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VAPOR-PHASE CORROSION INHIBITION

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The invention relates to improvements in vapor-phase corrosion inhibition, and more particularly, to improvements in vapor-phase corrosion inhibitors, in packaging materials containing the same and in the use thereof.

In general, vapor-phase corrosion inhibition is related to the packaging art. Metal articles tend to corrode when exposed to atmosphere and the packaging thereof should preferably prevent such corrosion as well as protect against mechanical damage.

The basic concepts of corrosion and its causes are fairly well understood. For example, steel rusts in the atmosphere because of a chemical reaction of the steel with moisture and oxygen in the air. The oxygen in the air is a relatively constant proportion, although the moisture content in the air varies considerably. It is generally understood that the presence of oxygen and water is required for rusting to occur. The removal of oxygen from an atmosphere in which a metal article is packaged is an extremely difficult and impractical operation. Heretofore, protective packaging of metals has usually been based upon the provisions of some sort of means for minimizing direct contact between moisture and the metal. Oil or grease coatings may be applied directly to the metal for this purpose. Waterproof wraps or packages have also been suggested. Other moisture-excluding methods include the use of strong moisture-absorbing materials placed within a waterproof package containing the metal articles.

Recently, however, there has developed a very great interest in what is known as "vapor-phase inhibitors," which are unique in that they prevent corrosion when both moisture and oxygen are present in the atmosphere in which a metal article is packaged. The exclusion of one or both of these essential corrosion inducing agents, viz. moisture and oxygen, is not necessary. Most preferably these vapor-phase corrosion inhibitors are applied to a suitable paper web or the like packaging means and the metal article is wrapped therein. It is not necessary to maintain the paper in contact with all of the surfaces of the metal article so wrapped, since the vapor-phase corrosion inhibitor apparently volatilizes very slowly so as to release agents into the atmosphere which effectively prevent corrosion of the metal that is adjacent to as well as touching the vapor-phase corrosion inhibitors. The rate of volatilization of a preferred corrosion inhibitor is extremely slow, in fact almost imperceptible. However, the reason that no rusting occurs is understood to be that the inhibitor volatilizes or releases a volatile material therefrom which permeates the air surrounding the metal article within the package. The inhibitor does not react with or remove water or oxygen, nor does it make any appreciable change in the determinable properties such as the pH of moisture in the vicinity, since such an inhibitor is preferably a substantially neutral compound. It may, however, and preferably does neutralize the slightly acid pH of, for example, a paper wrapper. Also, the inhibitor is not consumed to any appreciable extent by its action in protecting the metal article.

The foregoing discussion relates primarily to the desired properties of vapor-phase corrosion inhibitors, and not necessarily to the properties which various inhibitors that have been proposed or are actually in commercial use may possess. Instead, almost all of such inhibitors leave something to be desired, either in performance or in economic respects or both.

The instant invention is based upon the discovery of certain new, inexpensive and particularly suitable vapor-phase corrosion inhibitor compositions which comprise a mixture of a salt of a C_6–C_{10} alkanoic acid and a metal from the first two "A" groups of the periodic system (i. e. groups IA and IIA) such as sodium caprylate, and a salt of nitrous acid and a metal from the first two "A" groups of the periodic system, such as sodium nitrite. Neither of these two ingredients is a truly effective vapor-phase corrosion inhibitor per se (as a subsequently mentioned Government publication indicates), but the combination thereof gives you an equally superior result. Also, it has been found that the combination of these two ingredients is particularly effective with respect to ferrous metals; but not so effective particularly in direct contact with certain non-ferrous metals and the instant invention is further based upon an additional discovery that these two ingredients may be admixed with still a third ingredient (which is also not a vapor-phase corrosion inhibitor per se) so as to effectively improve the corrosion inhibiting features of these two ingredients with respect to non-ferrous metals; and the third ingredient is a di-alkali metal phosphate such as di-sodium phosphate.

In United States Patent No. 2,126,173, issued to Clapsadle on August 9, 1938, there is described an aqueous-alcoholic composition, such as an anti-freeze composition, which contains sodium nitrite and certain "higher fatty acids, such as oleic, palmitic and stearic acid" and/or triethanolamine salts thereof. The nitrite and the triethanolamine salts are presumably added for the purpose of preventing corrosion in the liquid phase.

In United States Patent No. 2,173,689, issued to Lamprey on September 19, 1939, another aqueous-alcohol composition is suggested containing, as liquid phase corrosion inhibitors, sodium nitrite plus a sodium salt of certain unsaturated organic acids. The specific acids suggested are crotonic, maleic, cinnamic and furyl acrylic acids.

A recently published Government publication (manuscript submitted January 29, 1954, and published March 10, 1954) entitled "Volatile Rust Inhibitors" by Hayward R. Baker of the Naval Research Laboratory, Washington, D. C., designated as NRL Report No. 4319 summarizes some aspects of the overall problem here involved and also summarizes the findings of the Naval Research Laboratory. This report shows, among other things, that so-called "inhibitors" useful in aqueous alcohol solutions are often not effective as vapor-phase corrosion inhibitors, and from this it could be concluded that a suggestion that an inhibitor may be used in aqueous alcohol media does not amount to a suggestion that this inhibitor is a vapor-phase inhibitor. For example, in the next to the last full paragraph on page 10 of the Baker report, it is pointed out that sodium nitrite is not a "vapor-corrosion inhibitor," although effective for liquid-phase inhibition. It will also be noticed that on page 15 of the Hayward report conclusion (5) points out that alkali metal salts of organic acids do not possess sufficient vapor pressure to be efficient rust inhibitors. The instant invention, however, is based upon the discovery of the unique effectiveness of the combination of these two materials, each of which is indicated by Hayward as not being effective for vapor-phase corrosion inhibition.

It is, therefore, an important object of the instant invention to provide a new and improved vapor-phase cor-

rosion inhibitor as well as an improved vapor-phase corrosin inhibiting procedure and packaging material.

It is another object of the instant invention to provide an improved composition consisting essentially of a mixture of (*a*) a salt of a C_6–C_{10} alkanoic acid and a metal from the first two "A" groups of the periodic system, and (*b*) a salt of nitrous acid and a metal from the first two "A" groups of the periodic system; the weight ratio of (*a*):(*b*) being 1:10 to 10:1; and to impart superior corrosion inhibition properties with respect to non-ferrous metals by the incorporation of a di-alkali metal phosphate in such composition; and to provide superior packaging materials which are impregnated with such compositions.

Other objects, features and advantages of the present invention will become apparent to those skilled in the art from the following detailed disclosure and examples of preferred embodiments of the invention.

The invention consists in a composition per se, a carrier or wrapping paper containing such composition, and a process using such composition for the protection of metal, which composition consists essentially of a mixture of (*a*) a salt of a C_6–C_{10} alkanoic acid and a metal from the first two "A" groups of the periodic system, and (*b*) a salt of nitrous acid and a metal from the first two "A" groups of the periodic system; the weight ratio of (*a*):(*b*) being 1:10 to 10:1; and, preferably, plus (*c*) a di-alkali metal phosphate, with the weight ratio of (*a*) plus (*b*):(*c*) being 20:1 to 2:1.

Although it is not desired to limit the invention to any particular theory, it is believed that certain aspects of the invention may be explained by certain chemical reactions and/or phenomenon. To begin with, it must be assumed that an effective vapor-phase inhibitor volatilizes and/or gives off a volatile material in order to obtain the resulting inhibiting effect. The "non-volatile" nitrites, such as sodium nitrite are well recognized as a group of compounds which have no appreciable vapor pressure. Because of the low vapor pressures of such compounds, it must be assumed that the nitrites owe their inhibitive effect in the vapor-phase to the decomposition thereof, probably as indicated in Equations 1, 2 and 3 below, using sodium nitrite:

(1) $NaNO_2+H_2O \rightleftharpoons NaOH+HNO_2$

(2) $2HNO_2 \rightleftharpoons H_2O+N_2O_3$

(3) $N_2O_3 \rightleftharpoons NO+NO_2$

The decomposition thus yields nitrogen trioxide (N_2O_3) which, in turn, yields nitric oxide (NO) and nitrogen dioxide (NO_2). Since only extremely small amounts of nitrogen oxides may thus be formed, it must be concluded that these oxides effect the formation of an extremely thin (molecular) impervious oxide film on the metal surface, as by the following Equations 4, 5 and 6:

(4) $Fe+NO_2 \rightarrow FeO+NO$

(5) $2FeO+NO_2 \rightarrow Fe_3O_4+NO$

(6) $2Fe_3O_4+NO_2 \rightarrow 3Fe_2O_3+NO$

The particular character of this impervious film is not clearly understood except that it tends to prevent corrosive action. The nitrogen dioxide must be consumed in this oxidation reaction so as to obtain a nitric oxide product; but nitrogen dioxide is immediately regenerated in the presence of atmospheric oxygen according to Equation 7 below:

(7) $2NO+O_2 \rightarrow 2NO_2$

As a result of this last reaction, it will be understood that a very small quantity of nitrogen dioxide may be required for the oxidation of a large amount of metal surface.

Although the nitrites employed in the instant invention exhibit a noticeable inhibiting effect when used alone (contrary to Baker's suggested results), such inhibiting effect is not ordinarily sufficient to meet standard requirements. In fact, it has been found that in many cases the carboxylic acid salts alone are capable of exhibiting as much or even more of an inhibiting effect (again, contrary to Baker's conclusions). The particular mechanics of the chemical reactions involved in producing an inhibiting effect using the instant carboxylic acid salts are not understood, although these reactions must also involve the formation of an effective volatile material. The instant invention is based upon a preliminary discovery that the instant carboxylic acid salts actually possess a certain amount of inhibiting properties, and further on the very significant discovery that a unique synergistic effect is obtained by the use of the instant salts, whereby a corrosion inhibiting effect substantially greater than that obtained by either may now be obtained. Also, the corrosion inhibiting effect resulting from the use of these two ingredients is substantially greater than would possibly be expected from the assumed "total effect" of these two ingredients.

The carboxylic (alkanoic) acid salts which may be used in the invention are salts of metals from the first two "A" groups of the periodic system, i. e., groups IA and IIA which are the more strongly basic metals of groups I and II. The metals of group IA are the alkali metals, the commercially significant members of which are lithium, potassium and sodium (rubidium and cesium, also operative members of the class, are considered to have no commercial or industrial significance). Sodium is the most preferred metal. The metals of group IIA, sometimes called the alkaline earth metals, are barium, strontium, calcium and magnesium. The alkanoic acid salts used may be salts (or mixtures of salts) of any of the foregoing metals with such acids as

(C_6)—Hexanoic—(caproic, methyl valeric, etc.)
(C_7)—Heptanoic—(oenanthic, methyl caproic, etc.)
(C_8)—Octanoic—(caprylic, methyl heptylic, etc.)
(C_9)—Nonanoic—(pelargonic, methyl caprylic, etc.)
(C_{10})—Decanoic—(capric, methyl pelargonic, etc.)

It has been found that the C_{12} fatty acids or higher are clearly inferior to the alkanoic acids herein recited and possibly this is because of a sharp reduction in the volatility or vapor pressure of such acids at approximately the C_{12} molecular weight. Also, these higher fatty acids are more inert with respect to the metal ion which reacts therewith to form the salt and possibly there is some other function not fully understood which also serves to explain the inferior performance of such higher fatty acids. Such higher fatty acids are not totally inoperative and perhaps may be more effective than the usual tests would indicate, if the materials were used at elevated temperatures, for example, to overcome deficiencies in volatility. The superiority of the present C_6–C_{10} alkanoic acid salts under ordinary conditions of storage is, however, very distinct. Fatty acids of C_5 or less molecular weight have been found to be distinctly inferior not only in their "lasting" powers, which might be attributed to excessive volatility causing loss of the compound, but also in actual function. This last feature of inferior corrosion inhibiting film formation may very well be attributed to the greater water solubility and reactivity of the lower molecular weight acid radicals. Again, for practical purposes the distinction is very clear between the lower molecular weight acids and the C_6–C_{10} alkanoic acids herein recited. Also, unsaturated fatty acids are distinctly inferior because of their tendency toward instability in the presence of heat and light. In fact, the lower molecular weight unsaturated acids are even capable of undergoing polymerization so as to effectively eliminate any volatility therein.

The nitrites or salts of nitrous acid used in the invention are preferably (like the carboxylic acid salts) nonvolatile and water-soluble. Also they are preferably salts of the metals hereinbefore mentioned in connection with the carboxylic acid salts. Such salts include sodi-

um, lithium, potassium, magnesium, calcium, strontium and barium nitrites.

The amount of nitrite used is, of course, that amount necessary to carry out (in conjunction with the carboxylic acid salt) its corrosion inhibiting function; and the same is true for the carboxylic acid salt, so the proportions of each may vary widely for certain special uses. Preferably the weight ratios of (*a*) carboxylic acid salt to (*b*) nitrite range from 1:10 to 10:1, and most preferably 1:5 to 5:1. The best cooperation is usually obtained using approximately equal amounts of (*a*) and (*b*). The salts (*a*) and (*b*) are used in intimate mixture, of course, and preferably on a surface or carrier (such as paper) which provides for maximum exposure of the mixture to the atmosphere, as in the case of thin films, layers, etc. Oustanding examples include (*a*) the sodium, lithium and potassium caproates, pelargonates and octanoates (caprylates and 2-ethylhexoates) or mixtures thereof, plus (*b*) sodium and/or potassium nitrite.

Example 1

A sheet of 60-lb. kraft paper is impregnated with a solution of 10 grams of sodium nitrite, 3.45 grams of sodium hydroxide and about 10 grams of caproic acid in 100 grams of water. (The solution is prepared by dissolving the acid in distilled water containing the calculated amount of sodium hydroxide, adjusting the pH until the solution was slightly alkaline to phenophthalein, and then adding the sodium nitrite.) The resulting paper is dried to obtain test paper having a total of 5.9 grams per square foot of the sodium nitrite-sodium caproate mixture thereon.

Steel specimens are polished with 6/0 garnet paper, cleaned in boiling benzene and placed on strips of kraft paper laid on the bottom of glass jars, using separate jars for untreated and treated (as per above paragraph) kraft paper. A small cup charged with 5 ml. of water is also placed in each jar and the jars are closed and stored in an oven maintained at 130° F. for two weeks. At this time the blank (untreated paper example) steel specimen showed severe corrosion whereas the specimen in the jar with the treated paper showed little or no corrosion.

Example 2

A procedure is carried out that is the same as that described in Example 1 except that, instead of the steel, cylinder head iron (0.73–1.16% Ni, 0.30–0.55%, Cr, 0.20–0.36 Mo, 0.10–0.17% V, and Fe balance) is used; and substantially the same results are obtained.

Example 3

A procedure is carried out that is the same as that described in Example 1 except that, instead of the steel, a zinc specimen is used and substantially the same results are obtained.

Example 4

A procedure is carried out that is the same as that described in Example 1 except that, instead of the steel, lead specimens are used and substantially the same results are obtained.

Example 5

A procedure is carried out that is the same as that described in Example 1 except that the test is "vapor-phase" instead of "contact" and the pieces are suspended in the jar lined with the test paper and not contacting the paper, and the amount of sodium hydroxide used is 6.9 grams and the amount of sodium nitrite used is 10 grams (in each case per 83 grams of water), the weight of the salt mixture on the paper is 6.6 grams per square foot, and it is noted that corrosion is noticeably inhibited, but there are rust spots appearing on the specimen after 168 hours at an oven temperature of 100° F.

Example 6

A procedure is carried out that is the same as that described in Example 5 except that the oven temperature is 150° F. and the time of exposure is only 120 hours, and it will be noted that corrosion has been inhibited, but there is definite evidence of corrosion in the form of several mottled dark brown rust areas. (The rather light corrosion described in connection with Examples 5 and 6 is very clearly and distinctly less than the extremely severe corrosion which will be noted using a control specimen in the absence of the instant inhibitors.)

Example 7

A procedure is carried out that is the same as that described in Example 5 except that 20 grams of sodium nitrite, 7 grams of sodium hydroxide and 20 grams of caproic acid are used and the amount of inhibitor-impregnant on the paper is 7.2 grams per square foot, and it is noted that after 168 hours at an oven temperature of 100° F. there are no signs of rust on the test specimen. This result, compared with the results of Examples 5 and 6 and substantiated by other test data, shows that the use of an excess of sodium hydroxide beyond that necessary to form substantially neutral sodium caproate, as well as extremely low proportions of sodium nitrite tend to reduce the effectiveness of the instant corrosion inhibitor.

It has been found that the amount of sodium hydroxide used to neutralize the carboxylic acid should be merely that amount which effectively increases the pH of the solution to approximately a neutral pH. The resulting pH range is preferably about 6–8, since extreme excesses of the base (sodium hydroxide) so as to obtain pH's of 10 or more apparently tends to reduce the effectiveness of the salt, perhaps by decreasing the volatilizing tendency of the carboxylic acid portion of the salt (which may involve an initial hydrolysis reaction). Also, if the amount of sodium hydroxide used is insufficient to effectively neutralize the carboxylic acid or increase the pH thereof to at least about 5, there is a sufficient amount of free acid in the salt to effectively reduce its corrosion inhibiting properties. The acids per se which are used in making the instant carboxylic acid salt are not corrosion inhibitors as such.

As previously indicated it is most preferable to use the carboxylic acid salt and the nitrite in approximately equal proportions, although the relative amounts of each may vary over a wide range if it is desired that they be so used. However, in the case of impregnation of paper or similar porous fibrous web materials which may act as an inert solid carrier which provides for maximum exposure of the impregnant to the atmosphere, it has been found that a certain minimum amount of nitrite (of approximately 0.05 gram and preferably 0.3 gram per square foot) should be used in order to obtain adequate effectiveness. The amount of the carboxylic acid salt used, as a minimum, should be about the same figure, although the criticality of the use of a minimum amount of the carboxylic acid salt is not as clearly established. The maximum amount of each of these ingredients which may be used may be as high as about 20 grams per square foot, although it is ordinarily not necessary to use so great an amount of these salts. Most preferably, the amount of each used is 1–10 grams per square foot of paper web; and the best results are obtained using a total of 2 to 8 grams per square foot of the mixture (wherein the salts have a weight ratio within the range of 1:2 to 2:1).

In order to show the unique effect obtained by the use of the two ingredients, however, it will be noted that if 40 grams of sodium nitrite are substituted for the other ingredients herein recited in this example, the resulting test piece exhibits a very substantial amount of red and brown mottled rust spots. Also, if the sodium

nitrite is omitted completely from the original formulation in this example it will be noted that the test specimen contains a number of brown spots or rust spots. In each of these two last mentioned demonstrations, it is clear that a corrosion inhibiting effect is being obtained, and also it appears that the carboxylic acid salt exhibits a stronger corrosion inhibiting effect than that shown by the nitrite; however, the amount shown by the use of either of these ingredients is very substantially less than that exhibited by the combination of the two.

Example 8

In order to further exhibit the effect of the combination of the two salts, a procedure is carried out that is the same as that initially described in connection with Example 7 except that only 10 grams of caproic acid are used and only 3.5 grams of sodium hydroxide are used (thereby obtaining the preferred neutrality), and it will be noted that no rust spots appear on the test specimen after the previously mentioned time of 168 hours. This shows that a reduction in the proportion of the carboxylic acid salt does not decrease the inhibiting effect as noticeably as a reduction in the amount of nitrite does. However, if only two grams of caproic acid and 0.7 gram of sodium hydroxide are used in the same procedure, it will be noted that a relatively small number of small brown rust spots appear on the test specimen, thereby indicating that the amount of the carboxylic acid salt has been reduced to such an extent that the optimum synergistic effect is no longer obtained. Still more noticeable corrosion is obtained if the amounts of caproic acid and sodium hydroxide are reduced to 0.4 gram and 0.14 gram, respectively; but even using this 50:1 nitrite to carboxylic acid ratio results in better corrosion resistance than that obtained using the nitrite alone. In this last demonstration, it was noted that the amount of impregnant on the paper was only about 0.34 gram per square foot.

Example 9

A procedure such as that described in Example 5 was carried out using the following formulations:

(I)

2-ethylhexoic acid	g.	10.0
Sodium hydroxide	g.	2.78
Sodium nitrite	g.	10.0
Water	g.	100.0
Total impregnant	g./sq. ft.	7

(II)

Pelargonic acid	g.	10.0
Sodium hydroxide	g.	2.53
Sodium nitrite	g.	10.0
Water	g.	100.0
Total impregnant	g./sq. ft.	7

(III)

Caproic acid	g.	5.0
Lithium hydroxide	g.	1.4
Sodium nitrite	g.	10.0
Water	g.	100.0
Total impregnant	g./sq. ft.	4

In each case, formulations I, II, and III yield substantially the same results, showing no corrosion on the test piece.

Other formulations which may be used in the practice of the invention, include:

(IV)

	G./sq. ft.
Sodium caprate	1
Sodium nitrite	2

(V)

Potassium caprate	1
Lithium nitrite	2

(VI)

Calcium caprylate	1
Potassium nitrite	1

(VII)

Strontium caproate	2
Sodium nitrite	2

(VIII)

Barium caprylate	2
Sodium nitrite	2

(IX)

Magnesium caproate	2
Sodium nitrite	2

Example 10

Another type of corrosion test known as the "Dynamic Performance Test" (MIL–P–3420) is a standard vapor-phase corrosion inhibitor test. This test involves the use of a temperature cycle such as (A) 2 hrs. at room temperature, 24 hrs. at 100° F. and 48 hrs. at 150° F. and (B) 2 hrs. at 75° F., 24 hrs. at 40° F., 24 hrs. at 100° F. and 48 hrs. at 150° F. Cycle (B) is the Government specification. In these tests the specimen is a steel rod polished at both ends which is positioned axially in a glass tube with one of its ends exposed and the other resting on the impregnated paper. Moist air is directed into the tube through a bubbler.

The following formulations are used; and the indicated results are obtained:

(X)

Caprylic acid	g.	10
Sodium hydroxide	g.	2.78
Sodium nitrite	g.	10
Water	g.	100
Impregnant	g./sq. ft. kraft	3.4

Cycle (B)—no rust.

(XI)

Caprylic acid	g.	10
Sodium hydroxide	g.	2.78
Sodium nitrite	g.	20
Water	g.	100
Impregnant	g./sq. ft. kraft	7.2

Cycle (B)—no rust.

(XII)

Caproic acid	g.	10
Sodium hydroxide	g.	3.45
Sodium nitrite	g.	10
Water	g.	100
Impregnant	g./sq. ft. kraft	5.9

Cycle (B)—no rust.

(XIII)

2-ethyhexoic acid	g.	10
Sodium hydroxide	g.	2.78
Sodium nitrite	g.	10
Water	g.	100
Impregnant	g./sq. ft. kraft	6.6

Cycle (B)—no rust.

(XIV)

Pelargonic acid	g.	10
Sodium hydroxide	g.	2.53
Sodium nitrite	g.	10
Water	g.	100
Impregnant	g./sq. ft. kraft	7

Cycle (B)—no rust.

(XV)

Caproic acid	g.	5
Lithium hydroxide	g.	1.4
Sodium nitrite	g.	10
Water	g.	50
Impregnant	g./sq. ft.	4

Cycle (B)—no rust.

The foregoing "Dynamic" test results are clearly su-

perior to those obtained using commercially accepted vaporphase corrosion inhibitors presently known.

As will be appreciated, the instant invention does not apply merely to wrapping papers but also adapts itself to such uses as stuffing materials for closed bearings, etc. Thus an inert porous solid carrier such as cotton flocking might be impregnated with the instant inhibitors and used as padding in a sealed package, or used as a bearing stuffing. The amount of inhibitor used is, of course, an effective amount to carry out the function; and the preferred amounts have been given for 60-lb. kraft. Such amounts can be translated to weight proportions, but they are here given in g./sq. ft. because the concept of exposing the inhibitor to the atmosphere is thus emphasized. The porous fibrous web preferably employed thus has (for all practical purposes) no thickness, only area. It is also preferably a water-insoluble substantially non-hygroscopic body; in fact, water resistant or water-impermeable wrapping materials are most preferred (for example, paper with a wax outside coating).

As will be appreciated, the instant invention provides a method for protecting metal or metal objects from atmospheric corrosion. Most preferably, the metal is a ferrous metal, with which the problem of corrosion is most acute from a commercial point of view. In carrying out the instant method, it is necessary merely to position the metal in the immediate vicinity of an effective amount of the instant inhibitor mixture and to expose the metal and the inhibitor mixture to atmospheric conditions (which would otherwise cause corrosion). The inhibitor is carried on a suitable surface (even in powder form) so that it is, in turn, exposed to the atmosphere. In the preferred method the metal article is wrapped or otherwise enclosed in some sort of protective material so that the atmosphere has only limited access thereto and the vapor-phase inhibiting "atmosphere" which results from the presence of the instant inhibitors may be retained in the immediate location of the metal article. This is accomplished, for example, by wrapping the metal article in a suitably impregnated sheet of wrapping paper. Such wrapping paper need not be sealed (although it preferably is) and it need not be a so-called "moisture proof" wrap, although a substantially vapor impermeable wrap (whether it be as a result of a coating on the paper or the use of a second wrapping material) is definitely preferred and this type of wrap results in a much more prolonged corrosion inhibiting effect.

As will be appreciated, the instant compositions are applied to the packaging material so as to, in effect, impregnate such material. Actually, the instant compositions may be applied to the wrapping material in the form of a wax composition containing the same and consisting primarily of wax, pitch, rubber hydrochloride and/or similar moisture and vapor barrier materials.

Another important aspect of the instant invention resides in the incorporation in the instant corrosion inhibition composition of a di-alkali metal phosphate, such as di-sodium phosphate, di-potassium phosphate, or the like. The addition of such alkali metal phosphate salt results in still another unique synergistic effect, in that corrosion inhibition of ferrous metal parts is not affected to an appreciable extent one way or the other, but the tendency of the first two corrosion inhibition ingredients here mentioned to cause mild attack when in direct contact with aluminum parts, for example, is substantially eliminated by the presence of the phosphate salt. This effect is less noticeable if there is no contact between the aluminum and the composition or a wrap containing the same. The overall corrosion inhibition effect of the composition thus is materially increased, with respect to non-ferrous metals, by the addition of the phosphate salt. It will be appreciated that a number of complex metal articles may be made primarily of the ferrous metal but may also include aluminum parts. In the protection of such complex articles, the instant wrapping material is impregnated with the carboxylic acid salt, the nitrous acid salt and the alkali metal phosphate salt, in combination, so that corrosion inhibition of all of the metal parts may be effected. For example, a procedure is carried out using the procedure of Example 1 herein except that 1 gram of di-sodium phosphate is added to the solution before pH adjustment and aluminum test pieces are included; and the results obtained are the same as those described in Example 1. Similar results are obtained (using combinations of ferrous and aluminum metal pieces) using the following formulations:

(XVI)

Caprylic acid	g.	10
Sodium hydroxide	g.	2.78
Sodium nitrite	g.	10
Di-Sodium phosphate	g.	1
Water	g.	100.0
Total impregnant	g./sq. ft.	5

(XVII)

Pelargonic acid	g.	10
Sodium hydroxide	g.	2.53
Sodium nitrite	g.	10
Di-Potassium phosphate	g.	1
Water	g.	100
Total impregnant	g./sq. ft.	4

(XVIII)

Sodium caprate	g./sq. ft.	2
Potassium nitrite	g./sq. ft.	2
Di-Sodium phosphate	g./sq. ft.	0.1

(XIX)

		(approx.)
Caprylic acid	7.77 g.	8 g.
Sodium hydroxide	2.14 g.	2 g.
Sodium nitrite	15.54 g.	16 g.
Di-Sodium phosphate	1.02 g.	1 g.
Water	73.55 g.	Bal.
Total impregnant	3 g./sq. ft.	

The foregoing corrosion inhibitor compositions are found to effectively inhibit corrosion on ferrous metal articles and also to prevent any tendency toward staining when in contact with the aluminum or comparable non-ferrous metal parts. In general, the amount of alkaline metal phosphate required is smaller than the amount of either of the other two ingredients, and in any event, this addition should not take the composition out of the pH range of 5–10 and preferably 6–8. The weight ratio of (*a*) the carboxylic acid salt plus (*b*) the nitrite to (*c*) the alkali metal phosphate may range from about 50:1 to about 10:1; and in preferred compositions containing 1–2 parts of (*a*) and 1–2 parts of (*b*), the amount of (*c*) the di-sodium phosphate is preferably about 0.01–0.1 part. Expressed in other terms, the amount of either (*a*) or (*b*) on the fibrous wrap may be within the range of about 0.3 to 20 grams per square foot and the amount of (*c*) alkali metal phosphate should be about 1%–10% of (*a*) plus (*b*), while in the preferred wrapping paper the total amount of impregnant, including (*a*), (*b*) and (*c*) is about 2 to about 8 grams per square foot.

This is a continuation-in-part of our application Serial No. 378,668, filed September 4, 1953, and now abandoned.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the present invention.

We claim as our invention:

1. A composition consisting essentially of a mixture of (*a*) a salt of a C_6—C_{10} alkanoic acid and a metal selected from the first two "A" groups of the periodic system, and (*b*) a salt of nitrous acid and a metal selected from the first two "A" groups of the periodic system; the weight ratio of (*a*):(*b*) being 1:10 to 10:1.

2. A composition consisting essentially of a mixture of (*a*) a salt of a C_6—C_{10} alkanoic acid and a metal selected from the first two "A" groups of the periodic system, (*b*) a salt of nitrous acid and a metal selected from the first two "A" groups of the periodic system, and (*c*) a di-alkali metal phosphate; the weight ration of (*a*):(*b*) being 1:10 to 10:1 and the weight ratio of (*a*) plus (*b*):(*c*) being 50:1 to 10:1.

3. A composition consisting essentially of a mixture of 1–2 parts of sodium caprylate and 1–2 parts of sodium nitrite.

4. A composition consisting essentially of a mixture of 1–2 parts of sodium caproate and 1–2 parts of sodium nitrite.

5. A composition consisting essentially of a mixture of 1–2 parts of sodium octanoate and 1–2 parts of sodium nitrite.

6. A composition consisting essentially of a mixture of 1–2 parts of sodium pelargonate and 1–2 parts of sodium nitrite.

7. A composition consisting essentially of a mixture of 1–2 parts of sodium caprylate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

8. A composition consisting essentially of a mixture of 1–2 parts of sodium caproate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

9. A composition consisting essentially of a mixture of 1–2 parts of sodium octanoate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

10. A composition consisting essentially of a mixture of 1–2 parts of sodium pelargonate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

11. A packaging material for inhibiting rusting and corrosion of metallic articles packaged therein, comprising an inert porous solid carrier containing, in a quantity effective to protect against corrosion, a vaporphase corrosion inhibitor consisting essentially of a mixture of (*a*) a salt of a C_6–C_{10} alkanoic acid and a metal selected from the first two "A" groups of the periodic system, and (*b*) a salt of nitrous acid and a metal selected from the first two "A" groups of the periodic system; the weight ratio of (*a*):(*b*) being 1:10 to 10:1.

12. A porous fibrous web impregnated with a vapor-phase corrosion inhibitor consisting essentially of a mixture of (*a*) a salt of a C_6–C_{10} alkanoic acid and a metal selected from the first two "A" groups of the periodic system, (*b*) a salt of nitrous acid and a metal selected from the first two "A" groups of the periodic system, and (*c*) a di-alkali metal phosphate; salts (*a*) and (*b*) each being present in amounts ranging from 0.3 to 20 g. per square foot of web and the weight ratio of (*a*) plus (*b*):(*c*) being 50:1 to 10:1.

13. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture of 1–2 parts of sodium caprylate and 1–2 parts of sodium nitrite.

14. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture of 1–2 parts of sodium caproate and 1–2 parts of sodium nitrite.

15. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture of 1–2 parts of sodium octanoate and 1–2 parts of sodium nitrite.

16. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture 1–2 parts of sodium pelargonate and 1–2 parts of sodium nitrite.

17. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture of 1–2 parts of sodium caprylate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

18. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture of 1–2 parts of sodium caproate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

19. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture of 1–2 parts of sodium octanoate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

20. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture of 1–2 parts of sodium pelargonate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

21. A method of protecting metal from atmospheric corrosion that comprises positioning in the immediate vicinity of the metal, in an amount effective to protect against atmospheric corrosion, a composition consisting essentially of a mixture of (*a*) a salt of a C_6—C_{10} alkanoic acid and a metal selected from the first two "A" groups of the periodic system, and (*b*) a salt of nitrous acid and a metal selected from the first two "A" groups of the periodic system; the weight ratio of (*a*):(*b*) being 1:10 to 10:1.

22. A method of protecting metal from atmospheric corrosion that comprises positioning in the immediate vicinity of the metal, in an amount effective to protect against corrosion, a composition consisting essentially of a mixture of (*a*) a salt of a C_6–C_{10} alkanoic acid and a metal selected from the first two "A" groups of the periodic system, (*b*) a salt of nitrous acid and a metal selected from the first two "A" groups of the periodic system, and (*c*) a di-alkali metal phosphate; the weight ratio of (*a*):(*b*):(*c*) being 1:10 to 10:1 and the weight ratio of (*a*) plus (*b*):(*c*) being 50:1 to 10:1.

23. A composition consisting essentially of 1–2 parts of sodium caprate and 1–2 parts of sodium nitrite.

24. A composition consisting essentially of 1–2 parts of sodium caprate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

25. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture of 1–2 parts of sodium caprate and 1–2 parts of sodium nitrite.

26. A sheet of wrapping paper impregnated with 2 to 8 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a mixture of 1–2 parts of sodium caprate, 0.01–0.1 part of di-sodium phosphate and 1–2 parts of sodium nitrite.

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