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# MULTIPURPOSE CORROSION INHIBITORS FOR AEROSPACE MATERIALS IN NAVAL ENVIRONMENTS

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19. A multidisciplinary approach was taken to solve the complex problem of premature failure of high strength aircraft alloys from the effects of environment. Principles concerning the time dependent macroscopic interfacial processes occurring at fine geometries (defect sites etc.) and responsible for sub-critical crack growth were isolated to envolve new methods for arresting cracking. It has been shown that a synergistically combined chemical system can be formulated which can modify in-situ interfacial chemistry of the crack propagation process such that the life of the material is enhanced significantly. Results show crack growth retardation effects on both steels and aluminum alloys when tested for corrosion fatigue and/or stress corrosion cracking in high humidity and saline environment.

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# INTRODUCTION

High humidity, salts and acid pH are the most corrosive elements for structural alloys such as steels and aluminum alloys. In particular, aircraft materials (critical parts like landing gear, bolts and hinges) when subjected to high stresses in these environments fail catastrophically. Most of these failures appear in the form of corrosion fatigue, stress corrosion cracking and/or hydrogen (environmental) embrittlement. The effects of environment reduce the fracture toughness of the material significantly and sometimes by a factor of ten or more, for high strength alloys (1). Thus, whenever the design stress levels are exceeded during service the part can fail catastrophically. For example, naval aircraft landing gear which are generally designed to approximately 40% of the yield strength often exceed this limit during landing. In the present work, consideration has been given to the interaction of corrosion and stress in service. Additionally, the processes occurring in fine crevices or small geometries are emphasized.

Corrosion and other interfacial phenomena which occur at bulk surfaces are quite different from those taking place at restricted geometries, specifically because of the differences in mass transport, surface tension and pH. It has been well established that conditions of low pH occur inside a crevice when species like chloride ions come in contact with the metal surface. Therefore, methods of corrosion inhibition normally applicable to large surfaces, are usually inadequate for restricted geometries such as crack tips. Additionally, high stress (produced from service) at the apex of a fine crack or crevice form a plastic zone, i.e. generation of new active surface, which is generally anodic to the rest of the surface (2). This combination of anodic susceptibility and low pH causes corrosion to occur at the tip of the crack. The surface adjacent to the crack-tip where the corresponding cathodic reaction is taking place becomes the site for hydrogen evolution. Initially, only atomic hydrogen is formed, which being nascent, is readily absorbed at the surface and diffuses to locations called traps in the bulk of the metal. These traps can develop at a variety of heterogenieties such as grain boundaries, microvoids, dislocation sites (slip plane pile-ups) and elastic-plastic interfaces. Under stress the diffusion of hydrogen (diffusion coefficient) is very fast, sometimes a few orders of magnitude higher than what is measured conventionally (3). The interaction of hydrogen with these heterogenieties or its build-up, can cause embrittlement and thereby reduce fracture toughness. For high strength aerospace alloys this is perhaps the most common failure mechanism. Earlier investigations performed on high strength steels (AISI 4340) and aluminum alloy (7075-T6) support this conclusion (4,5). The effects of hydrogen are more severe on new higher strength materials (300M steel) as higher strength is concomitant with higher sensitivity to embrittlement failure (6).

In this work the control of mechanical damage due to environment has been approached through the use of chemical compounds. The principles employed are based on the corrosion reactions occuring in crevices (low pH) and on processes which may affect the emergence of slip-steps or new surfaces during deformation. Electrochemical and surface tension concepts have been used to devise an inhibitor system which can protect high strength alloys from corrosion fatigue, stress corrosion cracking and/or hydrogen embrittlement. In particular, chemical compounds with certain specific properties have been employed to modify the interfacial chemistry of the crack-tip. Reduction-oxidation (redox) type inorganic chemicals which control anodic and cathodic processes have been considered.

Organic chemicals which affect surface tension (surface free-energy) have been also incorporated in the formula (inhibitors) to delay or suppress the emergence of new surfaces during cracking. It has been suggested that surface active adsorbates affect the mechanical behavior of metals, hardness and cracking (7,8). Surface active substances which offer lower interfacial tension (compared to water), such as non-polar solvents, have been reported to inhibit crack growth rate in high strength steels (9). Organic solvents are used to enhance the mobility of the corrosion inhibiting species and thus reach the crack-tip. These organic solvents are also capable of displacing moisture and hence eliminating the hydration shells which serve as barriers to inhibiting ions.

## EXPERIMENTAL PROCEDURE AND RESULTS

The selection and screening of chemical compounds as potential inhibitors of environmental cracking were based on their abilities to do one or more of the following:

(a) Reduce anodic dissolution of metal.

$$M \longrightarrow M^{+n} + ne \xrightarrow{O_2} M.O \text{ (passive film).} \qquad (1)$$

This is primarily achieved by producing spontaneous passivity. A number of assivating-type inhibitors such as chromates, dichromates, cerates, permanganates, nitrites and molybdates are good oxidizers and can also provide oxygen to the crack tip for passivation (10,11).

(b) Resist pitting or effects of chloride ions.

$$M.O + 2H^{+} \xrightarrow{Cl^{-}} M^{+} + H_2O \qquad (2)$$

Reactions of this nature break down the passive film when the environment becomes acidic, as is the case at the crack-tip. Molybdates, tungstates, vanadates, bismuthates, antimonates, peroxycarbonates are the compounds most commonly used for this purpose.

(c) Buffer pH at the crack-tip to neutral or slightly alkaline pH. In steels, slightly alkaline pH is preferred. Chemicals like borates, phosphates, acetates, silicates and carbonates are most widely used for this purpose. Neutral solutions also resist attack of chloride ions, which cause pitting.

(d) Inhibit hydrogen absorption in the metal. This is possible by either retarding the hydrogen evolution reaction in its entirety or

$$H^{+} + e^{-} \longrightarrow H \longrightarrow \tfrac{1}{2}H_2 \qquad (3)$$

accelerating the hydrogen recombination reactions (equations (4) and (5)) so hydrogen molecules (gas) are formed (evolved) as soon as hydrogen atoms are produced.

$$H + H \longrightarrow H_2 \qquad (4)$$

$$H + H^{+} + e^{-} \longrightarrow H_2 \qquad (5)$$

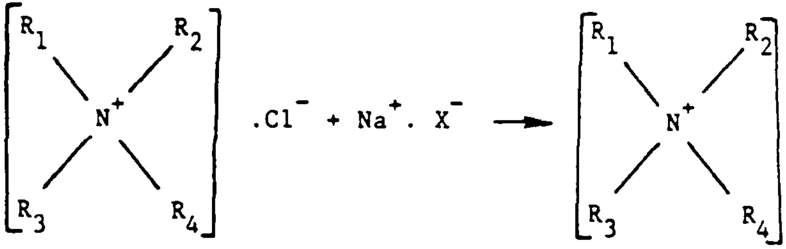
It is only the hydrogen atoms which diffuse into the metal causing embrittlement. A number of platinum group oxyanions like osmiates, platinates, palladates are effective hydrogen recombinants. There is another category of compounds known as rare earths; they inhibit hydrogen entry in metals by forming hydrides. Salts of La, Y, Ce and Sm have been considered in this study.

(e) Facilitate transport of inhibitors to the crack-tip, i.e. keep inhibitor ions devoid of hydration shells. This requires converting inorganic substances into a chelate complex with an organic group. Quaternary ammonium chlorides of either methyl trialkyl or tricapryl methyl groups have been used as phase transfer catalysts.

(f) Displace water and serve as good carriers (solvent) for inhibitors. Low surface tension solvents like mineral spirits, xylene or hexane have been tested. Inorganic complexes dissolved in these solvents become free of hydration shells (compared with aqueous ions) and reach reaction sites very effectively.

Since inhibition of crack propagation is a multifunctional task, a synergistic combination of several chemicals was mandatory. Inorganic substances in an organic medium provide the best option to formulate a multicomponent system without much fear of mutual interactions.

The phase transfer of inorganic compounds into organo-metallic complexes has been achieved by a direct method where anionic exchanges occur as follows;



(6)

where $X^-$ is the inhibitor anion and [N−Cl] is the alkyl-aryl quaternary ammonium chloride, the phase transfer catalyst. A 0.1M stock solution of the phase transfer catalyst in mineral spirits or m-xylene is used to mix 1 gm of solid inorganic inhibitor per 20 ml of stock solution. The mixtures are thoroughly agitated for several hours. The supernatant liquids are then studied for their crack growth inhibition properties. To prepare mixtures of several inhibitors into one solution each compound was solubilized separately and then mixed before evaluation. Generally 100 ppm of inhibitors has been solubilized by this method. The details of these procedures are described elsewhere (12). The principles of complexing or heteroconjugation of inorganic anions with organic molecules have been reported in detail by Barcza and Pope (13). In the present work the effect of various inhibitors in modifying the crack-tip chemistry is discussed in terms of crack growth rate inhibition and how incorporation of various functional properties of the additives affects the overall results.

The materials selected for mechanical testing were high strength 4340 and 300M steel and 7075 alloy. The nominal compositions of these alloys are given in handbooks (14). Two types of mechanical tests have been performed — the stress corrosion cracking (static) and corrosion fatigue (dynamic) — to study the inhibitors.

## CORROSION FATIGUE (CF) TESTS

For CF tests fracture mechanics type notched bend bars and/or compact tension specimens were fabricated according to the ASTM E-399 test method. All steel specimens were heat treated to their highest yield strength (14). 7075 aluminum alloy specimens were aged to T6 temper and specimens machined so that the plane of cracking would be in the longitudinal direction. Fatigue specimens were pre-cracked under high frequency until crack lengths of approximately 0.50 cm were obtained. This provided a starting stress intensity of approximately 25MPa $\sqrt{m}$ and 12MPa $\sqrt{m}$ for steel and aluminum respectively. Based on ASTM method E-399, CF tests were conducted at approximately 0.1 Hz in an environmental chamber of high humidity (moist air) and chloride. Specimens were injected with the inhibitors in the notch area only, both before and during the test at fixed periodic intervals. More details of these tests are described elsewhere (1, 15). Control tests are conducted without inhibitors under similar conditions of moist air and chloride. Tables I and II describe the results of the fatigue tests for 4340 steel in moist air, and moist air and chloride-containing environments respectively. The presence and absence of solvent in 'no inhibitor' control tests showed no appreciable difference in the corrosion fatigue behavior of 4340 steel.

Table I. Effect of Inhibitors on Corrosion Fatigue Behavior of High Strength 4340 Steel in Moist Air Test Environment

| Inhibitor System Dissolved in Mineral Spirits by Phase Transfer Catalysis | Crack Growth Rate, $\left(\frac{da}{dN}\right)$, $\mu$m/cycle (At $\Delta K$ of 40 MPa$\sqrt{m}$) | Stress Intensity, $\Delta K$, MPa$\sqrt{m}$ (At Plateau Velocity of 2.5 $\mu$m/cycle) | Total Fatigue Life, N, Cycles |
|---|---|---|---|
| No Inhibitor (Dry Air Only) | 0.3 | 77 | 17,000 |
| No Inhibitor | 2.8 | 36 | 1,800 |
| Dichromate | 1.0 | 57 | 6,800 |
| Hexapalladate | 1.1 | 45 | 4,600 |
| Cerate | 1.2 | 45 | 4,000 |
| Lanthanum Nitrate | 1.3 | 44 | 4,000 |
| Nitrite + Borate | 1.6 | 38 | 3,300 |
| Cerate + Nitrite + Borate | 1.0 | 49 | 6,400 |
| Dichromate + Nitrite + Borate | 0.7 | 60 | 9,000 |
| Dichromate + Nitrite + Borate + Molybdate | 0.7 | 60 | 9,000 |

All results have a scatter band of approximately 15% and are average values of at least 2 tests.

Table II. Effect of Inhibitors on Corrosion Fatigue Behavior of High Strength 4340 Steel in Chloride-Containing Test Environment

| Inhibitor System Dissolved in Mineral Spirits by Phase Transfer Catalysis. | Crack Growth Rate, $\left(\frac{da}{dN}\right)$, μm/cycle (At ΔK of 40 $MPa\sqrt{m}$) | Stress Intensity ΔK, $MPa\sqrt{m}$ (At Plateau Velocity of 2.5 μm/cycle) | Total Fatigue Life, N, Cycles |
|---|---|---|---|
| *No Inhibitor (Dry Air Only) | 0.3 | 77 | 17,000 |
| No Inhibitor | 3.8 | 35 | 1,200 |
| Dichromate | 4.2 | 36 | 1,200 |
| Molybdate | 1.5 | 50 | 4,500 |
| Molybdate + Nitrite | 1.3 | 50 | 4,800 |
| Dichromate + Nitrite + Borate | 4.0 | 37 | 1,400 |
| Dichromate + Nitrite + Borate + Molybdate | 0.8 | 55 | 6,500 |
| Cerate + Nitrite + Borate + Molybdate | 1.5 | 50 | 4,800 |

All results have a scatter band of approximately 15% and are average values of at least 2 tests.

*Tested in less than 15% R.H., without chloride.

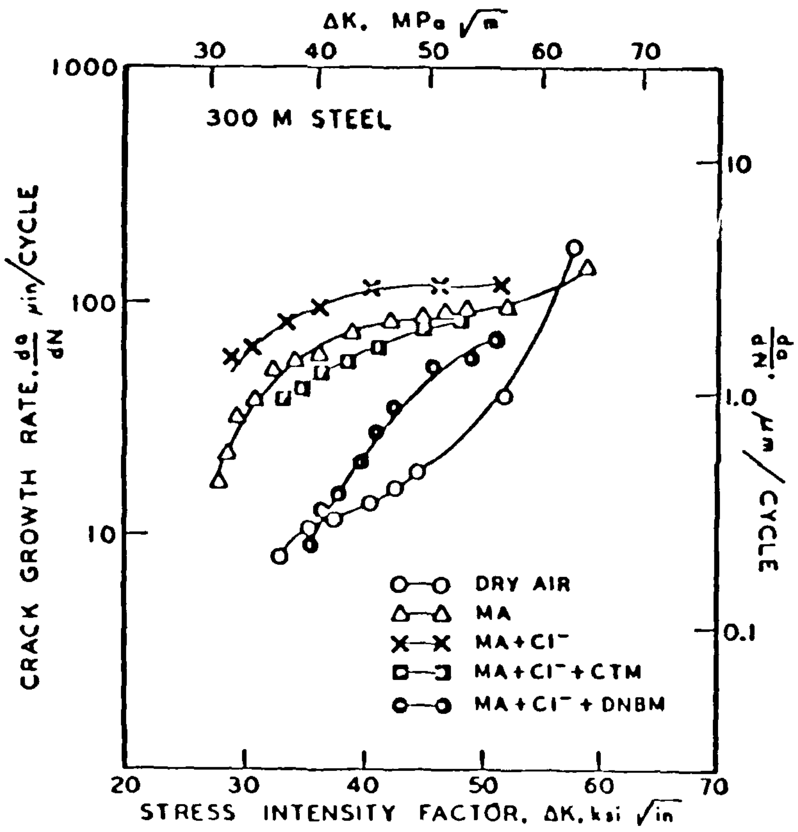


Figure 1. Effect of inhibitors on crack growth rate and stress intensity relationship of 300M steel during corrosion fatigue.

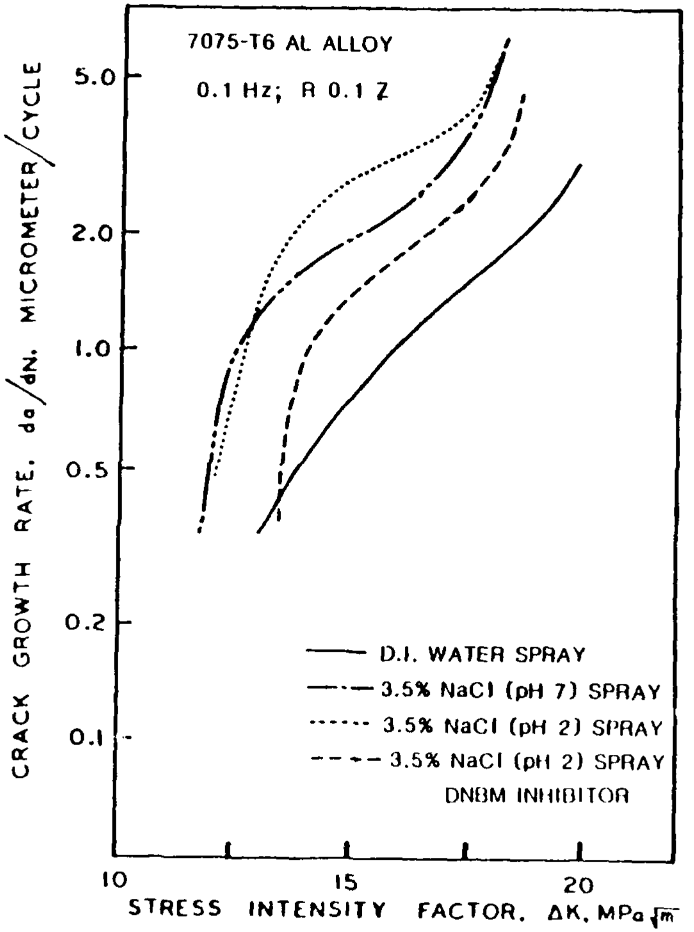


Figure 2. Effect of DNBM on crack growth rate (da/dN) and stress intensity (ΔK) relationship of Al 7075-T6 alloy during corrosion fatigue.

Table III. Effect of Inhibitors on Stress Corrosion Cracking Behavior of Al 7075-T6 Alloy in Chloride-Containing Test Environment

| Inhibitor System Dissolved in Mineral Spirits by Phase Transfer Catalysis | Crack Growth Rate, μm/hr. at 1000 hrs Elapsed (Exposure) Time | Threshold $K_{Iscc}$, MPa $\sqrt{m}$ | Crack Growth** During 2000 hrs. of Exposure, mm |
|---|---|---|---|
| *No Inhibitor, Lab Air (≃50% R.H.) Only | 0.2 | 25 | 2 8 ± 0.5 |
| *No Inhibitor, Moist Air Only | 1.9 | 15 | 6.5 ± 1.5 |
| No Inhibitor | 2.4 | 9 | 18.0 ± 1.7 |
| Dichromate | 1.6 | 12 | 16.5 ± 1.5 |
| Dichromate + Molybdate | 1.8 | 12 | 15.5 ± 1.5 |
| Dichromate + Molybdate + Nitrite | 1.8 | 13 | 14.0 ± 1.0 |
| Dichromate + Nitrite + Borate | 2.0 | 13 | 13.0 ± 2.0 |
| Dichromate + Nitrite + Borate + Molybdate | 0.8 | 17 | 4.0 ± 0.5 |

Results are averages of 2-4 tests with scatter band of approximately 20%. All specimens were pretreated with inhibitor before pre-cracking.

* These tests contained no chloride.

** Measured at the end of 2000 hours exposure.

Corrosion fatigue tests were also performed on 300M steel (1900-2000 MPa strength) which was slightly higher in strength than the 4340. Results show similar behavior as 4340 steel. For brevity, only the results of the best inhibitor combinations are illustrated in Figure 1. The (da/dN) vs. $\Delta K$ plot is typical of the curves obtained. The abbreviations MA, CTM and DNBM stand for moist air, dichromate + tellurate + molybdate and dichromate + nitrite + borate + molybdate respectively indicating the test environment. Typical results of the CF tests for Al 7075-T6 alloy are shown in Figure 2. Here, only the combination DNBM was studied and the test environments were atomized spray with 3.5% NaCl solution at various pH's.

STRESS CORROSION CRACKING (SCC) TESTS

For SCC tests notched double contilever beam (DCB) specimens of Al 7075 alloy were fabricated and tested according to the method described by Hyatt (16). The alloy was tempered to its highest strength (500 MPa) which is also its most susceptible conditon for SCC. For every test the notch area was pre-treated with the desired test environment before pre-cracking. Grain orientation of the specimen was selected so that the plane of crack growth was always longitudinal and the load applied in the short transverse direction. A number of inhibitors were evaluated using these DCB specimens. The details of the procedure for measuring crack growth and calculation of $K_I$, the stress intensity, have been reported elsewhere (15). During the test, specimens are kept in a controlled environmental chamber of moist air. Inhibitors and 3.5% NaCl solution are applied periodically in the notch. After monitoring for over 2000 hours and when no appreciable crack growth was observed the test was stopped. The tested specimens were then split apart by overloading and their fracture surfaces examined. The length of the fracture face due to SCC was measured. Approximately, this is the length of the crack from the line of pre-crack to the line of over-load fracture. In Table III these observations have been reported as 'crack growth during 2000 hours exposure.' Table III also reports the summarized results of the SCC tests in the presence of various inhibitors.

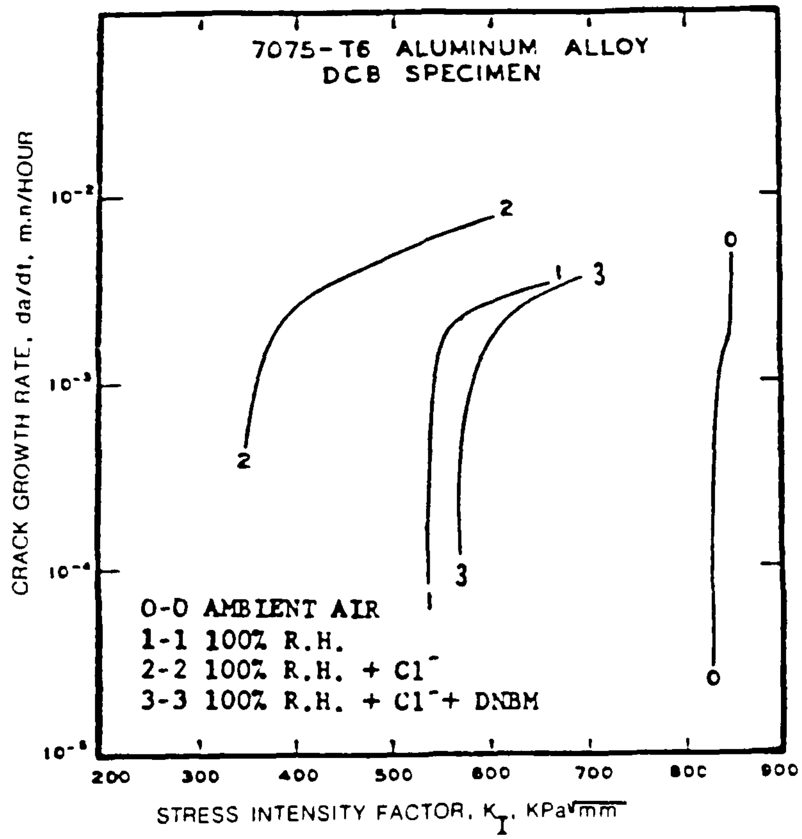


Figure 3. Effect of Combination Inhibitor, DNBM on (da/dt) vs $K_I$ Relationship of Al 7075-T6 Alloy During Corrosion Cracking

The crack growth rate (da/dt) vs. stress intensity ($K_I$) plots are shown in Figure 3 for the best inhibitor combination (DNBM). The SCC threshold value, $K_{ISCC}$, reported in Table III is determined from the above plot (Figure 3). It is the value when the stress intensity becomes almost independent of crack growth rate, the higher $K_{ISCC}$, the higher the resistance to SCC of the material in that test environment.

## ELECTROCHEMICAL POLARIZATION TESTS

To simulate the crack-tip environment for the study of inhibitors, the results of Parrish et al (17) have been used. A one percent solution of sodium chloride at pH 2, suggested as an extreme possible condition, was chosen to simulate the condition in pits or cracks of steel. In non-aqueous systems electrochemical studies of the inhibitors could not be performed due to their high electrolytic resistance (approximately $10^6$ ohms). Thus, aqueous solutions of the inhibitors have been used. Potentiostatic anodic and cathodic polarization measurements were performed according to the ASTM method G3-74. A potential stepping rate of 20 mV/min was used. All polarization measurements were started from the open-circuit or corrosion potential. Test solutions were not deaerated and contained dissolved oxygen (less than 50 ppm). To simulate the active nature of crack tip 1020 steel was chosen instead of more corrosion resistant 4340 steel. It was believed that the inhibitors would perform better on 4340 than 1020 steel. The log I/potential plots of the anodic polarization measurements are shown in Figure 4. Since the effects of inhibitors on the cathodic polarization behavior of 1020 steel were insignificant, they were not plotted. Instead, a Tafel slope (straight line) has been drawn to show a typical cathodic behavior. The anodic plots for both $MoO_4^{--}$ and $MoO_4^{--}$ + $NO_2^-$ solutions (0.01M) show an active-passive behavior with an anodic current density peak at −0.440 volt The passive region for $MoO_4^{--}$ only shows up as a sharp minimum, but in combination with $NO_2^-$ it was extended significantly (up to −0.10 volt) although the corrosion potential still remained at −0.50 volt (curve —●—, Figure 4). At 0.5M concentration of $MoO_4^{--}$ + $NO_2^-$ solution 1020 steel was spontaneously passivated (curve —✕—✕) as its corrosion potential was shifted to −0.1 volt. Results with dichromate were similar to nitrate but when combined with molybdate showed spontaneous passivity (not shown).

## ELECTROCHEMICAL HYDROGREN PERMEATION TESTS

Since changes in the cathodic reactions due to the presence of the inhibitors may reflect kinetics of the hydrogen evolution reaction, it becomes of interest to know their effect on hydrogen permeation through the metal. Thus, an electrochemical hydrogen permeation technique (18) was used to study the effect of inhibitors. Among the inhibitors investigated, sodium dichromate and sodium molybdate were found to significantly inhibit hydrogen entry into the metal. The results are shown as breakthrough times in Table IV. The longer the breakthrough time, the longer the delay in hydrogen diffusing through the metal or the better the efficiency of the inhibitor for hydrogen permeation inhibition.

# DISCUSSION

It is believed that plastic deformation which occurs by the movement of dislocations to the surface (19) is the precursor of the cracking process in metals. Since dislocations in metals may be considered to possess an electric field, the emergence of dislocations to the surface may result in the change of surface charge density, therefore a change in the potential difference across the double layer and in surface tension. According to Rebinder et al (7) the presence of surface active organic molecules on the surface causes metal to soften and thereby affects its mechanical behavior. Thus, reduction of some plasticity at the surface can be interpreted as enhancement of cracking resistance. The use of mineral spirits and incorporation of inorganic inhibitors into the organic complexes provides the proper surface active system which can adsorb readily on the surface. The surface tension measured for the chemicals in mineral spirits give a range of 25

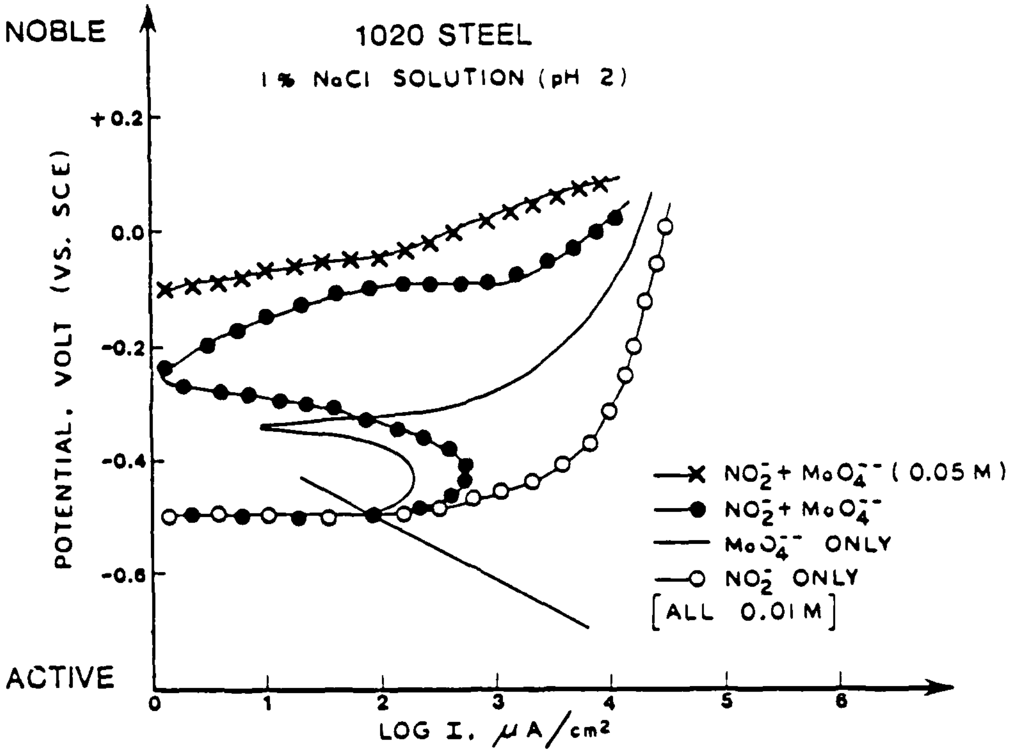


Figure 4. Effect of Inhibitors on Anodic Polarization Behavior of 1020 Steel in 1% NaCl Solution Modified to pH2

to 28 dynes/cm compared to approximately 73 dynes/cm for an aqueous system. In addition to adsorbing specifically, the carrier substance displaces water, thus retarding the ingress of water to the crack-tip. Inhibitors are carried to the crack-tip easily because of the lower surface tension of the solvent system. This was demonstrated by observing that liquid oozed out from the crack tip during compression cycle; whereas without the organic solvent this did not happen.

Table. IV. Effect of Inhibitors on Break-Through Times of Hydrogen in Armco Iron in Alkaline Catholyte

| Inhibitor | Breakthrough Time, seconds At Cathodic Current Density, mA/$cm^2$ | | | |
|---|---|---|---|---|
| | 1.0 | 2.0 | 3.0 | 5.0 |
| None | 36 sec. | 30 sec. | 28 sec. | 27 sec. |
| Sodium Dichromate | 273 | 216 | 201 | 101 |
| Sodium Molybdate | 122 | 43 | 40 | 29 |

A review of results in Table I shows a progressive increase in fatigue life of 4340 steel in moist air due to the inhibitors. The presence of a good passivator (dichromate), a pH modifier (borate) and an oxygen scavenger (nitrate, refs. 10 and 20) changes the crack tip chemistry in a synergistic way such that crack growth rate inhibition is observed. The addition of molybdate to this system (Table I) does not further enhance the CF life of the specimen. However, the results given in Table II show that the dichromate, nitrite and borate (DNB) combination is useless without molybdate when chloride is present. In other words, passivating properties of this system are not adequate to repair the film breakdown due to $Cl^-$. The additon of molybdate (M) to the DNB combination reinforces the passivity, probably by shifting the breakdown potential for pitting to a more noble value. The results with DNBM in Table II show a more than 5-fold increase in CF life of steel; i.e. from 1400 to 6500 cycles and the crack growth rates decrease from 4.0 to 0.8 $\mu$m/cycle. It is also interesting to note that cerate (Table II) functions in the same way as dichromate although not as efficiently. Cerate or Ce (IV) is a less potent oxidizer than Cr (VI) as shown in Table I. The performance of DNBM in even higher strength steel (300M) has been a success as shown in Figure 1. The (da/dN) vs. $\Delta K$ curves show a shift to lower crack growth rates in the presence of inhibitors. Similar observations are also recorded for Al 7075-T6 alloy when DNBM shifts the (da/dN) vs. $\Delta K$ curves to lower values. Neutral aqueous environment in the absence of chloride has virtually no effect on the fatigue properties of aluminum. It is simply because the oxides of aluminum in neutral solutions are very stable and protective. The influence of pH can be appreciated from the results obtained even in the presence of $Cl^-$ (Figure 2). Use of borates alone has also inhibited cracking in aluminum to some extent.

The performance of inhibitors on aluminum alloys has been better demonstrated in SCC tests. Table III reports the results of these tests. Here, the $K_{ISCC}$ values determined for various inhibitors show a progressive increase as more functional inhibitors are combined leading to a higher value of 17 MPa$\sqrt{M}$ for the DNBM combination. The length of crack growth measured after fracture also shows the smallest value, 4.0 mm compared to 18.0 mm during the 2000 hours of test (last column, Table III). As in the CF test of Al 7075-T6, the static test (SCC) also shows very little effect of moisture on SCC resistance, although its properties are a little better in laboratory air. Figure 3 shows the nature of the (da/dt) vs. $K_I$ plot for DNBM (curve 3-3) demonstrating the magnitude of shift compared to curve 2-2. Again, it can be interpreted that the formula DNBM in the organic phase contains almost every possible ingredient which is necessary to alter the chemistry of the advancing crack tip. At least the concept in principle has been shown to work to our advantage.

Electrochemical polarization studies of the various functional compounds in the aqueous medium at pH2 (simulating crack-tip acidity) show that none of the inhibitors can cause spontaneous passivity by themselves even up to 0.01M concentration. The least singular effect is that provided by molybdate (curve ◆—◆ Figure 4), where an active to passive transition behavior is demonstrated. In all cases, only anodic polarization curves are affected by the compounds. Effects of inhibitors are insignificant on cathodic processes.

The combination ($NO_2^-$ + $MoO_4^{--}$) shifts the anodic polarization curves to lower current densities and when their concentrations are increased, the steel becomes spontaneously passive (curve ✱—✱ in Figure 4). Spontaneous passivity is also achieved when dichromate is combined with molybdate (not shown). However, when all four chemicals (DNBM) are mixed together in the aqueous medium, the results are disastrous, the corrosion potential remains very active (−0.580V) and the anodic current density continues to increase even up to 0.00 Volt on the SCE scale. This is a direct indication of the interference among the chemicals when mixed in the aqueous medium and showing non-compatibility. In non-aqueous medium, i.e. in organic solvents, the functional properties of each compound are retained and become effective when required in inhibiting the cracking process.

In addition to the surface tension and electrochemical modifications achieved by the inhibitors, the dichrommate and molybdate also inhibit hydrogen permeation through steel. This is shown as delay in breakthrough times for hydrogen in Table IV. For instance, it takes only 36 secs for hydrogen to pass through a 25.4 µm Armco iron foil when the catholyte is only 0.2 M NaOH and 0.2M NaCN. But when molybdate or dichromate salts are added, the same process takes 122 secs and 273 secs respectively. In other words, the delay in hydrogen absorption means a delay in its embrittling effects on the metal. An evidence of this reduced embrittling effect of dichromate and molybdate has been found in the morphology of the fracture surface. Both the high strength steels and aluminum alloys have shown more retained ductile phase during fractography when these inhibitors are used (15). In their absence, the fracture surface shows intergranular and rock-candy appearance typical of brittle fracture. Other substances like palladates, cerates and lanthanum (II) also inhibit hydrogen absorption in steel; their effects are indirectly seen on enhanced fatigue life of the material.

## CONCLUSIONS

It has been shown that a multicomponent system is necessary to achieve effective retardation of crack growth. Use of inorganic redox chemicals controls the anodic and cathodic reactions, i.e. passivation and hydrogen inhibition, as well as modifying the pH to neutral or near neutral conditions. Use of a phase transfer catalyst has been made to convert redox chemicals into organic complexes. This makes ionic species free of hydration shells. When solubilized in low surface tension organic solvents, surface and active properties of ionic species are enhanced. The multi-functional properties of the so-developed DNBM formulation have been able to increase the corrosion fatigue life of high strength steels (4340 and 300M) as well as the Al 7075-T6 significantly in moist chloride environments. The formula has also been shown to inhibit stress corrosion cracking of Al 7075-T6. Generally it has been concluded that in-situ control of crack growth factors will inhibit cracking whether the stress conditions are static or dynamic.

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