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CORROSION INHIBITORS AND METHOD

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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. 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 consist essentially of an acid salt having the formula:

RCOOH.RCOOM

wherein M is an alkali metal and each RCO is a long chain fatty acyl group, and one of said R's is a C_5–C_{11} radical and the other R is a C_5–C_{17} radical. The acid soaps or salts are a known class of compounds as established, for example, by Dr. A. W. Ralston in "Fatty Acids and Derivatives," page 888, and they are understood to have the formula above shown resulting from 50% neutralization of a fatty acid wih a suitable alkali. The fatty acids per se are substantially ineffective as corrosion inhibitors. Certain salts of the fatty acids (i. e., completely neutralized salts) have shown some corrosion inhibiting properties, but the instant acid salts possess a unique combination of properties most advantageous for the so-called vapor-phase corrosion inhibition.

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, and there is no teaching in Clapsadle concerning the use of these ingredients in vapor-phase corrosion inhibition. Moreover, the applicants have tested sodium salts of these higher fatty acids (with or without sodium nitrite) and found them to be definitely inferior to the compositions of the instant invention as vapor-phase corrosion inhibitors.

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. Again, there is no suggestion concerning the use of such corrosion inhibitors in vapor-phase corrosion, rather than the liquid phase corrosion described by Lamprey. Moreover, it has been found that aryl and heterocyclic carboxylic acid salts (such as the cinnamic and furyl acrylic acid salts suggested by Lamprey) are not operative as vapor-phase corrosion inhibitors, when used alone or in conjunction with sodium nitrite.

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. It will 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 certain acid salts as vapor-phase corrosion inhibitors.

It is, therefore, an important object of the instant invention to provide a new and improved vapor-phase corrosion inhibitor as well as an improved vapor phase corrosion inhibiting procedure and packaging material.

Another object of the instant invention is to provide an improved packaging material for inhibiting rusting and corrosion of metallic articles packaged therein, which comprises an inert porous solid carrier such as a paper web containing an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of a certain specific acid salt.

A further object of the instant invention is to provide an improved method of protecting metal from atmospheric corrosion, that comprises positioning in the immediate vicinity of the metal an effective quantity of a certan specific acid salt to be described in detail hereinafter.

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

The invention consists in a carrier or wrapping paper containing a vapor-phase corrosion inhibiting composition and a process using such composition for the protection of metal, which composition consists essentially of an acid salt having the formula:

RCOOH.RCOOM

wherein M is an alkali metal and each RCO is a long chain fatty acyl group, and one of said R's is a C_5–C_{11} radical and the other of said R's is a C_5–C_{17} radical.

Although it is not desired to limit the instant invention to any particular theory, it is believed that certain aspects of the instant invention can be explained by certain chemical reactions and/or phenomena. 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 volatile material is further believed to form an extremely thin (monomolecular) impervious film on the metal surface. The particular character of this impervious film is not clearly understood except that it tends to prevent corrosive action. The particular mechanics of the chemical reactions involved in producing an inhibiting effect using the instant acid salts is not understood, although these reactions must also involve the formation of an effective volatile material. The acids per se in most cases exhibit little or no inhibiting effect and appear to be far too volatile for use in this field. In contrast, completely neutralized salts of the fatty acids exhibit very low vapor pressures such as to indicate that an insufficient amount of volatile material can be provided thereby. The instant acid salts are recognized compounds and it is understood that they differ from mere mixtures of a fully neutralized salt and the acid. There is some apparent linkage between the alkali and all of the acid present in the instant acid salts so that these compounds are definite chemical entities, differing from normal soaps in melting point, solubility, and other properties. The corrosion inhibiting effect resulting from the use of the instant acid salts is much greater than that obtained using either the acid or the fully neutralized salt.

Throughout the instant specification the term "acid salt" is used generically to mean the alkali metal acid salts of fatty acids, which have the following formula:

RCOOH.RCOOM

wherein M is an alkali metal (the predominant members of this group being sodium, potassium and lithium) and each RCO is an acyl group derived from a long chain fatty acid which may be a C_6–C_{18} fatty acid, although one

of the RCO groups must be a C_6–C_{12} fatty acyl group (preferably a C_8–C_{11} fatty acyl group). Expressed in other terms, each of the R's is preferably a straight chain hydrocarbon radical having from 5 to 17 carbon atoms therein, and one of the R's must contain 5 to 11 carbon atoms therein (although the other R may contain as many as 17 carbon atoms). It will thus be seen that the instant acid salts may be formed of mixed acids, an example being sodium acid caprylate stearate which is formed by 50% neutralization with sodium hydroxide of an equimolar mixture of caprylic and stearic acids. The acid salts may also, of course, be salts of a single acid as in the case of sodium acid caprate or sodium acid caprylate, each formed by 50% neutralization with sodium hydroxide of capric or caprylic acids, respectively. The acids which may be used in the practice of the instant invention include the following:

(C_6) Hexanoic (caproic), hexenoic, etc.
(C_7) Heptanoic (oenanthic), heptenoic, etc.
(C_8) Octanoic (caprylic), octenoic, etc.
(C_9) Nonanoic (pelargonic), nonenoic, etc.
(C_{10}) Decanoic (capric), decenoic, etc.
(C_{11}) Hendedecanoic, hendecenoic (undecylenic), etc.
(C_{12}) Dodecanoic (lauric), etc.
(C_{14}) Tetradecanoic (myristic)
(C_{16}) Hexadecanoic (palmitic)
(C_{18}) Octadecanoic (stearic), octadecenoic (oleic), etc.

But at least one of the acyl groups used must be a C_6–C_{12} group, and the other can be a C_6–C_{18} group. Most preferably both R's are C_7–C_{10} n-alkyl groups. The best results have been obtained using caprylyl, capryl and undecylenyl acyl groups.

Examples of the preparation of the instant acid salts include the following:

Salt A.—Sodium acid caprylate

A charge of 28.8 g. (0.2 mol) of caprylic acid and 4.0 g. (0.1 mol) of sodium hydroxide is added to 100 ml. of distilled water and a soft, opalescent gel is formed. The addition of 20 ml. of methanol produces a clear solution of the acid salt.

Salt B.—Sodium acid caprylate

A clear solution is also produced by dissolving 28.8 g. (0.2 mol) of caprylic acid and 4 g. (0.1 mol) of sodium hydroxide in a mixture of 45 ml. of methanol and 5 ml. of distilled water.

Salt C.—Sodium acid laurate

A clear solution of the salt is produced by adding a warm (50° C.) solution of 2 g. (0.05 mol) of sodium hydroxide in 10 ml. of water plus 40 ml. of methanol to a warm (50° C.) solution of 20 g. (0.1 mol) of lauric acid in 30 ml. of methanol. A precipitate forms when the solution cools below 40° C.

Salt D.—Sodium acid caprylate stearate

The acid salt is formed by adding a solution of 4 g. (0.1 mol) of sodium hydroxide in a mixture of 10 ml. of water plus 20 ml. of methanol to a hot (60° C.) solution of 28.4 g. (0.1 mol) of stearic acid and 14.4 g. (0.1 mol) of caprylic acid in 100 ml. of methanol; and a precipitate is produced which does not dissolve even at the boiling point; and a solid mass results when the solution is cooled to room temperature.

Salt E.—Sodium acid caprylate oleate

A clear solution is produced when a solution of 4 g. (0.1 mol) of sodium hydroxide in a mixture of 10 ml. of water and 20 ml. of methanol is added to a solution of 28 g. (0.1 mol) of oleic acid and 14.4 g (0.1 mol) of caprylic acid in 50 ml. of methanol at 40° C.

Salt F.—Sodium acid caprate

A clear solution of the acid salt is prepared by dissolving 17.2 g. (0.1 mol) of capric acid and 2 g. (0.05 mol) of sodium hydroxide in a hot (60° C.) mixture of 30 ml. of isopropyl alcohol and 20 ml. of distilled water. This salt is insoluble in aqueous isopropyl alcohol mixtures containing less than 30% or more than 80% isopropyl alcohol by volume.

Salt G.—Potassium acid caprate

A solution of the acid salt is prepared by dissolving 0.1 mol of capric acid and 0.05 mol of potassium hydroxide in a hot (60° C.) mixture of 30 ml. of isopropyl alcohol and 20 ml. of distilled water.

Salt H.—Lithium acid caprate

A clear solution of the acid salt is prepared by dissolving 0.1 mol of capric acid and 0.05 mol of lithium hydroxide in a hot (60° C.) mixture of 30 ml. of isopropyl alcohol and 20 ml. of distilled water.

Salt I.—Sodium acid undecylenate

A solution of the acid salt is prepared by dissolving 0.2 mol of undecylenic acid and 0.1 mol of sodium hydroxide in a hot (60° C.) mixture of 60 ml. of isopropyl alcohol and 40 ml. of distilled water.

Salt J.—Sodium acid caprate caprylate

A clear solution of the instant acid salt is prepared by dissolving 15.8 g. (approximately 0.1 mol) of a commercially available approximately equal mixture of caprylic and capric acids ("Aliphat 3B") and 2 g. (0.05 mol) of sodium hydroxide in hot (60° C.) 50% aqueous isopropyl alcohol.

Salt K.—Sodium acid caproate

A solution is prepared by dissolving 0.1 mol of caproic acid and 0.05 mol of sodium hydroxide in 30 ml. of isopropyl alcohol and 20 ml. of H_2O.

Salt L.—Sodium acid pelargonate

A solution is prepared by dissolving 0.1 mol of pelargonic acid and 0.05 mol of sodium hydroxide in 30 ml. of isopropyl alcohol and 20 ml. of H_2O.

Static performance tests were run for each of the acid salts. In the static performance tests, strips of 30 lbs. neutral kraft paper measuring 4 inches by 5 inches were impregnated with solutions of the acid salts. The strips were used to line 8 ounce glass jars measuring approximately 15 centimeters in height and 6 centimeters in diameter, and a bakelite cup containing 5 ml. of distilled water was placed in each jar. A rubber stopper with a stainless steel hook therein for holding the steel specimen was employed to close the jar. The steel panels or specimen tests panels, measuring ⅛ inch by 1 inch by 3 inches, were cleaned by sand-blasting and washed with hot benzene, weighed and suspended in the jars so as not to contact the paper. For comparison, blanks were run with untreated 30 lb. neutral kraft paper. Three series of tests were carried out using the following temperature cycles:

(1) 72 hours at 140° F.,
2 hours at room temperature,
96 hours at 140° F.
(2) 48 hours at 140° F.,
2 hours at room temperature,
120 hours at 140° F.
(3) 72 hours at 140° F.,
5 hours at room temperature,
91 hours at 140° F.

After the corrosion cycle, the steel panels were removed from the jars in the oven, cooled and weighed without cleaning. The results obtained in the test are shown in Table I below:

TABLE 1

Salt (acid)	Results[1]
K (C_6)	Fair: Adherent greasy film; some rust.
A (C_8)	Excellent: No corrosion.
L (C_9)	Good: Oily coating; but no apparent corrosion.
J (C_8—C_{10})	Excellent: No corrosion.
F (C_{10})	Do.
G (C_{10})	Do.
H (C_{10})	Good: Greasy coating; but no apparent corrosion.
I (C_{11})	Excellent: No corrosion.
C (C_{12})	Fair: Some rust; but far less than blank.
Blank	Poor: Substantial amount of rust.

[1] Concentrations or "loads" used are 1 to 10 g. per sq. ft. of paper.

From the foregoing it is apparent that improved results are obtained using C_6–C_{12} acid salts, but the best results are obtained using C_8–C_{11} acid salts.

As will be appreciated, for economic purposes it is most advantageous to use as little as possible of the instant acid salts. 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 minimum amount of approximately 0.05 gram per square foot (and preferably about 0.3 gram per square foot) should be used in order to obtain adequate effectiveness. The amount of the acid salt used may be as high as about 20 grams per square foot, although it is not ordinarily necessary to use so great an amount of these acid salts. Most preferably, the amount of acid salt used is 1 to 10 grams per square foot of paper web, and the best results are usually obtained using a total of about 2 to 8 grams per square foot of the instant acid salts.

Another type of corrosion test known as the "Dynamic Performance Test (MIL–P–3420)" is a standard vapor-phase corrosion inhibitor test. Using this test the temperature cycle for Government specifications is two hours at 75° F., 24 hours at 40° F., 24 hours at 100° F. and 48 hours at 150° F. 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 instant acid salts pass the dynamic performance test (i. e. preventing any corrosion), and particularly, it has been found that the caprylate salts (salts A and B) and the caprate salts (salts F and G) give unusually satisfactory results in this test, which also involves a proof that the instant salts are capable of giving off a minimum amount of volatile (corrosion inhibiting) material during the test. The mixed salts D and E also pass this test and give good to excellent results in the static test.

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 30-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 contemplates the use of mixtures of the instant acid salts, such

as a mixture of sodium acid caprate, sodium acid caprylate and sodium acid caprylate-caproate (which is salt J).

It will further be appreciated that this invention contemplates the use of the solution or dispersion of the instant acid salts in an oil vehicle which may be subsequently sprayed or flowed into cavities, etc. of machinery or engines or metallic parts thereof so that the volatile inhibitor can deposit upon the interior metallic surfaces to inhibit corrosion thereof.

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

We claim as our invention:

1. A packaging material for inhibiting rusting and corrosion of metallic articles packaged therein, comprising an inert porous solid carrier containing an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of an acid salt having the formula:

RCOOH.RCOOM

wherein M is an alkali metal and each RCO is a long chain fatty acyl group, and one of said R's is a C_5–C_{11} radical and the other of said R's is a C_5–C_{17} radical.

2. A packaging material for inhibiting rusting and corrosion of metallic articles packaged therein, comprising an inert porous solid carrier containing an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of sodium acid caprate.

3. A packaging material for inhibiting rusting and corrosion of metallic articles packaged therein, comprising an inert porous solid carrier containing an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of sodium acid caprylate.

4. A packaging material for inhibiting rusting and corrosion of metallic articles packaged therein, comprising an inert porous solid carrier containing an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of sodium acid caprylate-stearate.

5. A packaging material for inhibiting rusting and corrosion of metallic articles packaged therein, comprising an inert porous solid carrier containing an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of sodium acid caprylate-oleate.

6. A sheet of wrapping paper impregnated with 1 to 10 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of an acid salt having the formula:

RCOOH.RCOOM

wherein M is an alkali metal and each RCO is a long chain fatty acyl group, and one of said R's is a C_7–C_{10} radical and the other of said R's is a C_7–C_{17} radical.

7. A sheet of wrapping paper impregnated with 1 to 10 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of sodium acid caprate.

8. A sheet of wrapping paper impregnated with 1 to 10 g. per square foot of a vapor-phase corrosion inhibitor consisting essentially of a sodium acid caprylate.

9. A method of protecting metal from atmospheric corrosion, that comprises positioning in the immediate vicinity of the metal an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of an acid salt having the formula:

RCOOH.RCOOM

wherein M is an alkali metal and each RCO is a long chain fatty acyl group, and one of said R's is a C_5–C_{11} radical and the other of said R's is a C_5–C_{17} radical.

10. A method of protecting metal from atmospheric corrosion, that comprises positioning in the immediate vicinity of the metal an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of sodium acid caprate.

11. A method of protecting metal from atmospheric corrosion, that comprises positioning in the immediate vicinity of the metal an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of sodium acid caprylate.

12. A method of protecting metal from atmospheric corrosion, that comprises positioning in the immediate vicinity of the metal an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of sodium acid caprylate-oleate.

13. A method of protecting metal from atmospheric corrosion, that comprises positioning in the immediate vicinity of the metal an effective quantity of a vapor-phase corrosion inhibitor consisting essentially of an equimolar mixture of sodium acid caprate and sodium acid caprylate.

14. A method of protecting metal from atmospheric corrosion, that comprises positioning in the immediate vicinity of the metal an effective quantity of a vapor phase corrosion inhibitor consisting essentially of a mixture of caprylic and capric acids 50% neutralized with an alkali metal hydroxide.

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