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STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

The present invention relates to compositions of matter and more particularly to an improved composition for protecting high-strength metals from the harmful effects of corrosion.

It is well known that corrosive environments have a drastic influence on the structural strength of metallic materials. In atmospheres of high humidity, salt and other pollutants, the nominal design strengths of metal parts are considerably reduced in service thereby leading to premature failures. In particular, the high strength structural alloys used in the aircraft industry are highly susceptible to such failures with the fatigue life of AISI 4340 steel, for example, being decreased by more than an order of magnitude upon exposure to merely a high-humidity atmosphere. Presence of chlorides and gases, such as $\text{SO}_2$, even further reduce the fatigue strengths of
these high strength structural alloys, increasing the occurrence of stress corrosion cracking. Accordingly, the sudden failure of such structural aircraft parts, especially those of naval aircraft, and the potential catastrophic damages caused thereby due to highly corrosive environmental effects are a constant and major concern.

While early emphasis focused on improving mechanical properties of the structural alloys to compensate for environmental effects, it was soon realized that increasing the strength of the alloys also increased their susceptibility to stress corrosion cracking and corrosion fatigue. Subsequent studies concentrated on the interplay of corrosion processes occurring at crack tips and other areas of high stress concentrations, it being learned from such studies that the most common and damaging electrochemical reaction occurring at these areas is the hydrogen reduction process where hydrated protons are discharged to neutral hydrogen atoms. The hydrogen embrittlement caused by diffusion of adsorbed atomic hydrogen into the metal reduce its toughness and ductility and becomes a major source of premature failure.

Various corrosion inhibitors have been developed and utilized to decrease or prevent the corrosive reaction of a metal with its environment. Organic chemical compounds have long been used in coatings, such as primers, paints and varnishes, to inhibit the corrosion of an underlying metal surface. While organic chemical inhibitors in such coatings have proven to be
a satisfactory temporary barrier to the environment, inorganic chemical inhibitors are preferred, despite current limitations in their applicability, for their long range protection and high efficiency. These inorganic inhibitors have commonly been used in aqueous solutions wherein the inorganic ions exist as hydrated molecules, surrounded by a shell of water molecules which increases their size, restricts their migration to the reaction interface, and limits their full effectiveness. When applied to non-aqueous systems, these inorganic chemicals have proven to be incompatible due to a general immiscibility and insolubility in organic solvents. While recent developments have made it possible to solubilize metal anions in organic media using phase transfer catalysts, most inorganic corrosion inhibitors currently used in organic coatings are finely dispersed solids which prove less efficient in action since the solid inhibitors tend to leach out of their dispersed phase by rain and washings, and in turn, become impeded in their action by hydration shells. In addition, existing corrosion-inhibiting coating compositions have not proven entirely satisfactory in dynamic fracture conditions, such conditions causing a breakdown of the coating films that lead to the formulation of potentially hazardous areas of localized corrosion.

SUMMARY OF THE INVENTION

Accordingly, it is a general purpose and object of the present invention to formulate an improved composition
effectively using inorganic inhibitors to protect metals from the damaging effects of corrosion.

Another object of the present invention is to provide an inorganically-based corrosion-inhibiting composition that protects high strength structural alloys from catastrophic failures due to stress corrosion cracking, corrosion fatigue, hydrogen embrittlement, exfoliation and wear.

Still another object of the present invention is to provide a corrosion protective composition that effectively reduces corrosion fatigue and stress corrosion cracking in high strength structural alloys subjected to highly corrosive environments, particularly those containing chloride salts.

A further object of the present invention is to provide a corrosion protective composition that can be applied in situ to retard cracking of high strength steels and aluminum alloys in both static and cyclic stress conditions.

A still further object of the present invention is to provide a corrosion protective composition that is safe and easy to use, and economical to manufacture.

Briefly, these and other objects of the present invention are accomplished by a corrosion protective composition, particularly useful for crack arrestment, wherein finely divided solid inorganic inhibitor compounds are solubilized in a 0.1M stock solution of an alkyl or alkyl-aryl group, organo-substituted quaternary ammonium salt and an organic solvent, the approximate
ratio of the compound to the solution being 0.75 – 1.00 g/10 ml. The inorganic compounds, including sodium dichromate, sodium borate, sodium nitrite, sodium molybdate, ammonium hexanitratocerate, potassium hexachloro palladate and lanthanum nitrate, are mixed in specific combinations and dissolved in the organic solvent by phase transfer catalysis involving an anion exchange reaction between the salt and the inorganic compounds. Quaternary ammonium salts used as the phase transfer catalyst include methyl trialkyl (C₈ – C₁₀) ammonium chloride and tricapryl methyl ammonium chloride, while effective organic solvents include xylene and mineral spirits.

Solubilization of the compounds produces a clear, supernatant liquid which, when decanted and applied to the surfaces of high-strength steels and aluminum alloys, arrests corrosion fatigue and retards stress corrosion cracking of the metal surfaces exposed to high-humidity and chloride-containing environments.

Other objects, advantages and novel features of the present invention will become apparent from the following detailed description thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the present invention, inorganic inhibitor compounds of an anionic nature are selected for inclusion in the protective coating composition based on certain functional characteristics, particularly relating to a mechanistic
consideration of the corrosive electrochemical electrode process occurring on a metal surface at the tip of an advancing crack formed during corrosion fatigue or stress corrosion cracking. The selected compounds should: inhibit moisture entry and displace moisture at the crack tip, neutralize formation of $H^+$, impede entry of atomic hydrogen into the metal, create a passive film barrier at the crack surface, and control anodic dissolution of the metal. Based on these prerequisite characteristics, the following inorganic compounds were screened and selected according to their known functional properties in retarding corrosion reactions, both individually and collectively:
sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$), sodium borate ($Na_2B_4O_7 \cdot 10H_2O$), sodium nitrate ($NaNO_3$), sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), potassium hexachloro palladate ($K_2PdCl_6$), ammonium hexanitrato-cerate ($\left(\text{NH}_4\right)_2\left[\text{Ce}(\text{NO}_3)_6\right]$), and lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$).

The selected inorganic inhibitor compounds are solubilized into an organic phase by a conventional method of phase transfer catalysis. Using an organo-substituted, quaternary ammonium salt of the alkyl or alkyl-aryl group as the phase transfer catalyst, an exchange reaction is effected that forms an organic complex having the anionic radical of the inorganic compound. This phase transfer reaction is shown generally as follows:

$$Q^+X^- + Y^+(\text{INH})^- \rightarrow Q^+(\text{INH})^- + Y^+X^-$$
where
\[ Q^+ X^- = \text{quaternary ammonium salt}, \]
\[ Y^+(\text{INH})^- = \text{inorganic compound with inhibitor anion}, \] and
\[ Q^+(\text{INH})^- = \text{organic complex with inhibitor anion}. \]

Effective quaternary ammonium salts used as the phase transfer catalyst in the present invention include a methyl trialkyl \((C_8 - C_{10}) \) ammonium chloride, commercially available as Adogen 464 from the Aldrich Chemical Company, and a tricapryl methyl ammonium chloride commercially available from Tridom Chemical Inc. It should be understood that hydroxide, bromide and iodide salts of the quaternary ammonium complex may be likewise effectively employed as the phase transfer catalyst in the present invention.

A nonpolar organic solvent is included in the present composition both to dissolve the quaternary ammonium salt used as the phase transfer catalyst and then, after the exchange reaction, to dissolve the organic complex thereby serving as carrier vehicle for the inhibitor anions in the composition. Effective solvents used in the present composition include mineral spirits having a flash point in the range of 140°F-160°F and xylene, with xylene being found to be the more stable carrier solvent due to oxidation of unsaturated hydrocarbons in the mineral spirits by the inorganic anions dissolved therein. Although other solvents can be used, such as aliphatic and aromatic naphthas, esters, and ketones, only those solvents having high resistance to oxidation and unlikely
to change during periods of storage are recommended. It should be noted that these organic solvents, being generally effective as water-displacing agents, provide an additional corrosion control advantage to the present composition as the carrier vehicle therefor.

In the preparation of the composition, a 0.1M stock solution is initially made of the quaternary ammonium salt in the organic solvent. The inorganic inhibitor compounds, in finely-divided solids, are then added to the solution in specific combination and proportions, as described in specific detail hereinbelow, and mixed thoroughly for a period of time to dissolve the compounds and effect the phase transfer reaction. Typically, an hour of mixing was sufficient to obtain a phase transfer reaction. The resulting mixture is then allowed to settle leaving a clear supernatant liquid which may be decanted and applied to a particular metal surface requiring corrosion protection.

Testing of the present composition was conducted using notched bend bar specimens (10" X 1" X 1/2" size, fracture mechanics type) fatigue precracked and fabricated from a vacuum-arc remelted type 4340 steel of 260 to 280 ksi ultimate tensile strength. Small drops of the formulated composition, as specifically described in the examples below, were introduced to the inverted notched areas of the respective specimens before and after loading on an Instron machine. Loaded in tension-
tension on the Instron, the specimens were enclosed in a controlled humidity chamber having the capability of ranging between a dry air (< 15% relative humidity) and a moist air (> 90% relative humidity) environment, with additional provision for inclusion of chloride (NaCl) to the moist air to simulate a highly corrosive naval environment. A three-point load configuration was used for cycling the specimens between 150 and 1500 pounds at a frequency of 10 cycles per minute, and the crack growth of each specimen was monitored periodically after every 500 cycles to determine the crack growth rate.

It should be noted that the test conditions described yielded a minimum fracture mechanics stress intensity factor of approximately 25 ksi \(\sqrt{\text{inch}}\) for the dry air environment. Further details of the mechanical testing and fracture mechanics calculations are set forth in V. S. Agarwala and J. J. DeLuccia, "New Inhibitors for Crack Arrestment in Corrosion Fatigue of High Strength Steels", *Corrosion*, Vol. 36, No. 4, April 1980, pp. 208-218.

The following specific examples of the composition formulated and tested, are intended to illustrate the invention but not limit it in any way.

**EXAMPLE I**

To a 20 ml 0.1M solution of methyl trialkyl ammonium chloride in xylene, 0.5 gram each of sodium dichromate, sodium nitrite, and sodium borate was added and vigorously
shaken for 20 minutes. The resultant supernatant liquid containing approximately 0.1% of the dissolved inorganic compounds was tested for arrestment of cracks during corrosion fatigue testing in a high humidity environment with and without presence of a chloride salt.

EXAMPLE II

A mixture of sodium borate and sodium nitrate, 0.5 gram of each, was dissolved in 10 ml of a 0.1M solution of methyl trialkyl ammonium chloride in mineral spirits. The resultant supernatant liquid was applied to a test specimen and exposed to the corrosion fatigue testing in moist air only.

EXAMPLE III

One gram amounts of each of the following inorganic inhibitor compounds:

a. lanthanum nitrate,
b. potassium hexachloro palladate,
c. sodium molybdate, and
d. sodium dichromate

were separately dissolved in respective 10 ml 0.1M solutions of methyl trialkyl ammonium chloride in mineral spirits. Respective test specimens were coated with the formulated compositions and tested in the high humidity environment, the composition containing sodium dichromate being also exposed to the moist air containing chloride.
EXAMPLE IV

A mixture of ammonium hexanitratocerate, sodium nitrite, and sodium borate, 0.5 gram of each, was dissolved in 20 ml of a 0.1M solution of tricapryl methyl ammonium chloride in xylene. The resultant liquid composition was applied to a test specimen and subjected to corrosion fatigue testing in moist air only.

EXAMPLE V

A mixture of sodium molybdate, sodium nitrite and sodium borate, 0.5 gram of each, was added to 20 ml of a 0.1M solution of methyl trialkyl ammonium chloride in mineral spirits, and the formulation vigorously agitated for 10 minutes. Thereafter, 0.5 gram of sodium dichromate was added and the combined formulation agitated again for another 10 minutes. The combined formulation was allowed to settle and the supernatant liquid was decanted and applied to test specimens for corrosion fatigue testing in moist air as well as a 100% relative humidity environment containing approximately 1000 ppm chloride.

Results of the corrosion fatigue testing conducted upon the respective test specimens coated with the abovedescribed examples of the composition, as well as those test results obtained on uncoated specimens for baseline comparison purposes, are summarized in the following Table I. These results are
shown in terms of total fatigue life before overload fracture, the crack growth rate independent of the stress intensity factor, and the stress intensity factor independent of crack growth rate.
<table>
<thead>
<tr>
<th>Test Sample</th>
<th>Fatigue Life Cycles</th>
<th>Crack Growth Rate, μ in./cycle</th>
<th>Stress Intensity Factor, ksi√in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>Dry Air</td>
<td>17,000</td>
<td>70</td>
</tr>
<tr>
<td>Uncoated</td>
<td>Moist Air</td>
<td>1,800</td>
<td>33</td>
</tr>
<tr>
<td>Uncoated</td>
<td>Moist Air + Cl−</td>
<td>9,000</td>
<td>32</td>
</tr>
<tr>
<td>Example I</td>
<td>Moist Air</td>
<td>1,200</td>
<td>27</td>
</tr>
<tr>
<td>Example I</td>
<td>Moist Air + Cl−</td>
<td>3,300</td>
<td>35</td>
</tr>
<tr>
<td>Example II</td>
<td>Moist Air</td>
<td>4,600</td>
<td>&gt;40</td>
</tr>
<tr>
<td>Example III(a)</td>
<td>Moist Air</td>
<td>4,300</td>
<td>45</td>
</tr>
<tr>
<td>Example III(b)</td>
<td>Moist Air</td>
<td>1,300</td>
<td>48</td>
</tr>
<tr>
<td>Example III(c)</td>
<td>Moist Air</td>
<td>6,800</td>
<td>52</td>
</tr>
<tr>
<td>Example III(d)</td>
<td>Moist Air + Cl−</td>
<td>6,400</td>
<td>34</td>
</tr>
<tr>
<td>Example IV</td>
<td>Moist Air</td>
<td>9,000</td>
<td>45</td>
</tr>
<tr>
<td>Example V</td>
<td>Moist Air + Cl−</td>
<td>6,500</td>
<td>45</td>
</tr>
</tbody>
</table>

TABLE I
Referring to Table I, it should be noted that the corrosion fatigue test results evidenced a five-fold increase in the high-humidity life expectancy of the specimen applied with the formulation of Example I along with a retardation of the crack growth rate from 110 to 27 µin per cycle. With chloride added to the moist air environment, however, Example I showed increased crack growth rate and decreased life expectancy. In moist air, the formulation of Example II showed improvement, although somewhat less significant than Example I, in the corrosion fatigue life of the baseline specimen, retarding crack growth rate from 110 to 65 µin per cycle and increasing life expectancy by a factor of 2. Each of the formulations of Example III (a)-(d) evidenced retardation of crack growth rates and better than two-fold increases in life expectancy of the high-strength steel specimen in the moist air environment. However, with chloride added to the environment, the formulation of Example III(d) did not retard crack growth rate and did not significantly increase life expectancy. The formulation of Example IV showed a significant retardation of crack growth rate (110 to 38 µin/cycle) and a substantial increase (1800 to 6400 cycles) in life expectancy before failure. The most significant results of the corrosion fatigue testing were evidenced by the formulation of Example V which of particular note, when compared to a baseline no-treatment condition in a chloride-containing environment,
increased the fatigue life of the high strength steel by a factor of 5 and retarded crack growth rate from 150 to 28 μin per cycle.

It should be noted that further evaluation of the formulation of Example V was conducted on a high strength aluminum alloy specimen, Type 7075-T6, to study the stress corrosion inhibition properties of the formulation as applied to non-ferrous metals. In this evaluation, double cantilever beam specimens of the aluminum alloy were used and pop-in cracked under a constant load applied by two bolts in accordance with a conventional technique for determining stress corrosion cracking resistance of aluminum alloys. A test chamber was kept at room temperature and a high relative humidity (>95%) was maintained at all times. A salt solution (3.5% NaCl) was added to the notch areas of selected specimens to simulate the effect of a chloride-containing environment. Drops of the formulation were applied to the specimens once a week and their crack growth monitored periodically. The results of this testing are summarized in Table II below and evidence a marked crack growth retardation effect for the formulation of Example V in comparison to a baseline specimen and those specimens applied with formulations of Examples I and III(d). Particularly noteworthy is the nearly two-fold increase in the threshold value of the stress intensity factor ($K_{ISCC}$) for the aluminum alloy in the moist chloride environment.
### TABLE II

<table>
<thead>
<tr>
<th>TEST SAMPLE</th>
<th>ENVIRONMENT</th>
<th>CRACK GROWTH RATE, (\text{um/hr.})</th>
<th>1000-1500 hrs. elapsed</th>
<th>THRESHOLD (K_{\text{ISCC}}), MPa(\sqrt{\text{m}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>Air(=50% R.H.)</td>
<td>0.2</td>
<td></td>
<td>25.0</td>
</tr>
<tr>
<td>Uncoated</td>
<td>Moist Air (100% R.H.)</td>
<td>1.9</td>
<td></td>
<td>15.0</td>
</tr>
<tr>
<td>Uncoated</td>
<td>Moist Air + Cl(^-)</td>
<td>2.4</td>
<td></td>
<td>9.5</td>
</tr>
<tr>
<td>Example I</td>
<td>Moist Air + Cl(^-)</td>
<td>2.3</td>
<td></td>
<td>12.5</td>
</tr>
<tr>
<td>Example III(d)</td>
<td>Moist Air + Cl(^-)</td>
<td>1.6</td>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>Example V</td>
<td>Moist Air + Cl(^-)</td>
<td>0.75</td>
<td></td>
<td>17.5</td>
</tr>
</tbody>
</table>
Therefore, it is now apparent that the disclosed invention provides an improved composition using inorganic inhibitors in organic phase to protect high-strength metals from the harmful effects of corrosion and the resulting risks of catastrophic failures caused by stress corrosion cracking, corrosion fatigue, hydrogen embrittlement, exfoliation and wear. In particular, the disclosed protective composition effectively reduces corrosion fatigue and stress corrosion cracking in high-strength structural alloys exposed to highly corrosive environments including chlorides, increasing the fatigue life of the alloys in both static and cyclic stress conditions. Furthermore, the described inorganically-based corrosion protective composition is safe and easy to use, and can be economically manufactured.
ABSTRACT OF THE DISCLOSURE

A corrosion protective composition, particularly useful for crack arrestment, is disclosed wherein a mixture of finely divided solid inorganic inhibitor compounds are solubilized in a 0.1M stock solution of an alkyl or alkyl-aryl group, organo-substituted quaternary ammonium salt and an organic solvent, the approximate ratio of the compound to the solution being 1.00 g/10 ml. The inorganic compounds, including sodium dichromate, sodium borate, sodium nitrite and sodium molybdate, are mixed in specific combinations and dissolved in the organic solvent by phase transfer catalysis involving an anion exchange reaction between the salt and the inorganic compounds. Quaternary ammonium salts used as the phase transfer catalyst include methyl trialkyl (C_8 - C_10) ammonium chloride and tricapryl methyl ammonium chloride, while effective organic solvents include xylene and mineral spirits.