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1 ENVIRONMENTAL CRACK ARRESTMENT COMPOSITION

5 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.

10 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.

15 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
20 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
25 gases, such as SO₂, even further reduce the fatigue strengths of

1 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
5 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
10 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
15 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.

20 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
25 organic chemical inhibitors in such coatings have proven to be

1 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
5 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
10 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
15 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
20 dynamic fracture conditions, such conditions causing a break-
down 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
25 the present invention to formulate an improved composition

1 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
5 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
10 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
15 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.

20 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
25 quaternary ammonium salt and an organic solvent, the approximate

1 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 hexanitrate
5 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 tricaprlyl
10 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
15 corrosion fatigue and retards stress corrosion cracking of the
metal surfaces exposed to high-humidity and chloride-containing
environments.

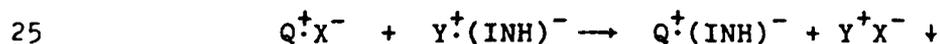
Other objects, advantages and novel features of the
present invention will become apparent from the following
20 detailed description thereof.

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
25 functional characteristics, particularly relating to a mechanistic

1 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
5 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
10 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 ($NaNO_2$), sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$),
potassium hexachloro palladate (K_2PdCl_6), ammonium hexanitrate-
15 cerate ($(NH_4)_2[Ce(NO_3)_6]$), 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
20 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:



1 where

$Q^+ X^-$ = quaternary ammonium salt,

$Y^+(INH)^-$ = inorganic compound with inhibitor anion, and

$Q^+(INH)^-$ = organic complex with inhibitor anion.

5 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
10 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
15 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 $140^\circ - 160^\circ F$
20 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
25 those solvents having high resistance to oxidation and unlikely

1 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
5 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
10 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
15 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
20 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
25 and after loading on an Instron machine. Loaded in tension-

1 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
5 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
10 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
15 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
20 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,
25 sodium nitrite, and sodium borate was added and vigorously

1 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
5 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
10 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:

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

were separately dissolved in respective 10 ml 0.1M solutions
20 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.

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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.

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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.

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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

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1 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.

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T A B L E I

Test Sample	Environment	Fatigue Life Cycles	Crack Growth Rate, μ in./cycle	Stress Intensity Factor, ksi $\sqrt{\text{in.}}$
Uncoated	Dry Air	17,000	12	70
Uncoated	Moist Air	1,800	110	33
Uncoated	Moist Air + Cl ⁻	1,200	150	32
Example I	Moist Air	9,000	27	55
Example I	Moist Air + Cl ⁻	1,200	200	34
Example II	Moist Air	3,300	65	35
Example III(a)	Moist Air	4,600	50	>40
Example III(b)	Moist Air	4,000	45	>40
Example III(c)	Moist Air	4,300	62	48
Example III(d)	Moist Air	6,800	42	52
Example III(d)	Moist Air + Cl ⁻	1,300	180	34
Example IV	Moist Air	6,400	38	45
Example V	Moist Air	9,000	25	55
Example V	Moist Air + Cl ⁻	6,500	28	45

1 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
5 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
10 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
15 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
20 retardation of crack growth rate (110 to 38 $\mu\text{in}/\text{cycle}$) 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-
25 treatment condition in a chloride-containing environment,

1 increased the fatigue life of the high strength steel by a
factor of 5 and retarded crack growth rate from 150 to 28
uin. per cycle.

5 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
10 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
15 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
20 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
25 alloy in the moist chloride environment.

TABLE II

TEST SAMPLE	ENVIRONMENT	CRACK GROWTH RATE, $\mu\text{m/hr.}$		THRESHOLD K_{ISCC} , $\text{MPa}\sqrt{\text{m}}$
		1000-1500 hrs. elapsed		
Uncoated	Air ($\approx 50\%$ R.H.)	0.2		25.0
Uncoated	Moist Air (100% R.H.)	1.9		15.0
Uncoated	Moist Air + Cl^-	2.4		9.5
Example I	Moist Air + Cl^-	2.3		12.5
Example III(d)	Moist Air + Cl^-	1.6		10.0
Example V	Moist Air + Cl^-	0.75		17.5

1 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
5 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 environ-
10 ments 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.

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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 tricaprlyl methyl ammonium chloride, while effective organic solvents include xylene and mineral spirits.

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