metal-containing surfaces, especially those of various steels, aluminum, etc., it is often necessary to prevent the 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 the packaging.

It is an object of the present invention to obviate the above and other defects, and to provide novel products or materials, which may be used as the enclosing or packaging means per se, or therein, and which materials are capable of inhibiting corrosion of metal parts stored or disposed in such enclosing or packaging means and/or in said enclosure means containing said novel materials.

It has now been discovered that a product or composition comprising a substantially solid (particularly fibrous) material having disposed thereon or therein one or more vapor phase corrosion-inhibitors, the vapors of which have access to the contiguous vapor space, prevents corrosion of corrodible metals disposed in the proximity of said compositions even in the presence of water vapor and oxygen. Suitable vapor phase inhibitors which are applicable according to this invention include salts of an organic nitrogen base with nitrous acid (organic base nitrites). Corrosion prevention was found to be effectively provided particularly by compositions comprising substantially solid covering materials containing organic nitrogen-base nitrites. It was also found that the vapor phase inhibitor should preferably have at least a vapor pressure of about 0.00002 mm. Hg at 21° C. Better results are obtainable with a vapor phase inhibitor having a vapor pressure greater than about 0.0001 mm. Hg at 21° C. while a more complete inhibition of corrosion is obtainable with a vapor phase inhibitor having a vapor pressure greater than about 0.001 mm. Hg at 21° C. The above mentioned compositions provide a highly satisfactory means for maintaining a corrosion-inhibiting atmosphere in the proximity of the metal.

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The compositions of the present invention may be realized and/or utilized in a number of ways which may differ in detail but not in the essentialities of the invention. Thus, these compositions may be prepared: by impregnating various cellulosic formulations with the inhibitors, by impregnating any sheet, film, fabric, or other partially porous or absorbent material with the inhibitors. Preferably the solid material chosen for impregnation has at least a fibrous structure so as to allow for absorption of the vapor phase inhibitors between the individual fibers of the carrier material. Where a carrier material is not particularly absorbent, it may advantageously be coated with the present inhibitors.

It was found particularly effective to impregnate the vapor phase inhibitors into a kraft paper which is either substantially neutral or which may be rendered neutral or somewhat basic in reaction by incorporation or impregnation therein of basic-acting materials, preferably an organic amine or other organic nitrogenous base.

Representative examples of solid materials which are suitable for use in conjunction with the vapor phase inhibitors include: paper; textile fabrics, e. g. of cotton, wool, or silk; wood; modified or stiffened papers such as card-board, fibre-board, and laminated papers; synthetic fabrics or spun textiles such as rayons, polyamides, nylons, polyvinylbutyral, and polyethylene; asbestos, charcoal, activated charcoal, alumina gel, silica gel, etc. Any sheet or strip material made of the above fibrous substances may

be used to prepare the novel compositions e. g. by coating these substances with a solution, emulsion, or dispersion of the organic vapor phase inhibitor(s) as long as the inhibitor may at least partially vaporize from the coating and thus be present in the contiguous atmosphere.

Impregnation or deposition of the vapor phase inhibitors described herein on any of the above solid materials is carried out by wetting, immersion, or soaking of the material with a dispersion or solution of the inhibitor(s), preferably in a relatively volatile organic solvent, in a mutual solution of water-soluble organic material and water, or in water alone. The impregnation may also be effected by distributing a melt of the inhibitor(s), with or without a melting-point lowering agent, upon the surface of the solid carrier material. The fibrous materials may also be impregnated by contact with the vapors of the inhibitors. The preferred method for impregnation, however, comprises deposition of the inhibitor(s) from a solution, the solvent or solvents used being evaporated by conventional methods, as by use of elevated temperatures, preferably not in excess of about 120° F. with or without air-blowing or the like. Suitable solvents include methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, acetone, methyl ethyl ketone, di-isopropyl ether, methyl acetate, and like volatile polar organic materials.

In many cases it is advantageous to treat or impregnate one or more paper laminates with the vapor phase inhibitor(s) and then fabricate these into a finished laminated composition which contains outer layers (laminates) which are much less porous or distinctly less impervious to the vapors of the inhibitor(s) than are the impregnated laminates which may be used for the interior of a package, or which are placed close to a corrodible metal. In such cases, the outer laminate may be a metal foil, such as tin or aluminum foil, preferably of sufficient thickness that it contains no pin holes. Similar results have also been obtained by coating one side of a vapor phase inhibitor-impregnated paper with a film of wax. With such wax paper containing the inhibitor(s), it is possible to enclose a metal object with one layer of the paper, and effectively prevent corrosion. In another embodiment of the invention, kraft paper waxed upon both sides was warmed to soften the surface layer on one side thereof, and crystals or powder of an organic nitrogen base nitrite was then sprinkled upon the softened wax. The latter was then cooled, and excess vapor phase inhibitor was shaken off. The resulting coated waxed paper was found to be an effective supplier of corrosion-inhibiting vapors. Other well-known coating materials may be used in place of wax for dispersion or incorporation of the present inhibitor(s) either before or after disposal of the coating material upon suitable solid materials. As such coating materials, reference may be made to: polyethylene, blends of polyethylene with waxes, polyalkylene resins, alkyd resins (e. g. of phthalic anhydride and glycerol), ethyl cellulose, polyamide resins, etc.

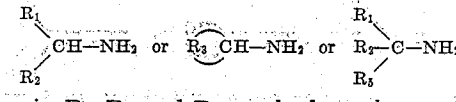
Vapor phase inhibitors which have been found applicable for use in the present compositions include salts of an organic nitrogen base with nitrous acid. Representative classes of nitrogenous bases which are suitable for preparing the present inhibitor-salts include such bases, for example, as: primary amines, secondary amines, tertiary amines, cyclic secondary amines of the type of piperidine, oxazines, morpholine, thiazolines and pyrrolidine; and various nitrogenous bases such as urea, thiourea, hydrazines, hydroxylamines, amidines, and guanidine. 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 nitrogenous compound is approximately equal to or greater than the acidity of nitrous acid with which it forms a salt. Among the substituent groups, the alkyl and cycloalkyl groups are preferred. Secondary amine nitrites, formed from nitrous acid and an amino nitrogen atom attached to a secondary carbon of an organic radical, as typified by di-isobutyl amine nitrite, di-isopropylamine nitrite, dicyclohexylamine nitrite, piperazine nitrite, morpholine nitrite, or 2,4,4,6-tetramethyl tetrahydro-3-oxazine nitrite are particularly effective vapor phase inhibitors.

The basicity of the various basic nitrogenous constituents of the class of salts disclosed herein is described, for example, the "The Organic Chemistry of Nitrogen" by N. V. Sidgwick, 1937 edition. The many various organic nitrogenous bases are also described in "Organic Chemistry" by Paul Karrer, 1938 edition.

More specifically and preferably, organic nitrogen base salts of nitrous acid 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:



wherein R_1, R_2 and R_5 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 hetero-cyclic-aliphatic ring radical R_3.

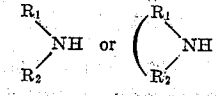
(*b*) primary amines in which the amine group is attached to an aralkyl group as in the following structural formula:

$$R_4—(CH_2)_n—NH_2$$

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, preferably a secondary or tertiary carbon atom, as represented by the following structural formulas:



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 wherein the amine group is attached to a secondary or tertiary carbon atom; cyclopentyl amine, alkylated cyclopentyl amines, cyclohexyl-amine, mono-methyl cyclohexylamines, dimethyl cyclohexylamines, trimethyl cyclohexylamines, other alkylated cyclohexylamines, bornyl amine, fenchyl amine, cycloterpenyl amines, pinyl amine, benzylamine, betaphenylethylamine, alkylated benzylamines, tetrahydrobetanaphthyl-amine, allyl amine, betamethyl allyl amine, beta-chloro allyl amine, 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)-menthyl amine, N-alkyl N-benzyl amines and their homologs and analogs; dicyclopentyl amine, dicyclohexyl amine, alkylated dicyclo-hexyl amines; diphenylamine, dibenzylamine, di-(beta phenyl ethyl) amine; piperidine, piperazine, alkylated piperidines or piperazines; 1,4-alkylated and unalkylated oxazines such as morpholine and 2,4,4,6-tetramethyl tetrahydrol-1,3-oxazine; alkylated-1,3-thiazine such as 2,4,4,6-tetramethyl tetrahydro-3-thiazine.

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 or propylene radical.

Tertiary amines: trimethyl amine, triethyl-amine, 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.

Various organic nitrogenous bases particularly guanidine, alkylated guanidines, alkylated thioureas, and also diazoles, imidazoles, imidazolines, e. g., 2-heptyl-2-imidazoline, diazines, pyrimidines, and the basic derivatives of these and other organic nitrogenous-base nuclei.

Quaternary ammonium bases: tetramethyl and higher tetra-alkyl 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 or analogs.

The various hydrocarbon radicals or groups of the above organic nitrogen bases 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 organic nitrogen-bases described above, may be prepared for example by a stoichiometric reaction of an organic nitrogen base with nitrous acid while maintaining the reaction mixture at least slightly basic in character.

The amount or concentration of the vapor phase inhibitor(s) which may be present in the compositions of this invention may vary within wide limits, but it is preferred to use them in the smallest effective concentrations. These are usually between about 0.05 gm. and about 5.0 gm. of the inhibitor per square foot of the surface of the substantially solid material employed therewith. Especially satisfactory results are attained when the inhibitor concentration is such as to allow between about 1.0 gm. and about 15 gm. (or for average conditions about 6 gm.) of the inhibitor for each cubic foot of enclosed vapor space.

Stability of the present vapor phase inhibitors, particularly the stability of organic nitrogen base nitrite salts, is usually adversely affected when they are present in a composition or an environment which, on contact with or dispersion in water, yields an aqueous phase having a pH value of less than about 6. Also this stability is frequently adversely affected by elevated temperatures, e. g., of the order of 120° F. or 150° F. These undesirable effects may be materially lessened or even entirely obviated by the simultaneous presence of a basic-acting agent, i. e. of an alkaline agent or a compound which reacts as a base in the presence of acidic-reacting materials. Preferably, it is advisable to use organic or inorganic compounds which, when dispersed in water, yield an aqueous phase having a pH value of at least 7. As such stabilizers, reference may be made to amines, guanidine, alkaline and alkaline earth metal hydroxides, carbonates and bicarbonates and the like basic materials. The amount of such stabilizer should be between about 0.1% and about 25% by weight of the vapor phase inhibitor, although larger or smaller amounts may also be used.

In cases where the absorbent, substantially solid material has a demand or chemical affinity for an organic base, particularly for the amine employed to prepare the nitrite salt thereof as the inhibitor, it is preferable to treat such solid absorbent material with the amine until this demand is satisfied.

The present compositions are improved, at least for certain corrosion-inhibiting purposes, by having them contain a mixture of vapor phase corrosion-inhibitors, at least one of which has a vapor pressure which is sufficiently high to provide immediate protection against corrosion while at least another inhibitor has a relatively low vapor pressure, which provides long-term corrosion-inhibition. The inhibitor with the low volatility is retained substantially in the vicinity

of the metal to be protected and does not escape to any material degree through the covering materials. In many cases, as with waxed paper or a metal foil enclosure, the high vapor pressure corrosion-inhibitor is also retained effectively in the vicinity of the metal.

The novel compositions of the present invention may be employed in a variety of ways for preventing corrosion of metals normally corrodible in the presence of air and water. The broad class of covering materials described herein containing the inhibitor(s) may be advantageously wrapped over, cloaked around, inserted near, draped over, or otherwise disposed in the immediate vicinity of the metal parts, so long as at least sufficient exterior covering is provided to keep an effective corrosion-inhibiting amount of the vapors arising from the present compositions in the proximity of the metal to be protected. As illustrative examples, a layer of vapor phase inhibitor-containing paper was inserted between every six or seven layers of steel ball bearings. About 16 sq. ft. of vapor phase inhibitor-paper was used per paper box containing approximately 250 steel bearings. The paper contained about 1 gm. of di-cyclohexylammonium nitrite per sq. ft. of paper. Inspection after one month showed the bearings were completely protected from rust, whereas the bearings in a control test were badly rusted. Also, a paper divider impregnated with di-isopropyl or di-cyclohexyl ammonium nitrite and used inside each package of two large steel half-bearings was found to keep the steel free from rusting. Also, a small piece of vapor phase inhibitor-containing paper was enclosed within a kraft-asphalt-kraft laminate paper package containing bright bar steel stock. The latter remained unrusted, while like steel stock packaged in the same type of a package, but without the present compositions, became rusted. Many forms of steel military equipment including artillery guns, tanks, etc. have been draped loosely with vapor phase inhibitor-containing paper, and kept within storage rooms. The equipment was found to have retained its initial rust-free condition during several months of such storage. On the other hand, like equipment stored in the same manner, but without the presence of the present compositions, was found to have corroded.

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.

Example I

Flat ¾ by 3 inch strips of thoroughly cleaned steel were wrapped in strong kraft paper which had been impregnated with di-cyclohexylammonium nitrite from a solution containing 20 weight percent of the amine nitrite in a mixture of 75 weight percent methyl alcohol and 25 weight percent water. The thus-wrapped pieces of steel were placed in an envelope made of kraft-asphalt-kraft laminated paper and then exposed in a humidity cabinet to a temperature of 100° F. and 100% humidity for a period of seven days. At the end of this time the packages were opened including those of control tests (in which kraft paper unimpregnated with a vapor phase inhibitor was employed). The steel strips wrapped with paper impregnated with the amine nitrite were found to be free of corrosion and shiny. The steel in the control test was very badly corroded with rust over practically its entire surface. A like test was carried out in exactly the same manner except 2 percent by weight of di-cyclohexylamine in addition to the 20 weight percent of the di-cyclohexylammonium nitrite in the impregnating solution was used to impregnate the wrapping paper. In this test the steel was also protected perfectly from rusting. Independent experiments indicated that the life of the di-cyclohexylammonium nitrite was increased materially by the impregnation of the paper with di-cyclohexylamine.

Example II

0.1 gm. pieces of 60 lb. kraft paper were immersed in a 2% by weight solution of dicyclohexylamine in 75% methanol-25% water solvent mixture for 10 seconds and then dried 5 minutes with warm air. One drop of 0.01 N sulfuric acid solution added to an entire extract of such treated paper changed phenolphthalein indicator over to the acid side. A sample of the described amine-impregnated paper was then tested in a sealed glass tube stability test wherein 0.1 gm. of the paper onto which was deposited 0.05 gm. of dicyclohexylammonium nitrite, was subjected to the vapors from 0.50 ml. of water. A tube for a control test was prepared using a sample of the untreated paper. After the testing periods indicated below, the contents of the tubes were analyzed for nitrite content, and the following results were obtained:

Duration at 212° F. in Hours	Percent of Nitrate Ions Present	
	Amine Treated Paper	Untreated Paper
2	90.0	75.5
4	87.5	51.0

Example III

The presence of guanidine nitrite in paper placed in the proximity of a strip of steel within an enclosure, completely prevents rusting and maintains the metal shiny. This test was carried out under conditions of 100% humidity at a temperature of 150° F. for a period of seven days. Similarly, it was found that a strip of brass was preserved free from corrosion when subjected to the conditions described herein. In the control tests the steel was badly rusted and the entire surface of the brass was covered with a blue-gray corrosion film.

Example IV

Kraft paper was passed twice through methyl alcohol containing 20 weight percent of di-cyclohexylammonium nitrite and 3 weight percent of di-cyclohexylamine. The solvent was removed by then passing the paper over a metal drum dryer internally heated by infra-red lamps. Flat machined pieces of steel were wrapped in the thus-treated paper, and then placed in separate paper envelopes, the edges of which were sealed with wax. These envelopes were then suspended in a cabinet under conditions of 100% humidity and a temperature of 120° F. After 300 hours of such exposure, only a few minute rust specks were present on the steel protected by the impregnated paper. On the other hand a like machined piece of steel in the control test was covered with rust specks over its entire surface.

Example V

The projecting outer surfaces of U-shaped machined steel strips were wrapped with kraft paper containing about 1 gm. of di-cyclohexylammonium nitrite per sq. ft. of the paper, and then overwrapped with aluminum foil having 0.005 inch thickness, the lapped edges of the foil being sealed with wax. A control sample of steel was wrapped in exactly the same manner except that plain unimpregnated kraft paper was used. These samples were then suspended in a cabinet having 100% of humidity, and maintained at 120° F. for 1000 hours. At the end of this period of time, there was no visible rust on any portion of the steel pieces packaged in the containers having the inhibitor. On the other hand, the steel of the control sample was badly rusted over more than 75% of its surface.

Example VI

Steel bearing parts were first wrapped in kraft paper impregnated with di-isopropylammonium nitrite, and then in light waxed paper. Control tests were wrapped likewise except that the kraft paper was not impregnated with any inhibitor. These packages were placed in large glass closed jars with water in the bottom and maintained at about room temperature for eleven months. At the end of this period of time it was found that there was no rust on the steel pieces wrapped in the impregnated paper, while the steel parts used in the control tests were badly rusted. For further comparison, like steel parts were first covered with a coating of a petroleum oil and then maintained at room temperature for eleven months. These steel parts showed a considerable number of rusted areas.

Example VII

By impregnating two parts by weight, of asbestos fiber with one part of di-cyclohexylammonium nitrite and then using this composition as dunnage for packaging steel articles, it is possible to keep the steel surfaces of such articles free from rust.

Example VIII

Four-ply spiral-wound kraft paper tubes, 18 inches long and 0.75 inch outside diameter were used in the following tests. The layers of the paper tubes were held together with casein glue, the pH of the tube was 9.4 and titration to a pH of 7 of the water extract of these paper tubes before impregnation showed that on the average each one of them contained approximately 0.002 equivalent of basic-reacting material.

One of these tubes was impregnated with a solution formed by dissolving 40% by weight of di-isopropylammonium nitrite in a 50 weight percent aqueous solution of isopropyl alcohol. The tube was found to contain 3.5 grams of di-isopropylammonium nitrite. Another one of these tubes was impregnated with a 20 weight percent solution of di-cyclohexylammonium nitrite in methyl alcohol, and was found to contain 1.6 grams of this organic nitrite salt inhibitor. A third tube (as a control) contained no inhibitor.

A 5-inch section of each of said three tubes was placed in a 1 inch by 6 inch Pyrex test tube. A ½ inch by 5 inch steel strip was placed inside each paper tube and the glass container test tube thereof was stoppered and maintained one hour at 120° F. Just before testing, the steel strip was polished with No. 2/0 emery paper. The tests were continued for one hour at 120° F., and then the solid stopper was replaced by a cork stopper having a ⅜ inch diameter hole, the test tube being then suspended open end down in a standard humidity cabinet held at 100° F. and 90% humidity. The results obtained are summarized in the following table:

Paper Tube Containing—	Appearance at Time in Hours					
	100 [a]	200	300	400	500	700
Di-isopropyl ammonium nitrite	no rust	no rust	no rust	no rust	no rust	no rust.
Di-cyclohexyl ammonium nitrite	do	do	do	do	do	Do.
None (control)	rusting on edges.	fine rust on faces, edges progressive rusting.	slightly more rust.	very little change.	little change	little change.

[a] The lower one inch of tubes were moist.

Example IX

Two steel bolt specimens were prepared by solvent washing, followed by wire brushing and then screwed into the fitting nut just far enough that the latter acted as a supporting base in which the bolt stood in a vertical position. Each of the prepared bolts was placed upright upon, the respective bottom of each of two 2-ounce sample bottles. In a prepared recess in the cork of the bottle containing the first of these specimens there was placed a small piece of cotton which had absorbed thereon 0.2 ml. of distilled water and 0.1 gm. of morpholine nitrite. The same amount of distilled water but without any vapor phase inhibitor, was absorbed in the same manner on a piece of cotton inserted into a prepared recess of the cork of the other of the two bottles. The respective bolts were not in contact with the cotton or the materials absorbed in the cotton. These corked bottles were allowed to stand at normal room temperature for a period of 76 days. At the end of this test period, the steel specimen which was subjected to the action of morpholine nitrite vapors was free from rust. The surface of this steel specimen was shiny as it had been at the start of the test. On the other hand, the other steel specimen was so severely rusted that the surface of it had a rusty appearance and had lost its original shiny polished surface.

Example X

Two $\frac{1}{16}$ inch low-carbon steel plates were machined to a ¾ inch by 3 inch strip and wire brushed to a bright metallic sheen. An inner wrap of neutral kraft paper and an outer wrap of laminated metal foil paper provided with an internal coating of a thermoplastic resin was provided around one of the described steel-plate specimens. The outer laminated metal foil wrap was heat sealed. The other steel plate was packaged in the identical manner except that the inner wrap of the neutral kraft paper, which in each instance measured 2 inches by 4 inches, was impregnated by dipping it in a 50% (by weight)

aqueous solution of morpholine nitrite. After dipping, the paper was dried by suspension for about 10 minutes in an air blast maintained at approximately 50° C. After such drying, the kraft paper contained approximately 0.1 gm. of the inhibitor.

Both specimens, after packaging, were immersed in synthetic sea water prepared according to U. S. Bureau of Ships Specification 14-0-15 (INT) (1934), for a period of 26 days, the water being maintained at a temperature of approximately 30° C. during the test. At the end of the test period these packages were opened. It was discovered that the steel plate wrapped in paper which did not contain any amine nitrite was badly corroded with rust. On the other hand, the steel plate packaged with the amine nitrite in the inner wrap retained its original polished and unblemished condition and appearance.

Example XI

Vapor phase corrosion tests were made with di-isopropylammonium nitrite to determine the effects on specimens of S. A. E. 1020 steel and 24 ST aluminum in coupled combination and also on the S. A. E. 1020 steel attached to a steel bolt. A one-half by one inch specimen of the metal alloy, coupled by a steel bolt through holes in each metal sample, was suspended in the vapor space of an 8 oz. wide-mouth bottle by means of a wire hook in a paraffined cork stopper of the bottle. A 16 sq. inch piece of kraft paper impregnated with approximately 0.2 gm. of di-isopropyl-ammonium nitrite, was placed on the bottom of a bottle of one series to be tested, while duplicate bottles containing the metals for control experiments were prepared containing the same amount of untreated kraft paper. To each of the containers was added 0.2 ml. of distilled water. All of the bottles were maintained at 30° C. for 73 days, after which time the specimens were removed, uncoupled, inspected and the weight loss determined after removal of any corrosion product, when present. It was found that, in the cases where di-isopropylammonium nitrite was used, there was no corrosion on either metal on the aluminum couple, and no corrosion (rust) on the S. A. E. 1020 steel . On the other hand, in the control experiment (in which no di-isopropyl-ammonium nitrite was used) there was bad and uniform rusting of the steel and some corrosion of the aluminum on the S. A. E. 1020 steel-24 ST aluminum couple, and fine rush specks over the entire surface of the steel.

Example XII

A ¾ by 3 inch specimen of aluminum was wrapped in 2 by 4 inch pieces of kraft paper impregnated with di-isopropylammonium nitrite which was then placed in another envelope made by folding 5 by 5 inch pieces of Grade A paper; the last envelope was then sealed with a pressure-sensitive, waterproof tape. Another aluminum specimen was similarly prepared, the only difference being that it was wrapped in an untreated piece of the said kraft paper. The envelopes or packages thus produced were suspended over water at 30° C. for 2 months, whereupon it was found that, whereas the aluminum specimen wrapped in the paper treated with di-isopropylammonium nitrite was not corroded, the aluminum specimen wrapped in the untreated paper had considerable white corrosion.

The term "hydrocarbyl" is used herein in accordance with the definition in Degering, "Outline of Organic Nitrogen Compounds," University Lithoprinters, Ypsilanti, Michigan (1945), page 59, namely, to designate a radical obtained by the loss of a hydrogen atom from any hydrocarbon.

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

We claim as our invention:

1. A substantially solid material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises paper containing between about 0.05 gram and about 5.0 grams per square foot of the surface of said paper, of di-isopropyl amine nitrite and a stabilizing amount of a basic-reacting agent.

2. A substantially solid material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises paper containing between about 0.05 gram and about 5.0 grams per square foot of the surface of said paper, of di-cyclohexyl amine nitrite and a stabilizing amount of a basic-reacting agent.

3. A material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises a substantially solid fibrous material containing between about 0.05 gram and about 5.0 grams per square foot of the surface of said fibrous material, of di-cyclohexy amine nitrite and a stabilizing amount of a basic-reacting agent.

4. A material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises a substantially solid fifrous material containing between about 0.05 gram and about 5.0 grams per square foot of the surface of said fibrous material, of di-isopropyl amine nitrite and a stabilizing amount of a basic-reacting agent.

5. A material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises a substantially solid fibrous material containing between about 0.05 gram and about 5.0 grams per square foot of the surface of said fibrous material, of di-cyclohexyl amine nitrite.

6. A material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises a substantially solid fibrous material containing between about 0.05 gram and about 5.0 grams per square foot of the surface of said fibrous material, of a di-cycloalkyl amine nitrite salt having a vapor pressure of at least about 0.00002 mm. Hg at 21° C.

7. A material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises a substantially solid fibrous material containing between about 0.05 gram and about 5 grams per square foot of the surface of said fibrous material, of di-isopropyl amine nitrite.

8. A material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises a substantially solid fibrous material containing between about 0.05 gram and about 5 grams per square foot of the surface of said fibrous material, of a secondary amine nitrite salt having a vapor pressure of at least about 0.00002 mm. Hg at 21° C.

9. A material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises a substantially

solid fibrous material containing a corrosion-inhibiting amount of an organic nitrogen-base nitrite salt of an unsubstituted hydrocarbyl amine, said salt having a vapor pressure of at least about 0.00002 mm. Hg at 21° C.

10. A material capable of inhibiting corrosion of a metal by an atmosphere containing oxygen and water vapor, which comprises a substantially solid fibrous material containing a corrosion-inhibiting amount of an organic nitrogen-base nitrite salt having a vapor pressure of at least about 0.00002 mm. Hg at 21° C.

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