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VAPOR PHASE CORROSION INHIBITION

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This invention relates to inhibiting the corrosion of metal surfaces in enclosed spaces, and specifically to effecting such inhibition by bringing at least two mutually reactive substances into contact with such surface and reacting them together thereon to form a layer or coating of the inhibiting substance, at least one and preferably all of said reactive substances being in the vapor phase. The present application is a continuation-in-part of my copending application Serial No. 483,837 filed January 24, 1955.

There are many pieces of mechanical equipment containing intricate metal parts which are used only intermittently. Engines, including gasoline, diesel, jet etc., farm and marine equipment, machine tools, containers, bins, etc., are illustrative of items which have intermittent periods of use. It is desirable to have a rapid and easy method for protecting metal surfaces forming a part of these items. Since many of them contain parts which because of their location or intricacy are inaccessible to the common methods of applying an anti-corrosion coating (such as painting, spraying or dipping) it is necessary to find a way of depositing a protective coating which may be carried into and around these intricate or inaccessible parts by means of a gas or easily introduced liquid.

There are a number of methods known for protecting metal surfaces against moisture and corrosive vapors, but many of them either deposit a permanent coating on the surface or use materials, such as heavy greases, which require a great deal of time to remove. The coating deposited by vapor phase corrosion inhibitors, on the other hand, is neither permanent nor does it have to be removed before operations can be continued.

The coatings of this invention are designed primarily to protect against water vapor and against the ordinary products of combustion, including those from leaded fuels, which remain in an engine or jet motor after shutdowns. These corrosion inhibitors are also very effective against atmospheres of excessively high humidities.

The idea of vapor phase inhibition of corrosion is not new since various compounds capable of being vaporized have been deposited on metal parts to prevent corrosion. In the usual process, the vaporized inhibiting compound is carried by means of air to contact the metal surfaces to be protected. Contrary to some contentions, it appears clear that the inhibitor is not effective while it is in the vapor phase but it must be deposited on the metal and subsequently dissolved in any drops of moisture, formed on the metal surface, so as to render said drops noncorrosive and harmless to the metal. The inhibitor which is actually active is that dissolved in the deposited moisture. This mechanism partially defeats the purpose of the commonly used vapor phase inhibitors since they may well revaporize from the metal surfaces before they have an opportunity to act in the manner described. In order to be completely effective under conditions of excessive humidity the vapor phase inhibitor should be hydrophobic in nature and preferably should be capable of forming a water-repelling coating.

The rate at which the inhibitor will evaporate depends upon the temperature involved, the vapor pressure of the inhibitor, and the rate at which air passes over the metal surface of the object. If better protection is sought at higher temperatures it is necessary to select vapor phase inhibitors which vaporize at higher temperatures and which are, accordingly, more difficult to apply if formed before application.

In the prior art many vapor phase inhibitors have been disclosed but their deposition on metal surfaces has simply been left to chance and no special means were used to cause them to deposit. This is particularly true since vapor phase corrosion inhibitors are commonly employed in equipment where other means of application such as brushing, spraying, etc., cannot be used because of inaccessibility to the surfaces. Normal temperature gradients throughout a typical piece of equipment, such as a jet engine for example, contribute to the spottiness of surface coatings, and hence to the lack of protection, attained. In addition, the more easily volatilized inhibitors which had to be used were less hydrophobic in nature.

A more desirable vapor phase corrosion inhibitor therefore, would be one which can be injected into a system or carried by air or some other suitable fluid carrier to be deposited at a relatively low temperature. It should also be one which would adhere in a continuous, thin coating to the metal surfaces even at elevated temperatures and preferably be hydrophobic in nature. I have found that by the process of this invention such desirable vapor phase corrosion inhibitors can be deposited on metal surfaces by forming the inhibitor in situ (i.e. on such surfaces) by reacting two, or more, substances on the metal surfaces. In this manner the inhibitor is formed directly on the metal and by proper choice of reactants it is possible to form an inhibitor which vaporizes at much higher temperatures than the reactants. This means that the temperatures at which the inhibitors are applied can be low while at the same time the resulting inhibitor coating maintains its efficiency at relatively high temperatures. It also makes possible the use of the more hydrophobic compounds as inhibitor coatings.

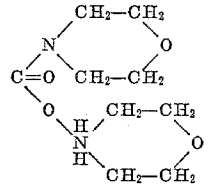
An object of this invention is to form a vapor phase corrosion inhibitor on enclosed metal surfaces which will adhere to the metal at elevated temperatures. Another object of this invention is to form on metal surfaces a corrosion inhibitor which will be continuous and of an even thickness. A further object of this invention is the formation of a vapor phase corrosion inhibitor in situ at temperatures lower than those required to vaporize the resulting vapor phase corrosion inhibitor. Still another object of this invention is to protect metal surfaces not only against corrosion due to contact with air and water but also against that due to the products of combustion encountered in engines and jet motors. An additional object of this invention is to provide vapor phase corrosion inhibitors which are hydrophobic in character. These and other objects will appear in the following discussion.

The improved vapor phase corrosion inhibitors of this invention are formed by introducing two or more reactants which are not in themselves inhibitors into the space containing or consisting of the metal surfaces to be coated and reacting these reactants with each other on the metal surfaces. One and preferably all of the reactants are in the vapor state, to promote ready introduction into small spaces or through intricate systems. One or more of the reactants may be carried by means of a suitable fluid such as air or lubricating oil. By thus forming the corrosion inhibitor in situ it is possible to de-

posit an inhibitor which is much less volatile than any of the reactants used in its formation.

At least one of the reactants is a basic amine, preferably strongly basic, and at least another of the reactants is a weak acid or an anhydride of a weak acid.

An example of a corrosion inhibitor formed in situ in accordance with this invention is morpholine carbamate which has the structure



and may be formed on a metal surface by introducing morpholine vapor and carbon dioxide or by first introducing the volatile amine carried by means of air, and then after the morpholine has deposited on the surfaces, introducing the gaseous carbon dioxide to react with the morpholine. The morpholine carbamate is much less volatile than either morpholine or carbon dioxide. However, morpholine carbamate is somewhat volatile and so it is frequently desirable to use less volatile amines and acids to form even less volatile inhibitors. For example, the use of benzoic or caprylic acid to give morpholine benzoate or caprylate results in a corrosion inhibitor which is only difficultly volatile and which is hydrophobic in character.

The amines suitable for this invention are preferably volatile at temperatures which can be conveniently handled under the circumstances in which the corrosion inhibitor is to be used. For example, if the vapor phase corrosion inhibitor is to be used in a jet engine, it is desirable that the amine be capable of volatilizing at or below the temperature reached by the internal surfaces of the jet engine at the time it is shut off. However, a difficultly volatile amine may be introduced without volatilizing by means of a suitable liquid such as oil which may be flushed through a mechanical system after it is turned off. In addition to possessing these physical properties, the amine should preferably be capable of forming a solid compound with carbon dioxide and should be sufficiently basic to give a stable solid salt with the acid used.

The use of an amine or acid dissolved in oil is particularly useful in reciprocating engines, either gasoline or diesel, where the internal surfaces are normally covered with oil which is pumped through the engine. In this case the special oil, containing amine or acid, can be fed to the oil circulating pump just before shutting down the engine. In other cases, it may be less convenient to apply the acid or amine in oil, but this can usually be done by oil sprays.

Since the inhibitor formed by the reaction will be much less soluble in oil than the component introduced in the oil, its formation will usually gel the oil so that both the oil and the inhibitor will remain as a film on the surface. This film will prevent the oil draining off as untreated oil would do. The amine may be dispersed or dissolved in the carrying liquid. When the engine is started up the heat generated, along with fresh oil flowing in, removes the inhibitors without any further steps being taken.

The amines should be stable in the vapor state and should not be substantially corrosive to the metal surface. They should preferably be strongly basic. Amines suitable for this invention may be aliphatic or aromatic and include, but are not limited to, morpholine, cyclohexyl amine and piperidine. Any amine of proper basicity and volatility is suitable. The stronger the acid, the less the required basic strength required in the base. For example, dicyclohexyl amine is too weak to use with carbon dioxide, but is satisfactory with caprylic acid. The three named above (morpholine, cycloehxyl amine and piperidine) have been found satisfactory with carbon dioxide and substantially all other acids.

The weak acid, or the anhydride of a weak acid, should not be substantially corrosive in itself. As in the case of the amine, the acid or acid anhydride should preferably be volatile under the conditions in which it is to be used. However, it is also possible to introduce it by using any suitable liquid as a carrier. For example, naphthenic acid which is substantially non-volatile can be dissolved in oil which is fed to the lubricating pump at the end of a run. The lubricating oil will distribute the naphthenic acid over the internal metal surfaces of the engine. The amine can then be introduced to form a difficultly volatile amine naphthenate on the metal surfaces.

Acids suitable for this invention include, but are not limited to, carbonic, benzoic, caprylic, and naphthenic. In addition, anhydrides of acids such as carbon dioxide may be used.

The sequence of introduction of the reactants into the enclosed space wherein are the metals to be protected is determined by considering several factors which include the relative corrosiveness of the reactants, the manner in which the reactants are to be introduced and the relative adhering qualities of the reactants.

When all the reactants are volatile, it is desirable to introduce them in order of increasing volatility, i.e., the less volatile reactant first. This allows the second reactant to be introduced at a lower temperature than that required to vaporize the first reactant, thus permitting the first reactant to remain intact on the surface for subsequent reaction with the second reactant. An additional reason for introducing the less volatile component first is that the engine is hot when first shut down but is cooling fairly rapidly, particularly with air-cooled engines. Therefore, the less volatile material should be introduced when the engine is hottest, that is first.

If the reactants in themselves are somewhat corrosive to the metal surfaces to be protected, then it is desirable to put the more corrosive reactant on first, i.e. in decreasing corrosiveness with respect to the surface to be protected. The second reactant may then be introduced in excess to react with all of the first reactant, leaving the less corrosive material to be present for a short time before removal.

If one reactant is carried in a solution or dispersion, and the other in a gas, it is preferable to introduce the solution or dispersion first to prevent "washing off" of a reactant deposited on the metal surface. As a corollary to this statement, it may be noted that if two reactants have different adhering qualities, the one which adheres better should be applied first.

The quantities of reactants introduced into the system to be protected are not critical but it is desirable, for economic reasons, to keep the ratios of reactants close to the stoichiometric ratios. If the metal surface is to be protected only under dry conditions, i.e., no liquid water will collect on the surface, it is not necessary to form a final coating of the corrosion inhibitor which is more than one to a few molecules thick. When water, or other liquid, deposits there must be sufficient inhibitor present to dissolve in the water and render it non-corrosive. The more water that deposits, the more inhibitor that is required. Also, the inhibitor must have sufficient solubility in the water droplets to render them non-corrosive. Where there are sufficient water deposits to cause "drip-off" even larger amounts of inhibitor are required.

The amount of liquid present, the ability of the first introduced reactant to adhere to the surfaces to be protected, the rate of reaction attained at the temperature of reaction, and the relative corrosiveness of the reactants, will be factors to be considered in setting the ratio of reactants used, as well as the total amounts of them used.

As pointed out above, the reactant amines and acids may be introduced as vapors or one of them may be dissolved or dispersed in a liquid. In any case if one reactant is introduced in a solvent or a dispersion, the other reactant must be introduced as a vapor or gas. The vapor or gas may be a pure vapor or gas of the reactant such as gaseous carbon dioxide or morpholine vapor, or may be gasses carried by an inert gas such as air or nitrogen. When the gaseous reactant or reactants are diluted with air or other gaseous diluent, rather than in the pure state, they should nevertheless be in effective concentration in the diluent in order to assure reaction of the components to form the desired corrosion inhibiting product. The reactions between the amines, on the one hand, and the acidic components, on the other, are more or less readily reversible, and unless there is an effective concentration of the vapor-phase reactants the reaction does not go sufficiently to completion to provide an effective quantity of the corrosion inhibitor upon the metal surface to be protected. I have found that the gaseous reactants to be effective for the purposes of this invention, should each constitute at least ten percent, and preferably at least fifteen percent, of the gaseous medium surrounding the metal surfaces to be treated and within the aforesaid enclosed spaces. As the concentrations are increased above the minima just specified, the reactions of this invention also proceed more rapidly and a heavier deposit will be obtained, other things being equal. If one reactant is gaseous and the other is in a liquid, the gaseous reactant will therefore be present in the concentration indicated (i.e. 10% and preferably 15% of the entire gaseous medium) and the other reactant will be present in an amount which, as indicated above, will preferably be stoichiometrically substantially equivalent to the gaseous reactant.

If a reactant is used as a liquid or in the form of small solid particles and is carried into the system by means of a gas, heat for vaporization of the reactant may be supplied by the gas carrier or by radiation from the hot metal surface to be coated. Thus the reactant may be preheated and applied to a cold surface where it condenses or sublimes or it may be applied in a relatively cold state on a hot surface which furnishes heat to vaporize it before depositing on the surface as the surface cools. To illustrate, morpholine, as a vapor or a dispersed liquid, can be injected into the intake of a jet engine and as it comes near the hot internal surfaces of the engine it will vaporize and deposit uniformly on the hot surfaces. As the engine cools, the morpholine will form a continuous coating on the surfaces. Subsequent introduction of gaseous carbon dioxide will form a coating of morpholine carbamate.

It may be desirable to introduce reactants to form more than one layer of inhibitors. Thus, it is possible to put in more than one amine and more than one acid to get a cumulative effect. For example a strong amine and a weaker one could be introduced with an acid to get quick protection which would not be so enduring, along with less immediate protection which would last over a longer period of time. Or, if the metal surfaces to be protected were a combination of ferrous and nonferrous metals a strongly hydrophobic material such as a caprylate could be formed first to protect the nonferrous surfaces and then a morpholine salt of carbon dioxide could be deposited on top, thus eliminating the possibility of the morpholine salt attacking the nonferrous surfaces.

This invention is illustrated by, but not limited to, the following examples:

Example 1

A piece of cast iron cut from an aircraft cylinder was introduced, at room temperature, into a flask containing a small amount of morpholine in the bottom and in which the air was fully saturated with morpholine vapor at 150° F. The flask and sample were allowed to cool so that the morpholine would deposit on the metal surface. The sample was then put into a flask containing a small piece of Dry Ice sufficient to provide at least ten percent concentration of CO_2 in the gaseous atmosphere in the flask; the subsequently generated carbon dioxide vapors reacted with the morpholine coating to form morpholine carbamate. The coated sample showed excellent resistance to moisture.

Example 2

Three sets of pieces of cast iron similar to that used in Example 1 were dipped in oil containing ten percent by weight of naphthenic acid and the excess oil solution was allowed to drain off. The three sets of oiled pieces were then separately suspended in three atmospheres consisting principally of piperidine, morpholine and cyclohexylamine respectively, and piperidine, morpholine and cyclohexylamine naphthenates gelled on the surfaces. The coated pieces were placed in flasks containing water vapor at 150° F. and at room temperature. Good protection was achieved at both temperatures.

Example 3

Several pieces of cast iron similar to that used in Example 1 were dipped in oil containing ten percent by weight of cyclohexylamine and the excess oil solution was allowed to drain off. Some of these oiled pieces were placed in atmospheres constituted of at least 15% caprylic acid at about 150° F., others were placed in atmospheres constituted of at least 15% benzoic acid, at about 150° F., and still others were placed in an atmosphere constituted of at least 15% carbon dioxide, at room temperature. In each instance, the gaseous acidic component reacted with the cyclohexylamine to form on the iron surfaces a corrosion-inhibiting substance which was fully protective even when the surfaces were exposed to water vapor under conditions which would ordinarily cause rusting.

Example 4

Gaseous vapors of morpholine, cyclohexylamine and carbon dioxide were injected into the intake of a diesel engine. Morpholine carbamate formed almost immediately giving rapid and extensive protection. Cyclohexylamine carbamate formed at a slower rate to give further and more lasting protection of the internal surfaces against moisture and the gaseous combustion products remaining in the engine.

It will be seen that by the use of this invention it is possible to deposit one or more coatings of a corrosion inhibitor on surfaces which would be otherwise unattainable or which could be reached only with difficulty. By forming a corrosion-inhibiting compound in situ, it is possible to protect a metal surface over longer intervals and at higher temperatures than those for which previous vapor phase corrosion inhibitors could be employed.

I claim:

1. A method for protecting an enclosed metal surface from corrosion which comprises reacting on said metal surface at least two reactants to form a coating of corrosion-inhibiting material in situ on said metal surface, one of said reactants being a basic amine and the other of said reactants being an acidic material selected from the group consisting of weak acids and anhydrides of weak acids, at least one of said reactants being in the vapor state at the time of application and being present in the gaseous medium around said surface in a concentration of at least ten percent, said amine and said acidic material being brought separately into contact with said surface for said reacting thereon.

2. A method for protecting a metal surface from corrosion which comprises reacting on said metal surface an amine and an acidic material selected from the group

consisting of weak acids and anhydrides of weak acids, to form a salt of the amine in situ, said amine being strongly basic, both said amine and said acid being in the vapor state at the time of application and each being present in the gaseous medium around said surface in a concentration of at least ten percent, said amine and said acidic material being brought separately into contact with said surface for said reacting thereon.

3. The method in accordance with claim 2 wherein the amine is morpholine and the acidic material is carbon dioxide.

4. The method in accordance with claim 2 wherein the amine and the acidic material are introduced in order of increasing volatility.

5. A method for protecting a metal surface from corrosion which comprises reacting on said metal surface a strongly basic amine and a weak acid to form a salt of the amine in situ upon said surface, said weak acid being in the vapor state at the time of application and being present in the vapor in a concentration of at least fifteen percent, said amine and said acid being brought separately into contact with said surface for said reacting thereon.

6. A method for protecting an enclosed metal surface from corrosion which comprises bringing into contact with said surface a first reactant, subsequently

bringing into contact with said surface a second reactant which is reactive with said first reactant, reacting on said metal surface said two reactants to form a coating of corrosion-inhibiting material in situ on said metal surface, one of said reactants being a basic amine and the other of said reactants being a member of the group consisting of weak acids and anhyrides of weak acids, at least one of said reactants being in the vapor state at the time of application and being present in the gaseous medium around said surface in a concentration of at least ten percent.

7. The method in accordance with claim 6 wherein said first reactant is introduced into contact with said surface in a liquid vehicle.

8. The method in accordance with claim 7 wherein said vehicle is lubricating oil.

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