

2,717,843

SHEET FOR PROTECTION OF METALS FROM CORROSION AND METHOD OF MAKING

Aaron Wachter, Oakland, and Nathan Stillman, El Cerrito, Calif., assignors to Shell Development Company, Emeryville, Calif., a corporation of Delaware

No Drawing. Application July 7, 1952,
Serial No. 297,562

17 Claims. (Cl. 117-156)

The present invention relates to novel vapor phase corrosion inhibiting compositions and products thereof. More particularly, it relates to articles comprising a substantially solid material which contains, or is impregnated or coated with a mixture of at least two salts which interact to form volatile corrosion-inhibiting substances capable of inhibiting the corrosion of corrodible metals in moist air. The materials impregnated with these mixtures may be of the kind suitable for packaging, inserting in a package, or for enclosing metals.

During storage, handling, transportation, etc. of objects comprising or consisting of a corrodible metal exposed to the atmosphere, specifically a ferrous metal, various steels, aluminum or alloys of these metals, it is often necessary to prevent their corrosion. Heretofore, 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 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 they enter later through the enclosure walls after packaging. This results in corrosion of the metal, particularly of steels.

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

It has now been discovered that the above and other objects may be attained and the corrosion of a corrodible metal by moisture and air is inhibited by providing for contact of said metal with vapors arising from substantially solid materials containing, coated upon, impregnated therein or otherwise physically incorporated therewith, both an ionic inorganic metal nitrite salt and an ionic organic base salt of an acid other than nitrous acid. A particularly useful organic base salt is an organic base phosphate salt. By the latter is meant a salt of an organic base and a phosphoric acid wherein at least approximately two of the acid (hydroxyl) radicals of the latter have been combined with at least two molecules of the same or different organic bases. The term "ionic" means capable of ionizing in a conventional ionizing medium, such as an aqueous medium.

It has further been discovered that said corrosion-inhibition is effected by one or more of the present mixtures in proximity to the metal to be protected, which mixture comprises essentially an ionic organic nitrogen-base phosphate salt and an ionic metal nitrite contained in, or impregnated within a substantially solid organic material. It is believed that the vapors which arise from one or more of the present mixtures are a result of ion interchange between the at least two essential component

salts of the mixture, and that these vapors are composed essentially of a volatile organic base nitrite.

It was further discovered that said corrosion-inhibition of steel is preferably effected by the proximity of organic fibrous materials impregnated with first: an amine phosphate, particularly a secondary amine phosphate, and second: a water-soluble ionic metal nitrite. More particularly, in such a preferred case, the fibrous material, such as paper, is impregnated with an aqueous solution of an amine phosphate and then with a water solution of a metal nitrite, whereby an ion interchange takes place in the aqueous system of the wet fibrous material to yield a volatile organic base nitrite.

As to the referred-to ionic metal nitrites, any water-soluble metal nitrite may be used, but most preferred are the base metal nitrites, i. e., the alkali metal nitrites, for instance sodium nitrite, potassium nitrite, and lithium nitrite or alkaline earth metal nitrites such as calcium nitrite, barium nitrite and magnesium nitrite.

The term "present mixtures" or the term "mixtures of salts" as used herein mean mixtures of a water-soluble metal nitrite salt and a water-soluble organic base salt of an acid other than nitrous acid. Preferably, a "present mixture" comprises essentially a water-soluble organic base-phosphate salt mixed with a metal nitrite.

In general, the organic phosphate salt and the metal nitrite may be introduced into the substantially solid organic material by solutions, suspensions, dispersions, or emulsions in any media so long as sufficient water is present therein to promote at least a partial ion interchange between the phosphate and the nitrite spoken of above and so long as the pH value of the resultant combination is at least approximately 6, and preferably at least about 7. The pH range should in general preferably not extend higher than about a pH of 12, and is most desirable within a range of a pH of 6 to a pH of about 9. The organic material acts as a carrier of the present corrosion-inhibiting composition and may also act as a means of enclosure for a metal. The organic material employed is simply a material not containing functional groups which are conventionally known to chemically react with the functional groups of the present active corrosion-inhibiting ingredients. In general, then, the organic material referred to herein is substantially non-reactive chemically with the present cooperating mixture of corrosion-inhibitors under the conditions of use of said mixture.

With reference to the above-described media for the present corrosion-inhibitors, these media are also substantially non-reactive chemically with the inhibitors under the conditions of impregnation, etc. If some slight reaction does take place in unusual instances, in general, it will not be sufficient to negative the positive results obtained from the present invention.

In general, the present compositions of an organic phosphate salt and a metal nitrite salt function in any atmosphere in contact with a metal so long as condensation of the atmosphere and/or dispersion of same in water forms a liquid having a pH value of at least approximately 6, and preferably a pH of at least about 7. The pH value of the compositions and/or atmosphere should preferably in general not extend higher than a pH of about 12, and is particularly more effective when within a range of a pH of 6 to a pH of about 9. By an atmosphere is meant a gas (commonly moist air), a liquid, a gel, a semi-solid, a grease, or an at least partially permeable solid, or a mixture of any one or all of these, so long as the atmosphere permits the volatile organic base nitrites (formed from the present compositions) to diffuse or be transferred by other natural forces to the surface of the metal.

In general, the organic phosphate and the metal nitrite

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can be introduced or impregnated into a suitable carrier, preferably an organic material, either approximately simultaneously or in a stepwise fashion, one after the other. Either the phosphate or the nitrite may be introduced first, the order of introduction not being material in the invention so long as both the phosphate and the nitrite are retained in sufficient quantities in the material impregnated. Insofar as manner of impregnation is concerned, any practicable manner known heretofore to those skilled in the art of impregnation, may be used. One may impregnate the organic material or any substantially neutral material retentive of the organic phosphates, by simply immersing or soaking the material in, impressing or spraying upon it first a simple water solution of the organic phosphates(s) followed by a similar or like manner of introducing the nitrite(s) into the organic material. This is a preferred order of impregnation in that usually the organic material retains the organic phosphate better from an initial aqueous impregnation and then reacts better with the metal nitrite when it is impregnated, then precipitating the relatively water-insoluble organic base nitrite salt into the organic material.

For purposes of impregnation, the organic base phosphate salt and the metal nitrite salt generally cannot be mixed in the same water solution prior to impregnation because the low solubility of the organic base nitrite salt causes it to precipitate out, thereby tending to prevent impregnation of a sufficient concentration of the nitrite in the solid organic material. Also, if both the phosphate salt and the nitrite salt are mixed in the same water solution, an important advantage is lost in that the precipitation of the organic nitrite salt does not take place intimately and in finely divided incipient form within the interstices and upon the fibers of the organic material. As a result, a strong attachment of the precipitate thereto does not occur in such a case. However, where a simple water solution is not used and the aqueous solvent is modified by having a sufficient quantity of an organic solvent therein for keeping any potential precipitate of organic base nitrite salt in solution, then the organic base phosphate and metal nitrite may be mixed in such a liquid organic solvent-water blend, and the resultant solution applied in a single step to the organic material. In this modified mode of impregnation, however, precipitation or fixing of the organic base nitrite salt in the organic material will not take place so long as the specified organic solvent-water blend is present. Therefore, in this case simple immersion of the organic material (e. g., paper, a synthetic textile fabric, or cloth) in the aqueous organic solvent will not be sufficient unless the concentrations of the organic base phosphate salt and the metal nitrite are higher than that used in the water impregnation or high enough that evaporation of the solvent from the immersed material leaves at least a minimum concentration therein of active ingredients. Minimum concentrations are later specified below. Suitable solvents for the organic base phosphate salts, besides water, include methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, as well as mixtures of these alcohols with water, benzene-alcohol-water mixture, etc. The water-soluble metal nitrites are also soluble in the lower alcohols, particularly when admixed with a relatively small ratio of water.

In using the latter modified impregnation procedure, it is often desirable to wet or soak a sheet of the organic material in a solution of the mixed organic phosphate salt and the metal nitrite, withdraw the wet sheet, and then dry it by any suitable means, such as a conventional steam-heated drying press.

A particularly advantageous modified form of the compositions of the present invention is obtained by coating the present mixtures of the salts as suspensions or pastes which contain a suitable binder, onto the solid organic material carrier, e. g., paper. In forming the resultant compositions, a surface-active agent or a colloid

may be employed advantageously with the suspension to stabilize it and impart improved wetting and adhering qualities to the suspension so that it is bound more effectively to the organic material carrier. The binder is used in adapted amounts suitable for a given finished coated paper, for example. Suitable binders, which bind the present "mixtures of salts" to the preferred fibrous materials (or other carriers), are glues, casein glues, mucilaginous materials, natural or synthetic adhesives, gums, and water-soluble or colloiddally dispersible resins including those conventionally employed in the paper-making and textile fabric-manufacturing industries. Starch, dextrin, and/or shellac may also be employed. It is not always essential that appreciable ionic interchange occurs between the salts of the "present mixtures" at the time of coating or impregnation so long as a later introduction of moisture gives sufficient interchange (yield of volatile organic base nitrite) to meet the corrosion-inhibiting purpose at hand.

The vapor phase inhibiting organic base nitrite salt liberated by interaction in the present mixtures should have preferably at least a vapor pressure of approximately 0.00002 mm. Hg at 21° C. Better results are obtainable from such a liberated organic base nitrite having a vapor pressure greater than about 0.0001 mm. Hg at 21° C. while a more rapid inhibition of corrosion is obtainable with such a liberated organic nitrite salt having a vapor pressure greater than about 0.001 mm. Hg at 21° C. The compositions described herein provide a highly satisfactory means for maintaining a corrosion-inhibiting atmosphere of organic base nitrite salt vapors in contact with a metal in the proximity of the compositions.

The compositions and articles 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 or coating any sheet, film, fabric, or other inert solid material with the present mixtures. Preferably the solid material chosen for impregnation has at least a fibrous structure so as to allow for absorption and adsorption of the present mixture of salts between and upon the individual fibers of the carrier material. Where a carrier material is not particularly absorbent, it may advantageously be coated with one of the present mixtures of salts.

It was found particularly effective to impregnate the present mixture of salts into a kraft paper or other strong papers, the composition as a whole being also impregnated, if necessary, with a sufficient amount of basic-reacting material, preferably an organic amine or other organic nitrogenous base, to render the composition with a pH value of at least approximately 6.

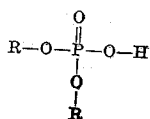
Representative examples of inert solid materials which are suitable for forming the present compositions with the present mixtures of salts, include: paper; textile fabrics, e. g., of cotton, wool, silk; wood; modified or stiffened papers such as card-board, fiber-board, and laminated papers; synthetic fabrics or fibers such as rayons, polyamides, nylons, polyvinylbutyral, polyethylene; asbestos, charcoal, alumina gel, silica gel, metal foils, etc.

In many cases it is advantageous to treat or impregnate one or more paper laminates with the mixture of organo base phosphate salt and water-soluble metal nitrite. Those laminates are then fabricated into a finished laminated product or article. The impregnated paper laminates may be used as corrosion-inhibiting means for the interior of a package, or may be placed close to a corrodible metal to protect it. In such cases, the outer laminate may be metal foil, such as tin or aluminum foil, preferably of sufficient thickness so as to contain no pinholes. Results similar to those with the above laminates have also been obtained by impregnating paper with the mixture of an organo base phosphate salt and a metal nitrite and having one side of the paper coated with a

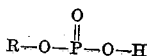
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film of wax. With this prepared paper, it is possible to enclose a metal object with one layer of this paper, and effectively prevent corrosion. An intimately ground mixture of the present mixtures of salts may be dispersed in wax and impregnated into paper. An aqueous wax emulsion may be used for this purpose and the water mechanically pressed out of the impregnated paper. Other well-known coating materials may be used in place of wax for dispersion or incorporation of the present mixtures whether before or after disposal of the coating material upon suitable solid materials. Among these, reference may be made to polyethylene, blends of polyethylene with waxes, polyalkylene resins, alkyl resins (e. g., of phthalic anhydride and glycerol), ethyl cellulose, polyamide resins, etc.

Although any ionic salt of an organic base and a non-nitrite anion may be employed as one of the essential components in the present mixtures, the preferred class of an acidic compound (i. e., source of anion) for forming such salts consists of acidic hydrogen oxyphosphorus-radical-containing compounds. The latter comprise or consist essentially of inorgano and organo compounds containing at least a mono acidic hydrogen phosphate radical or a mono acidic hydrogen phosphite radical, and preferably at least two such acidic hydrogens in an oxyphosphorus radical having the general formulas, respectively, of:



and



wherein each R may be the hydrogen atom or a suitable organic radical such as alkyl, aryl, phenyl, aralkyl, alkaryl, alkenyl, alicyclic and/or heterocyclic radicals. Among the many acidic phosphate or acidic phosphite nuclei-containing compounds which may thus be employed to form the non-volatile organic base salts, there are: the various phosphoric acids, the various phosphorous acids, mono- and di-alkyl ester-phosphoric acids wherein, for example, the alkyl group is an ethyl, propyl, dodecyl, etc., radical; also cycloalkyl (naphthenic, terpenic, bornyl, cyclohexyl) acidic phospho esters.

Although phosphate anions are preferred for forming the organic base, non-nitrite, anionate salt component of the present mixtures other water-solubilizing anions may be used. Organic anions can be used as well as inorganic anions. Of the organic anions, the carboxylate ions are preferred. Examples of suitable anions are oxalate, benzoate, acetate, propionate, citrate, tartrate, borate, nitrate, sulfate, chloride, chromate, iodate, carbonate, etc. The only limitation upon the anion is that it be from an acid sufficiently strong to form a salt with the organic base.

Organic base phosphates or other anionate salts which have been found applicable for use in conjunction with water-soluble metal nitrites in the present compositions include salts of the following representative types of organic bases: primary amines, secondary amines, tertiary amines, cyclic secondary amines of the type of piperidine, oxazines, morpholine, thiazines, thioxazines, pyrrolidines, diazoles, imidazolines, diazines, pyrimidines; and various nitrogenous bases such as guanidine, urea, thiourea, hydrazines, hydroxylamines, etc. The various known sulfonium organic bases are also suitable for forming sulfonium phosphate salts for use in the present invention. In any of the organic base nuclei (used to form the present organic base-anionate salts),

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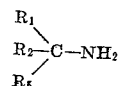
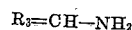
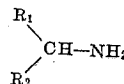
there may be present alkyl, cycloalkyl, terpinyl, bornyl, aralkyl, benzyl, phenyl, aryl, and various substituent groups or atomic radicals so long as the sum total basicity of the organic base is sufficient to form a salt with the phosphoric acid anion or other anion with which it is combined. Among the substituent groups, the alkyl and cycloalkyl groups are preferred. Secondary amine phosphates are preferred for the present purposes, and more particularly those formed from a phosphoric acid and an amino nitrogen atom attached to a secondary carbon atom of an organic radical, as typified by a di-isobutyl amine phosphate, a di-isopropylamine phosphate, a di-cyclohexylamine phosphate, a piperazine phosphate, a morpholine phosphate, a 2,4,4,6-tetramethyl tetrahydro-3-oxazine phosphate. These are particularly effective phosphates for the practice of the present invention.

The basicity of the various basic constituents of the salts disclosed herein is described, for example, in "The Organic Chemistry of Nitrogen" by N. V. Sidgwick, 1937 edition, in "Organic Chemistry" by Paul Karrer, 1938 edition, and in "Organic Chemistry" by Fieser and Fieser, 1944 edition.

More specifically and preferably, organic nitrogen-base salts of a phosphoric acid include phosphoric acid salts of the following:

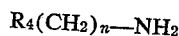
1. Primary amines such as

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



wherein R₁, R₂ and R₃ 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 R₁ and R₂ are joined as indicated by R₃ to form with the CH-group a cyclo-aliphatic or heterocyclic-aliphatic ring radical R₃=CH—.

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



wherein R₄ is an aromatic hydrocarbon radical, preferably a phenyl or substituted (preferably alkylated) phenyl radical and n is an integer which is preferably 1 or 2;

(c) Simple primary aliphatic amines, such as methyl amine.

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



wherein R₁ and R₂ are hydrocarbon radicals as in 1 (a) and wherein R₁ and R₂ may be joined to form with the

NH-group a nitrogen-containing heterocyclic ring represented as



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.

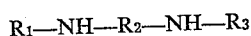
4. Quaternary ammonium bases including pyridinium bases.

Specific examples of organic nitrogen bases suitable for preparation of the organic nitrogen-base non-corrosive anionate salts for utility in the practice of the present invention include:

Primary amines: methylamine, isopropyl amine, 2-aminobutane, tertiary butyl amine, 2-amino-4-methylpentane, 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, cyclohexylamine, mono-methyl cyclohexylamines, dimethyl cyclohexylamines, trimethyl cyclohexylamines, other alkylated cyclohexylamines, bornyl amine, fenchyl amine, cyclo-terpenyl amines, pinyl amine, benzylamine, betaphenylethylamine, alkylated benzylamines, tetrahydrobetanaphthylamine, allyl amine, betamethyl allyl amine, betachloro 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-cyclo-terpenyl amine, N-isopropyl N-(1)-menthyl amine, N-alkyl N-benzyl amines and their homologs and analogs; dicyclopentyl amine, dicyclohexyl amine, alkylated dicyclohexyl 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 tetrahydro-1,3-oxazine; alkylated 1,3-thiazine such as 2,4,4,6-tetramethyl tetrahydro-3-thiazine.

Second amine type derivatives of alkylene diamines, such as:



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, triethylamine, tri-n-propylamine, 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.

In general the invention is preferably practiced by using as the non-nitrite salt, a phosphate salt formed by the addition of a phosphoric acid to a trivalent basic nitrogen atom of a nitrogenous organic compound.

The salts of a phosphoric acid or of other non-corrosive acid anions with the organic nitrogen-bases described above are preferably prepared by a relatively simple neutralization of such a base with the desired acid. If desired, it is effective to use two moles of an organo-nitrogen-base or an amine to react with one mole of a tribasic phosphoric acid, thus forming a diamino-hydrogen-phosphate.

The amount or concentration of each of the essential components of the present mixtures, namely water-soluble organic base salts and water-soluble metal nitrite salts respectively, which may be present in the compositions and articles of this invention, may vary within wide limits, but it is preferred to use them in the smallest effective concentrations. The concentrations of each of the respective salts are preferably so chosen that interaction between them in the impregnated fibrous material allows between approximately 0.05 gm. and about 5.0 gm. of the reaction product, a volatile organic base-nitrite salt, to form per square foot of the exposed or free surface of the substantially solid material employed therewith. The best or optimum results in most cases of fairly severe usage are obtained by having the respective salts present in amounts sufficient to form by ionic interchange between about 0.5 gm. and about 2 gm. of a volatile organic base-nitrite salt per each square foot of such a surface. It is preferable to adjust the respective concentrations of the organic base salt and the metal nitrite salt in the material so that the organic cations are approximately stoichiometrically equivalent to the nitrite anions provided by the metal nitrite salt, although slight excesses, up to about 10% or 20% of either of the salts can be used without serious adverse effects.

The range of concentrations of the organic base salt in the impregnating solution will usually vary from about 1 wt. per cent to about 25 wt. per cent (or saturation, whichever is higher) in a given solvent. More often it is preferred to impregnate a fibrous material with between about 5% and about 20% by weight in solution of one or more of the specified salts. Also, the same concentrations for impregnation are useful for the aqueous metal nitrite solutions; in general, it is preferable to employ a somewhat higher solution concentration of the metal nitrite, such as about two to three times that employed for the organo phosphate salt.

The time required for the dipping or impregnating operations is readily determined (as to meet specific conditions for final concentrations of salts desired in the impregnated material) by empirical aliquot tests. For most purposes, however, the time of immersion of a fibrous material in an impregnating solution need not be more than about one minute, although longer times may be used; and in many cases immersion for approximately about one to about ten seconds in about a 10 wt. per cent concentration of impregnant in water has been found to suffice.

Stability of the organic base-nitrite salts (i. e., vapor phase inhibitors), formed from interaction of the present mixtures of salts, is usually adversely affected when said organic nitrites are present in a composition or environment which, on contact with or dispersion in water, yields an aqueous phase which is appreciably acidic, that is has a pH value of less than approximately 6. Also this sta-

bility of the liberated organic nitrite salts 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, and even be entirely obviated by the simultaneous presence in the present mixtures of a basic-reacting agent, i. e., an alkaline agent or a compound which reacts as a base in the presence of acidic-reacting materials. As such basic-reacting stabilizers there may be used an organic or inorganic compound which, when dispersed in water, yields an aqueous phase having a pH of at least 7 and preferably somewhat higher than a pH of 7. As such stabilizers, reference is made to amines, guanidine, alkaline and alkaline earth metal hydroxides, carbonates and bicarbonates, organic bases, basic salts, etc. The amount of stabilizer, when necessary, should be between about 0.1% and about 25% by weight of the organic base nitrite salt to be liberated from the present mixtures, although larger or smaller amounts may 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 phosphate salt thereof, and which interacts in the impregnated material to liberate an amine nitrite, then it is preferable to treat such a solid absorbent material with the free amine until this demand is satisfied.

The novel compositions of substantially solid materials containing the present mixtures of metal nitrites and organic base salts may be employed in a variety of ways for preventing corrosion of metals normally corrodible in presence of an oxygen-containing gas and water. The broad class of covering or enveloping materials described herein containing said mixtures may be advantageously wrapped over, cloaked around, inserted near, draped over, or otherwise disposed in the immediate vicinity of metal parts, so long as at least sufficient exterior coating or enclosure is provided to keep an effective corrosion-inhibiting amount of organic base-nitrite vapors arising from the present compositions in contact with a metal to be protected. All that is necessary is this vapor phase contact.

Particular advantages of the utility of the present invention are: it eliminates entirely the prior necessity of having to synthesize an organic base nitrite salt before impregnation in a fibrous material; it eliminates the prior necessity of having to use an inflammable organic solvent for an organic base nitrite to impregnate it into a material because of the organic nitrite being insufficiently soluble in water or aqueous solutions; it eliminates the prior necessity for the production of nitrous acid formerly needed to prepare the organic base nitrite salts.

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 disclosed therein.

Example I

Samples of kraft wrapping paper were impregnated with certain salts as enumerated in the cases below by immersing 2½ by 3½ inch pieces of the paper for approximately ten seconds in water solutions (except where noted otherwise) containing approximately 10% by

weight, respectively, of: (1) disodium hydrogen phosphate, (2) sodium nitrite, and (3) dicyclohexylammonium phosphate (in methyl alcohol). In the case of (4) the sample of paper was first immersed in a solution of dicyclohexylammonium phosphate as in (3) but then followed by immersion for a few seconds in an approximately 20% by weight sodium nitrite solution in water. The thus impregnated samples were then dried. A control piece of paper was also employed which had not been impregnated. Separate steel strips (½ by 2 inches) were wrapped, respectively, inside the pieces of papers prepared as described above. The individual packages thus prepared were suspended by strings in separate glass bottles, each of which contained 0.5 ml. of water to provide a wet atmosphere of air. The bottles were closed with stoppers and maintained at 100° F. The results obtained from these tests are tabulated below:

Compound With Which Paper Impregnated	Appearance of Steel Test-Strip After 625 Hours
(1) Disodium Hydrogen Phosphate.....	Rust spots present—random distribution.
(2) Sodium Nitrite.....	Rust spots present, particularly near corners of wrap.
(3) Dicyclohexylammonium phosphate.....	Rust spots present—random distribution.
(4) Dicyclohexylammonium phosphate and sodium nitrite from dual impregnation.	No corrosion.
(5) Control (no impregnant).....	Rust spots present.

Example II

An aqueous slurry was prepared by adding to water about 8.0 wt. per cent of casein, about 15.4 wt. per cent of dicyclohexylamine, about 3.8 wt. per cent of phosphoric acid, and about 5.3 wt. per cent of sodium nitrite, in that order. A 5 x 5-inch piece of 30# kraft paper was coated with the slurry and then dried. The amount of slurry used was such that the total weight of dicyclohexylammonium and nitrite ions was equal to about 1 gram per square foot of kraft paper.

A second sheet of paper was coated like the first, except that about 4.6 wt. per cent of acetic acid was used instead of the phosphoric acid in the slurry.

A 1" by 1" by 3" SAE 1020 steel bar was loosely wrapped in each of the pieces of paper prepared as described above and placed in a cardboard carton which was stored outdoors for three months. There was also placed in the carton a third steel bar wrapped in an uncoated and otherwise untreated piece of 30% kraft paper.

At the end of the three month period the steel bar in the untreated paper had 30% of its surface rusted, the steel bar in the paper coated with the first slurry had only a very slight trace (a very small fraction of 1%) of its surface rusted, and the steel bar in the paper coated with the second slurry was completely free of rust.

Example III

Paper products were prepared as described above in Example II, but using aqueous slurries of the following compositions:

Slurry No.	Binder	wt. percent	Organic base	wt. percent	Acid	wt. percent	Metal nitrite	wt. percent
1.....	Casein.....	8.0	DICHA*	15.4	Phosphoric.....	3.8	NaNO ₂	5.3
2.....	do.....	7.7	DICHA.....	14.9	do.....	3.7	NaNO ₂	6.5
3.....	do.....	8.1	DICHA.....	15.6	do.....	3.9	NaNO ₂	4.8
4.....	do.....	8.0	DICHA.....	15.4	Boric.....	4.8	NaNO ₂	5.3
5.....	do.....	8.0	DICHA.....	15.4	Phosphoric.....	3.8	Ca(NO ₂) ₂	5.8
6.....	do.....	8.0	DICHA.....	15.4	do.....	3.8	KNO ₂	6.6
7.....	do.....	8.0	DICHA.....	15.4	Citric.....	4.9	NaNO ₂	5.3
8.....	do.....	8.0	DICHA.....	15.4	Acetic.....	4.6	NaNO ₂	5.3
9.....	do.....	8.0	DICHA.....	15.4	Carbonic.....	(**)	NaNO ₂	5.3

*Dicyclohexylamine.

**Treated with CO₂ until all of DICHA converted to water-soluble salt.

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Example IV

Other slurries suitable for coating paper as in Examples II and III, were prepared as follows:

Slurry No.	Binder	wt. percent	Organic base	wt. percent	Acid	wt. percent	Metal nitrite	wt. percent
10	Starch	6.0	DICHA	15.7	Phosphoric	3.8	NaNO ₂	5.4
11	Casein	8.0	DICHA	15.4	Sulfuric	3.7	NaNO ₂	5.3
12	do.	8.0	DICHA	15.4	Tartaric	5.8	NaNO ₂	5.3

This application is a continuation-in-part of our copending application, Serial No. 782,047, filed October 24, 1947, now abandoned, which is in turn a continuation-in-part of our copending application, Serial No. 557,358, filed October 5, 1944, now abandoned.

We claim as our invention:

1. The method of preparing a substantially solid composition capable of inhibiting metal corrosion in the presence of moisture and air, which method comprises coating a paper with a suspension obtained by mixing water, a dicyclohexylamine phosphate and sodium nitrite in the presence of adhesive casein used in an amount sufficient to bind the resultant mixture to said paper, the amounts of said phosphate and said nitrite being sufficient to form, by ionic interchange, between about 0.05 gram and about 5.0 grams of dicyclohexylamine nitrite per each square foot of paper surface thus coated, and drying the coated paper, said solid composition, when in contact with water, resulting in a liquid phase having a pH value of at least about 6.

2. The method of preparing a substantially solid composition capable of inhibiting metal corrosion in the presence of moisture and air, which method comprises coating a paper with a suspension obtained by mixing water, a secondary amine phosphate and an alkali metal nitrite in the presence of an effective binding amount of a colloiddally dispersible adhesive for the resultant mixture to said paper, the amounts of said phosphate and said nitrite being sufficient to form, by ionic interchange, between about 0.05 gram and about 5.0 grams of a volatile secondary amine nitrite having a vapor pressure of at least 0.00002 mm. Hg at 21° C. per each square foot of paper surface thus coated, and drying the coated paper, said solid composition, when in contact with water, resulting in a liquid phase having a pH value of at least about 6.

3. The method of preparing a substantially solid composition capable of inhibiting metal corrosion in the presence of moisture and air, which method comprises coating a substantially solid fibrous material with a suspension obtained by mixing water, a water-soluble organic nitrogen-base phosphate salt and a water-soluble metal nitrite in the presence of an effective binding amount of an adhesive for the resultant mixture to said paper, the amounts of said phosphate and said nitrite being sufficient to form, by ionic interchange, a corrosion-inhibiting amount of a volatile organic nitrogen-base nitrite having a vapor pressure of at least 0.00002 mm. Hg at 21° C., and drying the coated fibrous material, said solid composition, when in contact with water, resulting in a liquid phase having a pH value of at least about 6.

4. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises paper coated with a mixture of casein and the total product of ionic exchange of dicyclohexylamine phosphate and sodium nitrite in amounts such that the total of stoichiometrically equivalent amounts of dicyclohexylammonium ions and nitrite ions is between about 0.05 gram and about 5.0 grams per square foot of paper, said casein being present in an amount sufficient to bind said ionic exchange product to said paper, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

5. A material capable of inhibiting metal corrosion in

the presence of moisture and air, which material comprises paper coated with a mixture of an adhesive binding agent and the total product of ionic exchange of di-

cyclohexylamine phosphate and sodium nitrite in amounts such that the total of stoichiometrically equivalent amounts of dicyclohexylammonium ions and nitrite ions is between about 0.05 gram and about 5.0 grams per square foot of paper, said adhesive agent being present in an amount sufficient to bind said ionic exchange product to said paper, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

6. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises paper impregnated with the total product of ionic exchange of dicyclohexylamine phosphate and sodium nitrite in amounts such that the total of stoichiometrically equivalent quantities of dicyclohexylammonium ions and nitrite ions is between about 0.05 gram and about 5.0 grams per square foot of paper, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

7. A material capable of inhibiting metal corrosion in the presence of moisture and air which material comprises paper coated with a mixture of an adhesive binding agent and the total product of ionic exchange of amine phosphate and a water-soluble alkali metal nitrite salt in amounts such that the total of stoichiometrically equivalent quantities of ammonium cation and nitrite anion is sufficient to form a corrosion-inhibiting amount of a volatile amine nitrite having a vapor pressure of at least 0.00002 mm. Hg at 21° C., said adhesive agent being present in an amount sufficient to bind said ionic exchange product to said fibrous material, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

8. A material capable of inhibiting metal corrosion in the presence of moisture and air which material comprises paper coated with a mixture of an adhesive binding agent and the total product of ionic exchange of an organic nitrogen-base phosphate salt and a water-soluble metal nitrite salt in amounts such that the total of stoichiometrically equivalent quantities of organic nitrogen-base cation and nitrite anion is sufficient to form a corrosion-inhibiting amount of a volatile organic nitrogen-base nitrite having a vapor pressure of at least 0.00002 mm. Hg at 21° C., said adhesive agent being present in an amount sufficient to bind said ionic exchange product to said fibrous material, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

9. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises a substantially inert solid fibrous material having physically associated therewith the total product of ionic exchange of an organic nitrogen-base phosphate salt and a water-soluble metal nitrite salt in amounts such that the total of stoichiometrically equivalent quantities of organic nitrogen-base cation and nitrite anion is sufficient to form a corrosion-inhibiting amount of a volatile organic nitrogen-base nitrite having a vapor pressure of at least 0.00002 mm. Hg at 21° C., said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

10. A material capable of inhibiting metal corrosion in the presence of moisture and air which material comprises a substantially inert solid fibrous material coated

with a mixture of an adhesive binding agent and the total product of ionic exchange of an organic nitrogen base phosphate salt and a water-soluble metal nitrite salt in amounts such that the total of stoichiometrically equivalent quantities of organic base cation and nitrite anion is sufficient to form a corrosion-inhibiting amount of a volatile organic base nitrite having a vapor pressure of at least 0.00002 mm. Hg at 21° C., said adhesive agent being present in an amount sufficient to bind said ionic exchange product to said fibrous material, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

11. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises paper coated with a mixture of casein and the total product of ionic exchange of a dicyclohexylammonium carboxylate salt and sodium nitrite in amounts such that the total of stoichiometrically equivalent amounts of dicyclohexylammonium ions and nitrite ions is between about 0.05 gram and about 5.0 grams per square foot of paper, said casein being present in an amount sufficient to bind said ionic exchange product to said paper, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

12. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises paper coated with a mixture of casein and the total product of ionic exchange of the sodium salt of nitrous acid and the dicyclohexylammonium salt of the group consisting of phosphates and carboxylates in amounts such that the total of stoichiometrically equivalent amounts of dicyclohexylammonium ions and nitrite ions is between about 0.05 gram and about 5.0 grams per square foot of paper, said casein being present in an amount sufficient to bind said ionic exchange product to said paper, said material, when in contact with water, yielding a liquid having a pH value of at least about 6.

13. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises an inert solid sheet packaging material having physically attached thereto the total product of ionic exchange of a water-soluble metallic salt of nitrous acid and an organic nitrogen base salt of the group consisting of phosphates and carboxylates in amounts such that the total of stoichiometrically equivalent quantities of organic base cation and nitrite anion is sufficient to form a corrosion-inhibiting amount of a volatile organic base nitrite salt having a vapor pressure of at least 0.00002 mm. Hg at 21° C., said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

14. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises an inert sheet packaging material having physically associated thereto a metallic salt of the group consisting of phosphates and carboxylates having a vapor pressure of at least 0.00002 mm. Hg at 21° C. and an organic nitrogen-base salt of nitrous acid in amounts sufficient to form a corrosion inhibiting composition, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

15. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises an inert solid sheet packaging material having physically attached thereto a metal phosphate and an organic nitrogen-base nitrite having a vapor pressure of at least 0.00002 mm. Hg at 21° C. in amounts sufficient to form a corrosion inhibiting composition, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

16. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises an inert solid sheet packaging material having physically attached thereto an alkali metal phosphate and a hydrocarbon ammonium nitrite having a vapor pressure of at least 0.00002 mm. Hg at 21° C. in amounts sufficient to form a corrosion inhibiting composition, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

17. A material capable of inhibiting metal corrosion in the presence of moisture and air, which material comprises an inert solid sheet packaging material having physically attached thereto a sodium phosphate and a dicyclohexylammonium nitrite having a vapor pressure of at least 0.00002 mm. Hg at 21° C. in amounts sufficient to form a corrosion inhibiting composition, said material, when in contact with water, yielding a liquid phase having a pH value of at least about 6.

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