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VAPOR PHASE CORROSION INHIBITION OF METALS

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The present invention relates to methods of inhibiting corrosion of metals. More specifically this invention pertains to novel methods of enclosing metals in materials or containers which contain vapor phase inhibitors. A vapor phase inhibitor may be defined to comprise a compound which inhibits corrosion of metal parts in the presence of water vapor 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. More specifically, this invention relates to the enclosing or packaging of metal objects in a manner whereby corrosion thereof by water vapor and/or aqueous condensates is prevented due to the presence of said vapor phase corrosion inhibitors.

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, or alloys of these metals, it is often necessary to prevent the corrosion of these metals when in the presence of water vapor. Heretofore, the various methods tried to prevent such corrosion have been unsatisfactory because such methods did not adequately prevent the corrosion, were cumbersome, did not prevent corrosion over a sufficiently long period of time, and/or required an excessive amount of labor and expenditure of time.

It is an object of the present invention to provide a novel method for enclosing, packaging, or covering metals whereby the enclosed metal parts are prevented from corroding even when water vapor and/or aqueous condensates are present in such containers. Another object is to provide packaging or covering materials containing vapor phase corrosion inhibitors thereby providing adequate corrosion inhibition to metal parts contained therein.

It has now been discovered that enclosing, packaging, or surrounding of metal parts by enclosure in or with materials containing a vapor phase inhibitor, the vapors of which have access into the thus enclosed space, prevents corrosion of the metal parts even in the presence of water vapor and oxygen. It was found that the vapor phase inhibitor should preferably have at least a vapor pressure of approximately 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. More rapid inhibition of corrosion

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is obtainable with a vapor phase inhibitor having a vapor pressure greater than about 0.001 mm. Hg at 21° C. Also it was found that corrosion of metal parts is inhibited by enclosing them in containers so that the vapors of the vapor phase inhibitor are provided and/or maintained in the enclosed space prior to the time of substantially complete closing thereof. 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. Thus, a vapor phase inhibitor may be effectively applied: by placing it as powder or crystals per se, or mixed with inert material, 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 absorbent material coated or impregnated with the vapor phase inhibitor, by wrapping the metal parts with a wrapping material, such as paper, cloth, cellophane, ethylcellulose, polyvinylbutyral, any sheet material, or the like, which are coated with, or impregnated with the vapor phase inhibitor, 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 vapor phase inhibitor to the contiguous atmosphere, as in the case of a waxed paper coated on one side with the inhibitor. A laminated paper or an asphalt paper impregnated or containing one or more of the present vapor phase inhibitors may be used. After providing the containers with the inhibitor in any of the above, or like modes, these packages may then be closed or sealed. The resultant package does not have to be completely closed or impervious to vapors or gases, but only has to be impervious to the extent that a sufficiently high concentration of vapors of the inhibitor are maintained in the package.

Preferably the vapors of the inhibitor should have a solubility in water of at least approximately 1% by weight. In some cases the degree of water-solubility may be very low, 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.

Vapor phase inhibitors which have been found applicable according to the present invention 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 constituents of the class of salts disclosed herein is described, for example, in "The Organic Chemistry of Nitrogen" by N. V. Sidgwick, 1937 edition. The many various organic bases are also described in "Organic Chemistry" by Paul Karrer, 1938 edition.

Various specific examples of organic base nitrites suitable for use in the present invention are described in our copending application, Serial No. 663,608, filed April 19, 1946.

Table I below sets forth some of the representative organic nitrogen base nitrites as well as their respective vapor pressures.

TABLE I

Compound	Vapor Pressure, mm. Hg at 21° C.
1. 2-amino butane nitrite	.0038
2. cyclohexylamine nitrite	.0027
3. betaphenylethylamine nitrite	.0019
4. 3,3,5-trimethylcyclohexylamine nitrite	.0018
5. morpholine nitrite	.0030
6. 2,4,4,6-tetramethyl tetrahydro-3-oxazine nitrite	.0017
7. dicyclohexylamine nitrite	.00012
8. piperidine nitrite	.00057
9. dibenzylamine nitrite	.00087
10. di-isopropylamine nitrite	.0047
11. trimethylbenzyl ammonium nitrite	.00035

Of the above compounds, di-isopropylamine nitrite, 2-amino butane nitrite and morpholine nitrite are especially suitable vapor phase inhibitors of the present invention because of their relatively high vapor pressures, their relatively higher solubility in water, and in view of the fact that a higher vapor pressure of the inhibitor results in a more rapid distribution of its vapors throughout the contiguous atmosphere.

The concentration of amounts of the vapor phase inhibitor which is employed to inhibit corrosion of a metal under the above specified conditions may vary within wide limits, but it is preferred to apply the smallest effective concentration. This is usually between about 0.1 gm. to about 5.0 gm., and preferably approximately 1.0 gm. of the vapor phase inhibitor present per square foot of the inner container surface. Especially satisfactory results are attained when the inhibitor is provided in such concentration as to allow between about 1.0 gm. and about 15 gm. (or for average conditions about 6 gm.) thereof for each cubic foot of enclosed vapor space. These specified concentrations of inhibitor may be obtained by placing a substantially solid sheet of material, paper, a fibrous composition, or an adsorbent material coated with or impregnated with a vapor phase inhibitor in the proximity of, or partly in actual contact with, a metal enclosed by a package or other housing or enclosure means. In actual practice it has only been necessary to have the initially applied unvaporized form of the inhibitor sufficiently close to the metal so that vapors arising from the substantially solid or liquid form of the inhibitor transfer sufficiently rapidly into the atmosphere contiguous to the metal, thereby inhibiting metal corrosion. Partial or substantially complete contact of the vapor phase inhibitor (or of compositions containing it) with the metal surfaces of the object to be protected (e. g. when a thin film or coating of the vapor phase inhibitor is deposited upon a metal) and then packaged, achieves the present invention more effectively and economically in that the metal is protected with more certainty, completely and immediately, and in that somewhat less inhibitor may be required. In this connection, a metal article coated with a vapor phase inhibitor, when enclosed within a package or container, will gradually set up an equilibrium with the vapor or gaseous phase of the enclosed space, and with the packaging material, no matter how small the enclosed gas-containing space. At equilibrium, substantially the same result is achieved as if the interior walls of the enclosing box or package had been coated with the vapor phase inhibitor instead of the inhibitor coating being initially on the metal. The main difference is however, that the closer the vapors or the solid form of the present inhibitors are to the surface of a metal, the more quickly there is attained a complete inhibition of corrosion. Where an enclosing material impregnated with one or more of the present inhibitors is not applied to cover a metal, as for example when the inhibitor-containing material is simply placed in or distributed throughout the interior space enclosed by a container, satisfactory inhibition of corrosion is attained by applying approximately 1 gm. to 15 gm., or usually about 6 gm., of an unvaporized form of the inhibitor per cubic foot of enclosed vapor space. However, lesser concentrations of the inhibitor may give satisfactory results under milder conditions. As a minimum requirement, an atmosphere containing at least some of the vapor of the inhibitor must be present in contact with a metal. Better results are obtained by having the metal article surrounded with an atmosphere which is approximately saturated with the vapor of the inhibitor.

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 of less than about 5. In some instances the stability is also adversely affected by elevated temperatures, such as 120° F. or 150° F. Such factors, or others which may render an organic nitrite salt unstable, 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 of the inhibitor. This addition of the alkaline agent to the unvolatilized portion of the vapor phase inhibitor 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. Suitable stabilizing agents include alkaline materials having dissociation constants approximately equal to or slightly less than the dissociation constant of the alkaline material which was combined to form the nitrite salt which it is desired to stabilize.

Various alkaline stabilizing agents which were found to be effective are: di-isopropyl amine, dicyclohexyl amine, aliphatic primary amines containing from 16 to 18 carbon atoms, various high molecular weight amines, 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 a stabilizer (by weight of the vapor phase inhibitor) are effective. It will be seen from the above that many alkaline materials have been found to be effective in stabilizing a salt of an organic nitrogen base with nitrous acid. In this respect any organic or inorganic compound which is capable of removing acidity or maintaining an alkaline condition is suitable as the stabilizing agent.

The vapors of amine nitrite salts may contain, and in a number of cases have been found to contain, vapors of the corresponding nitrosamine. In studies on stability it was found that the decomposition of some secondary amine nitrite salts was of an autocatalytic type. Decomposition of such an amine nitrite was also accelerated by small amounts of water. Such decomposition as a whole, however, was readily prevented by the presence of an alkaline agent of the class defined above.

It was stated above that an amine nitrite salt may be in equilibrium with the nitrosamine and water which are formed from the corresponding nitrite, and that the shift of the equilibrium toward the nitrosamine is increased at increasingly higher temperatures. This equilibrium may be stated as follows:

$$(a) \qquad R_2NH{\cdot}HNO_2 \overset{\text{Heat}}{\rightleftarrows} R_2N{-}N{=}O + H_2O$$

wherein R represents an organic radical. According to the usual laws of equilibrium, an excess of either water or nitrosamine or both above the chemically equivalent amounts indicated in the above equation tends to force the equilibrium toward increasing concentrations 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 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.

The present vapor phase inhibitors can be applied either separately or in various mixtures of members of this class, or with other vapor phase inhibitors. In certain cases it is advantageous to apply a mixture of inhibitors containing an inhibitor with a relativley high vapor pressure and an inhibitor with a relatively low vapor pressure. In this way the highly volatile inhibitor more rapidly protects metals in its vicinity, whereas the less volatile inhibitor gradually builds up an atmosphere saturated with its vapor. The latter is either substantially not lost or only lost to a slight degree due to partial permeability of an enclosure, whereas the highly volatile inhibitor may escape from an enclosure to a relatively greater degree than the inhibitor having a lower volatility. Once initial rapid inhibition of corrosion by the highly volatile inhibitor has been provided, usually the best overall long-term inhibition is provided by an atmosphere sufficiently concentrated with an inhibitor having a relatively lower volatility, such as dicyclohexyl ammonium nitrite.

The vapor phase inhibitors of the present invention, whether as such, or disposed on or in inert substances, upon contact with water or dispersion therein should preferably yield a solution having a pH of at least about 6 Alkaline agents, either volatile or non-volatile may be used with the present inhibitors to maintain the desired pH.

The vapors of organic nitrogen salts of nitrous acid are more effective in preventing aqueous corrosion of various ferrous metals, e. g., steels, as well as couples of steels with aluminum or copper or other metals, and aluminum and alloys of these metals. More satisfactory inhibition of corrosion of copper, and copper alloys, such as brass and bronze, is obtained when small amounts of volatile carbonates, such as ammonium carbonate or an organic nitrogen base carbonate, for example, di-isopropyl ammonium bicarbonate or dicyclohexyl ammonium bicarbonate, are present in the vapor phase along with the inhibitor.

Various techniques have been practiced in the utilization of the vapor phase inhibitors disclosed herein. Within any enclosure means, preferably comprising a substantially impermeable material, corrosion of metal surfaces by moisture is prevented by enclosing, or making available therein, a vapor phase inhibitor. The latter can be originally introduced as a solid, a liquid, or a vapor, or in solution, as an emulsion, or a dispersion, etc., as long as the inhibitor may vaporize and thus be present in the atmosphere around the metal. In the alternative, the inhibitor may be introduced as a vapor. In the case of enclosed metal articles, the inhibitor may be disposed as crystals or as a powder in various porous containers; or the metal article or the wrapping material thereof may be coated with material containing the vapor phase inhibitor. In one of the preferred embodiments of the invention it was found advantageous to use wrapping material, such as paper which was first impregnated with the vapor phase inhibitor. In another embodiment, waxed paper was warmed to melt or soften the surface layer of one side thereof and crystals or powdered di-isopropyl ammonium nitrite, or the like were then sprinkled upon the partially melted wax. The latter was cooled, and the excess vapor phase inhibitor was shaken off. The resulting waxed paper coated with the vapor phase inhibitor was found to be an effective supplier of corrosion-inhibiting vapors. Absorbent materials such as paper, cotton, wool, cloth, silica gel, alumina gel, fuller's earth, asbestos, and activated carbon are some examples of materials which can be impregnated with the above vapor phase inhibitors. In cases wherein free circulation of air is prevented around metal articles in storage, the present inhibitors are effectively applied by introducing them as vapor, or by providing an atmosphere containing inhibitor vapor around such metal articles. Corrosion by circulation of air over

metal surfaces can be prevented by substantially saturating the introduced air with vapors of the present inhibitors. Metal objects can also be coated with the vapor phase inhibitor by depositing the latter from a solution or a dispersion or from heated vapors contacting the metal, or by incorporating the inhibitor in relatively non-volatile coating materials. The latter may be a paint, a resin, a varnish, a lacquer, etc.

The present invention also includes the enclosing or making available of the vapor phase inhibitors within the vapor spaces present within or enclosed by machines, mechanisms, or metal articles of manufacture. Prevention of corrosion from the vapors and/or liquids present within the spaces enclosed by various hydraulic mechanisms, may be secured for instance by the introduction of one or more of the vapor phase inhibitors into a liquid hydraulic fluid. Aerosols and the carriers used therewith are also effective in distributing the present vapor phase inhibitors into shipping, handling, or storage enclosures.

The present inhibitors have also been found to reduce the corrosive wear of moving engine parts, the inhibitors thus acting as antiwear agents.

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 condition disclosed therein. The percentages specified in the following examples are percentages by weight unless otherwise specified.

Example I

Seven steel bolts, each of which was $\frac{5}{16}$ inch in diameter and 3 inches long, were solvent washed, electrolytically cleaned, and the threaded ends inserted into corks. These corks were then used as stoppers for 2-ounce bottles. In this way the bolts were suspended in the vapor space of these bottles. Six of the bolts were suspended in bottles each of which contained 0.2 ml. of distilled water and 0.2 gm. of a vapor phase inhibitor. The bottle containing the seventh bolt was provided with 0.2 ml. of distilled water only. The bolts were not in contact with the walls, bottom or liquids contained in the sample bottles. The vapor phase inhibitors thus tested in the respective bottles were: di-isopropylamine nitrite, morpholine nitrite, cyclohexylamine nitrite, piperidine nitrite, dibenzylamine nitrite, dicyclohexylamine nitrite. For a period of 14 days all of the bottles were subjected to alternate heating and cooling cycles, each bottle being heated to 50° C. for a period of 10 minutes, followed by cooling to 0° C. for 10 minutes and then permitted to stand at room temperature. Three such cycles were carried out during each day of the test. At the end of this 14-day test period, examination of all of the seven bolt specimens showed that only the seventh specimen (which had not been subjected to the vapors of one of the amine nitrites), was badly rusted. The test with the sixth specimen in which dicyclohexylamine nitrite was used, showed over 90% protection (prevention of rusting) as compared to the control specimen. The tests with the other five specimens showed complete prevention of rusting due to the presence of the respective mentioned vapor phase inhibitors. Other tests showed that dicyclohexylamine nitrite also was 100% effective as a vapor phase inhibitor in preventing corrosion of steel.

Example II

Two steel-bolt specimens were given the same preparatory treatments and then tested by means of suspension in sample bottles in the same manner as described above for Example I, except for the following differences: In the bottom of each sample bottle there was placed a folded pad of kraft paper, in each instance amounting to 8 square inches of the paper. In one of the bottles, the kraft paper had absorbed therein 0.1 gm. of di-isopropylamine nitrite and 0.1 ml. of distilled water. In the other bottle the paper had absorbed therein only 0.1 ml. of distilled water (without any vapor phase inhibitor being present). These two specimens were suspended in the respective bottles, stoppered tightly, and subjected to the alternate heating and cooling cycles described in Example I for a period of 37 days. At the end of this test period, it was found that the specimen disposed in the bottle containing the vapor phase inhibitor was preserved in its original appearance. On the other hand, the other specimen was so severely rusted that very little of the surface of this steel bolt was visible; in fact, over 90% of said bolt was covered with a heavy growth of rust.

Example III

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 IV

Two $\frac{1}{16}$ inch low carbon steel plates were machined to a $\frac{3}{4}$ 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 or 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 im-

mersed in synthetic sea water prepared according to U. S. Bureau of Ships Specification 14–O–15 (INT) (1943), 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 V

A test similar to that described in connection with Example II was made with an assortment of steel nuts, screws and bolts in two small paper cardboard boxes, ⅝ by 1¾ by 2¼ inches. A liner was made for each box, one of untreated kraft paper, and the other of kraft paper impregnated with approximately 0.14 gm. of di-isopropylammonium nitrite. The top of the box was made of clear cellulose acetate sheet to allow observation of the contents. A small hole approximately $\frac{1}{32}$ inch in diameter was punched in the cellulose acetate window of each box in order to allow ample breathing. These two boxes were alternately chilled to 5° C. and warmed to 30° C. several times a day for six weeks. After this period of time it was found that considerable rust was evident on the steel parts in the box containing the untreated kraft paper liner, but that there was no rust on the steel parts in the box lined with the paper containing di-isopropylammonium nitrate.

Example VI

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 pipeces 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 the 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.

Example VII

A number of tests were effected: In each case a low-carbon steel specimen, ½ inch by 2 inches, was first cleaned electrolytically, neutralized with sodium carbonate, rinsed in distilled water, and then dried by carefully rinsing with acetone and drying. The steel specimen was then weighed and suspended in the vapor space of a 125-ml. bottle by means of a glass hook placed in a cork fitted into the under side of a hollow stopper. One-half gram of the compound to be tested and 0.5 ml. of distilled water were placed at the bottom of each bottle (maintained in the upright position) and then the stopper with the attached steel specimen was put into place. This stopper was sealed with a silicone stopcock grease. The thus-prepared bottle and contents were maintained at 150° F. for 7 days, after which the specimens were removed, washed with acetone, dried in a vacuum desiccator and the weight changes determined. The following results were obtained:

Inhibitor	Gain in Weight (in Grams)	Approximate Protection of Surface Area Against Rusting
None	.0579	5% protection.
Do	.1022	0%.
Di-Secondary-butylammonium nitrite.	.0026	90% protection.
Di-Cyclohexylammonium nitrite	.0101	99% protection.
Di-Isopropylammonium nitrite	.0052	90% protection.
Do	.0163	Do.
Guanidinium Nitrite	.0008	Do.

Example VIII

0.1 gm. pieces of 60 lb. kraft paper were immersed in a 2% by weight solution of discyclohexylamine 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 Nitrite Ions Present	
	Amine Treated Paper	Untreated Paper
2	90.0	75.5
4	87.5	51.0

Example IX

One tenth of a gram of di-isopropylammonium nitrite containing or intimately admixed with 10 per cent by weight of sodium bicarbonate was impregnated into 8 square inches of kraft paper, placed in the bottom of a glass bottle, and 0.1 ml. of distilled water added. In the vapor space of this wide-mouth bottle, a steel bolt was suspended by attaching it to the stopper of the bottle. The steel bolt specimens used in such a test were given the same preparatory treatment as that described for Example I. Control experiments on untreated kraft paper were run under the same conditions side by side for comparison. Twice each day the described sealed bottles with their contents were chilled to 0° C. for 20 to 30 minutes, warmed to 50° C. for 5 minutes and allowed to stand at room temperature (about 25° C.) the remainder of the time. The steel bolt in the stoppered bottle containing untreated kraft paper rusted during the first day of the control test, but the steel bolt in the stoppered bottle containing the kraft paper impregnated with 0.1 gm. of di-isopropylammonium nitrite containing 10 per cent by weight of sodium bicarbonate did not rust after four weeks of being subjected to the cycles of this test.

Example X

Tests were conducted to show the effect of paper tubes on the stability of di-isopropylam-

monium nitrite. Four-ply spiral-wound kraft paper tubes, 18 inches long and 0.75 inch outside diameter were used in these 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. The conditions of operation and the results obtained are summarized below.

A 5-inch section of the hollow ¾-inch diameter paper tube impregnated with a volatile organic amine nitrite to be tested was placed in a 1 by 6 inch Pyrex test tube. A ½ inch by 5 inch steel strip was placed inside the 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 test was 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:

Vapor Phase Inhibitor	Amt. Impregnated per 18 inch length tube	Appearance at Time in Hours					
		[b] 100	200	300	400	500	700
	Grams						
Di-isopropyl ammonium nitrite.	3.5	no rust	no rust	no rust	no rust	no rust	no rust.
Di-cyclohexyl ammonium nitrite.[a]	1.6	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] Tube impregnated with 20% solution di-cyclohexylamine nitrite in methyl alcohol.
[b] The lower one inch of tubes were moist.

As is apparent from the results in the above table, control steel specimens in paper tubes not impregnated with volatile corrosion inhibitors were rusted considerably even after the first few days of treatment. After 400 hours exposure, no rust was present on any of the steel specimens in the di-isopropylammonium nitrite-impregnated paper tubes. After 700 hours, the steel specimens in the di-isopropylammonium nitrite-impregnated paper tubes were free of rust. After this length of time (700 hours), there was no rust present on the steel specimen inside the paper tube impregnated with di-cyclohexylammonium nitrite.

The present invention 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. In a method for packaging a metal normally corrodible by contact with water vapor and oxygen, the step of enclosing said metal within a fibrous material containing dicyclohexyl amine nitrite in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

2. In a method for packaging a metal normally corrodible by contact with water vapor and oxygen, the step of enclosing said metal within a fibrous material containing di-isopropyl amine nitrite in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

3. In a method for enclosing a metal normally corrodible by contact with water vapor and oxygen, the step of enclosing said metal within a fibrous material containing a secondary amine nitrite having a vapor pressure of at least about 0.0001 mm. Hg at 21° C., said nitrite being present in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

4. In a method for packaging a metal normally corrodible by contact with water vapor and oxygen, the step of enclosing said metal within a substantially solid covering material containing a secondary amine nitrite salt having a vapor pressure of at least about 0.0001 mm. Hg at 21° C., said nitrite being present in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

5. In a method for packaging a metal normally corrodible by contact with water vapor and oxygen, the step of enclosing said metal within a substantially solid covering material containing an organic nitrogen-base nitrite having a vapor pressure of at least about 0.0001 mm. Hg at 21° C., said nitrite being present in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

6. The combination comprising a metal article normally corrodible by contact with water vapor and oxygen and a fibrous material enclosing said metal article, said fibrous material containing dicyclohexyl amine nitrite in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

7. The combination comprising a metal article normally corrodible by contact with water vapor and oxygen and a fibrous material enclosing said metal article, said fibrous material containing di-isopropyl amine nitrite in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

8. The combination comprising a metal article normally corrodible by contact with water vapor and oxygen and a fibrous material enclosing said metal article, said fibrous material containing a secondary amine nitrite having a vapor pressure of at least about 0.0001 mm. Hg at 21° C., said nitrite being present in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

9. The combination comprising a metal article normally corrodible by contact with water vapor and oxygen and a substantially solid covering material enclosing said metal article, said covering material containing a secondary amine nitrite having a vapor pressure of at least about 0.0001

mm. Hg at 21° C., said nitrite being present in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

10. The combination comprising a metal article normally corrodible by contact with water vapor and oxygen and a substantially solid covering material enclosing said metal article, said covering material containing an organic nitrogen-base nitrite having a vapor pressure of at least about 0.0001 mm. Hg at 21° C., said nitrite being present in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

11. In a method for packaging a metal normally corrodible by contact with water vapor and oxygen, the step of enclosing said metal within a fibrous material containing an N-hydrocarbyl ammonium nitrite salt having a vapor pressure of at least about 0.00002 mm. Hg at 21° C., said nitrite salt being present in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

12. The combination comprising a metal article normally corrodible by contact with water vapor and oxygen, and a substantially solid covering material enclosing said metal article, said covering material containing an organic ammonium nitrite salt having a vapor pressure of at least about 0.0001 mm. Hg at 21° C., said nitrite salt being present in an amount sufficient to maintain a corrosion-inhibiting atmosphere which, upon dispersion in water, yields a solution having a pH value of at least about 6.

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