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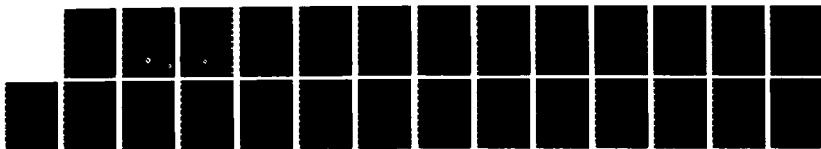
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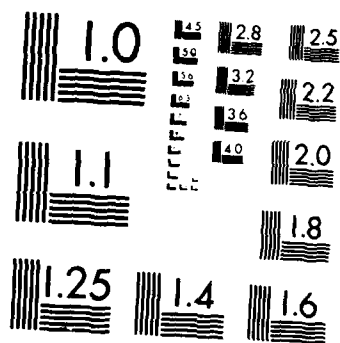
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FORCES SHIPS' AIR CONDITIONING
HYDRONIC WATER SYSTEMS

C. M. Hanham - D. E. Veinot
R. M. Armstrong - C. A. Shaw

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ABSTRACT

The air conditioning system on Canadian Forces Ships, utilizes air conditioning plants that supply hydronic water, and a network of pipes, fittings and pumps that distribute the water to fan coil units throughout the ship. Hydronic water is a 90:10 mixture of fresh water and ethylene glycol which is chilled to 4.4°C by the air conditioning plants, and used for cooling, or heated to 60°C by hot water converters, and used for heating. A hydronic water system is designed to be fabricated from copper or copper alloy components in order to minimize corrosion. As a result of an investigation of the plugging of hydronic system strainers and small orifices with hydrated iron oxide, which resulted in a reduction of the effectiveness of the air conditioning system, some parts of the system have been found to be fabricated from mild steel. Corrosion of steel parts produces hydrated iron oxide deposits and sludges, and additional corrosion control of these parts in either oxygen rich or oxygen deficient hydronic water environments is necessary.

This report describes the results of some corrosion rate measurements that were conducted using the polarization resistance technique, to evaluate the effectiveness of various chemical inhibitor combinations and concentrations for corrosion control of steel components in oxygen rich and oxygen deficient hydronic water.

SOMMAIRE

À bord des navires des Forces canadiennes, le conditionnement de l'air est assuré par des groupes à eau comprenant un réseau de tuyauterie, des accessoires et des pompes faisant circuler l'eau jusqu'à des ventilo-convecteurs dans tout le navire. La solution utilisée est un mélange 90:10 d'eau douce et d'éthylène-glycol qui est soit refroidi à 4.4°C par les groupes de climatisation et utilisé pour le refroidissement, soit chauffé à 60°C par des chauffe-eau à vapeur pour le chauffage. Les groupes de climatisation à eau sont conçus pour être construits en éléments de cuivre ou d'alliages de cuivre afin de réduire la corrosion au minimum. Lors d'une inspection à la suite de l'obturation des crépines et petits orifices par de l'oxyde de fer hydraté, ce qui causait une perte de rendement, on a découvert que certaines pièces étaient en acier doux. La corrosion des pièces en acier produit des boues et des dépôts d'oxyde de fer hydraté et il faut prévoir une protection supplémentaire contre la corrosion de ces pièces lorsqu'elles sont exposées à de l'eau riche ou pauvre en oxygène.

Ce rapport décrit les résultats de certaines mesures du taux de corrosion prises grâce à la technique de la résistance de polarisation dans le but d'évaluer l'efficacité de différentes combinaisons et concentrations d'inhibiteurs chimiques comme moyens de limiter la corrosion de pièces en acier dans de l'eau soit riche, soit pauvre en oxygène.

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1. INTRODUCTION

The hydronic water system on a Canadian Forces ship carries a mixture of fresh water and ethylene glycol. It has an important role in the supply and distribution of coolant for the exchange of heat to air conditioning fan coil units, converters and condensers. It is defined as a closed recirculating system because the cooling water is retained in the system and heat is given up via heat exchangers.

The hydronic water system was designed to be fabricated from copper base alloys. It was expected that because this system theoretically requires very little makeup water, corrosion should be minimal. Makeup water replacing even minute losses due to evaporation, leaks and overflows, however, can introduce dissolved solids to the system if high quality makeup water is not used¹. The system is therefore not as resistant to corrosion as its designer intended it to be because dissolved solids increase the conductivity of the water, thus favoring increased corrosion². Inhibitors were therefore added in order to prevent corrosion and blockage of coolant passages by corrosion products, and to maintain heat transfer efficiency by keeping metal surfaces free from adherent corrosion products.

Filters, orifices, and small valves in the DDH 280 Class hydronic water system are susceptible to clogging by solids. Examination and analysis of these solids show them to be iron oxide. Makeup water introduces some dissolved solids into the system but this cannot be responsible for the total extent of the solids which cause the clogging problems. Further investigation of the system has revealed the presence of at least three cast steel converter end bells with which the hydronic water comes into direct contact. These end bells show evidence of excessive pitting corrosion attack. It has been shown, therefore, that the system is not fabricated entirely from copper base alloys and that the solids problem is due to the corrosion of ferrous alloy components in the system.

The inhibitor package presently used in the DDH 280 Class hydronic water system is contained in the ethylene glycol itself, which until only recently have been commercial ethylene glycol mixtures more commonly known as automotive antifreeze. Inhibitor additions are therefore only made when the ethylene glycol level in the hydronic water becomes low and the system is replenished with "antifreeze". Tests for the actual inhibitor concentration are not made and, therefore, the rate at which the inhibitor is consumed is unknown. It has been suggested that uninhibited ethylene glycol be added to the hydronic water and that an inhibitor package be added and maintained separately. This would ensure that sufficient concentrations of inhibitor would be present to protect both the copper and steel hydronic water system components from corrosion. The accumulation of solids in the hydronic water system, which are responsible for the time consuming maintenance of filters and small valves, would be reduced, resulting in less down time in these systems.

A specific inhibitor package, CSW311, was recommended for the DDH 280 Class ships' hydronic water system by Specialty Chemicals Limited after the hydronic water and the corrosion products (deposits) found in the hydronic water system were analyzed. The recommended package contains three chemicals: sodium nitrite, borax decahydrate and mercaptobenzothiazole (MBT). It is marketed in a concentrated aqueous solution form. The new inhibitor package was recommended on the basis of its nitrite ion content. It was suggested that the nitrite ion concentration be maintained at 1200-1500 ppm in order to ensure adequate protection. CSW311 was designed to be used as a corrosion inhibitor in closed hot water, chilled water, or diesel cooling water systems. It inhibits corrosion of both ferrous and non-ferrous metals and is compatible with all common antifreeze solutions (ethylene glycol and alcohols). It has been suggested, however, that CSW311 should not be added to a phosphate ion inhibited ethylene glycol because of the incompatibility of the chemicals at higher concentrations. The presence of phosphate ion in the hydronic water from the prior use of inhibited antifreeze might interfere with the use of a new inhibitor package and if this were the case, hydronic water systems would have to be thoroughly drained and flushed prior to employing the CSW311 inhibitor system.

There is a long history of the effective use of inhibitors for the prevention of corrosion in cooling systems where a mixture of ethylene glycol and water is used as the coolant. The approach has been to incorporate inhibitors in antifreeze to ensure their addition to cooling systems. The ethylene glycol in the DDH 280 Class hydronic water system, for example, contains phosphate ion. Phosphate ion increases the reserve alkalinity and also has a buffering action. Phosphate ion is nonoxidizing however, and therefore requires the presence of oxygen in order to passivate steel³.

Many chemicals have been investigated for their inhibitive properties in engine coolants. Some of the commonly used chemicals include nitrites, nitrates, phosphates, borates, silicates, arsenates, chromates, amines, benzoates, mercaptans, organic phosphates, and polar or emulsifiable oils⁴. The three most common types of corrosion inhibitors used for closed cooling water systems are the chromate base inhibitors, the nitrite ion base inhibitors and the soluble oil inhibitors⁵. Ethylene glycol antifreezes and chromate base treatments are not compatible⁶. Soluble oil inhibitors, although being good corrosion inhibitors, pose other problems such as fouling, interference with heat transfer and degradation of natural rubber hoses and gaskets. Nitrite ion, on the other hand, is a suitable inhibitor for iron and steel when the pH value is maintained in the alkaline range. This treatment also has the advantage of being compatible with antifreeze solutions⁶.

CSW311, besides containing nitrite ion, also contains mercaptobenzothiazole (MBT) and borate ion from borax decahydrate. MBT must be used in combination with nitrite ion to give protection to copper and its alloys in the same system. It is again necessary to maintain the pH on the

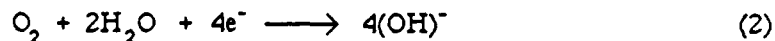
alkaline side. The principal function of borate ion is to provide reserve alkalinity and buffering action against acids; in other words, to maintain the pH in the alkaline range. Borate ion's inhibitive quality is its reinforcement of the effects of other inhibitors. Borate ion is also nonoxidizing and therefore makes conditions more favourable for the adsorption of oxygen⁶. Nitrite ion, on the other hand, is oxidizing and can passivate steel even in the absence of oxygen³.

Nitrite ion, from sodium nitrite, borate ion, from borax decahydrate, and phosphate ion act as anodic polarizers on steel in ethylene glycol/water solutions. An anodic polarizer or inhibitor is one that restrains an anodic corrosion reaction such as



These types of inhibitors which are also called passivating inhibitors, increase the polarization of the anode and cause the corrosion potential to shift to a more passive potential³. If insufficient amounts of anodic inhibitors are used, corrosion can be severely localized in the form of pitting. Nitrites are sometimes regarded as reducing agents. They do, however, possess oxidizing properties and tend to render metal surfaces passive to corrosive attack in weakly alkaline solutions. They do not render iron passive in acid solutions.

Mercaptobenzothiazole (MBT), on the other hand, acts as a cathodic polarizer. A cathodic polarizer or inhibitor restrains a cathodic corrosion reaction such as



by acting as a diffusion barrier layer. These types of inhibitors increase the polarization of the cathode, therefore reducing the rate of the cathodic reaction³. The cathodic reaction in an acidic solution would be the reduction of hydrogen ions to hydrogen gas. The reduction of oxygen, as in equation (2) above, is another cathodic reaction. Treatments which form an adherent coating on the metal surface, such as MBT, function as cathodic inhibitors. An ideal inhibitor would develop a dense protective coating of minimum thickness which would deposit evenly at both hot and cold sections of the system.

The purpose of inhibitor testing is to determine the effectiveness of an inhibitor in slowing down a corrosion process. In order to study the effects of inhibitors on corrosion, the corrosion process must be taking place. It is impossible to separate the inhibitor test from the corrosion test. Since many variables affect corrosion processes, the designs of available inhibitor tests are also numerous. The properties and performance of an inhibitor may be measured under relatively controlled conditions in a laboratory and under realistic, but usually more difficult, conditions in the field.

A corrosion inhibitor prevents attack by the formation of a barrier on the surface of a metal⁷. This barrier may interfere with either the anodic or the cathodic process occurring at the metal/solution interface. The measurement of the effect of an inhibitor on corrosion rate is a measure of the integrity of the barrier formed on the metal surface. The surface of the metal must be clean and uniform so that reproducible corrosion results may be obtained. This is necessary even though the condition of the metal surface may not be typical of metals exposed under field conditions.

Indirect methods of corrosion rate measurement which involve aspects of the electrochemical process, utilize current-potential relationships such as polarization curves. Polarization data will indicate the relative efficiency with which inhibitors control corrosion reactions. Anodic inhibitors control the anodic reactions while cathodic inhibitors control the cathodic reactions. Inhibitors under mixed control, control both the anodic and the cathodic reactions. In controlling these reactions, they reduce the corrosion current density, i_{corr} , which is directly proportional to the corrosion rate. Parameters, such as corrosion current density, can be determined from polarization data and used to determine corrosion rates and inhibitor performance.

Simulating actual field conditions is always difficult. The corrosion current densities or corrosion rates determined from accelerated electrochemical corrosion tests cannot be expected to be the same as those under field conditions. It is assumed⁷, however, that the same corrosion mechanisms are taking place, and that if an inhibitor is effective under accelerated conditions, it will also be effective under actual field conditions.

2. EXPERIMENTAL PROCEDURE

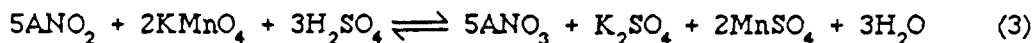
2.1 INHIBITOR ANALYSIS

Specialty Chemicals Limited CSW311 is a concentrated aqueous solution containing sodium nitrite, sodium borate decahydrate and mercaptobenzothiazole (MBT). It is designed for use in diesel engine cooling water systems. In order to be an effective corrosion inhibitor, the concentrations of the inhibiting ions in the cooling water must be maintained within certain limits and maintainers must therefore have an accurate means to monitor the necessary concentrations. Specialty Chemicals Limited have specified that for the most effective protection, the nitrite ion content in the cooling water should be maintained between 1200 and 1500 parts per million (ppm) and a field monitoring kit, The La Motte Chemicals Nitrite Test Kit is marketed by the company for this purpose. The analytical work described below was conducted in order to evaluate this test kit for use on hydronic water solutions. Additionally, in order to provide guidance on the quantities of CSW311 needed for hydronic systems, analytical procedures for determining

the concentrations of nitrite and borate ions in the CSW311 were established.

2.2 NITRITE ION ANALYSIS

Two methods were evaluated for the analysis of nitrite ion in aqueous solutions containing 10% ethylene glycol. The first of these methods was a wet chemical titrimetric procedure. This procedure involves the reaction between nitrite ion in the solution with potassium permanganate in sulfuric acid as describe by the following chemical reaction:



where A = hydrogen, sodium, potassium or any other cation.

2.2.1 Reagents Required

The procedure requires standardized 0.20N sodium oxalate, and standardized 0.20N potassium permanganate. Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) is a primary standard and the 0.20N standard solution was prepared by dissolving 13.4 grams of sodium oxalate in 1 litre of distilled water. This primary standard solution was then used to standardize the potassium permanganate (KMnO_4) solution. The KMnO_4 solution was prepared by dissolving 6.322 grams of KMnO_4 in 500 ml of distilled water. The solution was heated at 80°C for 1 hour and allowed to cool to room temperature for 12 hours, then filtered through glass wool to remove any colloidal manganese dioxide (MnO_2) and diluted to 1 litre with distilled water. The primary sodium oxalate standard was then used to standardize the resulting KMnO_4 solution.

2.2.2 Procedure For Nitrite Ion Determination

25 ml of the standardized KMnO_4 solution was pipetted into a 250 ml erlenmeyer flask and acidified with 10 ml of dilute (1:4) sulfuric acid. 20 ml of the solution to be tested was then added using a pipette and the resulting solution was heated to 80°C and 25 ml more of the dilute sulfuric acid was added. A colourless solution at this point indicated that either more potassium permanganate solution or less unknown solution was required. A deep purple colour at this stage indicated that excess potassium permanganate solution had been added. This excess was titrated with the 0.20N sodium oxalate solution until the purple colour was destroyed and then approximately 5 ml more of the oxalate solution was added to ensure that all the potassium permanganate was consumed. The exact excess of oxalate solution was determined by back titration with the standardized 0.20N KMnO_4 . The total quantity of KMnO_4 used minus the oxalate used equals the quantity

of KMnO_4 consumed by the total nitrite ion in the unknown. Using these solutions, then, 1 ml of KMnO_4 solution equals 4.6 milligrams of nitrite ion and 1 milligram nitrite ion per litre equals 1 ppm nitrite ion concentration.

This method is known to be accurate when no other oxidizable constituents are contained in the test solution. However, since the solution contains ethylene glycol, which may interfere with the procedure, another method which utilized the ultraviolet (UV) absorption of nitrite ion was developed. Nitrite ion in distilled water containing 10% ethylene glycol was found to absorb UV radiation at 211 nanometers (nm). This UV absorbance was found to vary linearly with nitrite ion concentration up to 20 ppm and other components of the solution, ie. ethylene glycol, borate ion, etc., did not interfere with the measurement of nitrite ion. A calibration curve of UV absorbance at 211 nm versus nitrite ion concentration was prepared and unknown solutions were diluted as required so that the UV absorbance from these solutions was within the limits of the calibration curve.

2.2.3 Evaluation of Nitrite Ion Test Kit

Three solutions of 10% ethylene glycol in distilled water containing known nitrite ion concentrations were prepared and these solutions were analyzed using the UV method and the La Motte Chemicals Test Kit. The results are shown in Table I. The results indicate that either method provides an acceptable measure of nitrite ion content. Therefore, the test kit should be useful for monitoring nitrite ion content in hydronic water solutions in field situations.

2.3 BORATE ION ANALYSIS

The total concentration of borate ion ($\text{B}_4\text{O}_7^{2-}$) in hydronic water solutions was measured by determining elemental boron content in solution by flame (nitrous oxide/acetylene) atomic absorption at an analytical wavelength of 249.7 nm. The method has an analytical sensitivity of approximately 10 ppm for boron and absorbance was linear with concentration up to approximately 500 ppm boron. The borate ion content in ppm was obtained by multiplying the boron content in ppm by a factor of 3.59 which is obtained by dividing the molecular weight of borate ion by the molecular weight of boron,

$$\text{ie. } \frac{155.23}{43.24} = 3.59 \quad (4)$$

2.4 ANALYSIS OF CSW311 CONCENTRATE

The concentration of nitrite ion in the concentrated CSW311 product was determined using both the titrimetric and ultraviolet absorption procedures described above and was found to be 152,000 ppm by both procedures. The concentration of borate ion in the CSW311 concentrate was found to be 10,800 ppm. Therefore, in order to obtain a nitrite ion concentration of 1500 ppm, approximately a one hundred fold dilution of the concentrate would be required. That is, for each 100 gallons of hydronic water, 1 gallon of CSW311 would be required to provide a nitrite ion concentration of at least 1500 ppm. This dilution of CSW311 would result in a borate ion concentration of approximately 100 ppm.

2.5 CORROSION RATE MEASUREMENTS

The copper and mild steel samples required for this inhibitor evaluation study were sectioned and machined from bar stock with compositions similar to UNS C10200 and UNS G10100 respectively, to a length of 2.1 cm and a diameter of 1.5 cm. One end of each sample was drilled and tapped for 3-48 N.C. threads to accommodate an electrode holder. Within one hour prior to immersion in a test solution, the sample was polished with 400, followed by 600, grit silicon carbide paper, washed with tap water, degreased in boiling toluene for five minutes, and then rinsed with distilled water.

The test solution was prepared with distilled water and ethylene glycol (Anachemia AC-4242) to a concentration of 10% by volume. The effects of nitrite ion additions and borate ion additions were studied independently by adding required amounts of reagent grade sodium nitrite (NaNO_2) and sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) respectively. The effect of their combined corrosion inhibiting effectiveness was studied by adding CSW311. The effect of residual phosphate ion on the inhibiting power of CSW311 was studied by adding required amounts of reagent grade sodium phosphate (NaH_2PO_4) to produce 100, 200 and 400 ppm phosphate ion (PO_4^{-3}) concentrations in a solution containing CSW311 at the manufacturer's recommended concentration of 1500 ppm nitrite ion. The corrosion cell containing the electrolyte was maintained at 25°C in a Haake Model F3-K water bath.

The inhibitor evaluations were carried out in both aerated and deaerated solutions. An aerated or deaerated condition was obtained by purging the electrolyte for one hour prior to and one hour after immersing the mild steel sample with zero zero grade air or nitrogen respectively. The purge was terminated for one hour prior to and also during the polarization experiment.

The polarization resistance experiments were conducted in an EG&G

Princeton Applied Research (PAR) Model K47 Corrosion Cell which accommodates two high-density graphite counter electrodes, a working electrode (mild steel sample), a reference electrode bridge tube (Luggin probe) with a fitted saturated calomel (mercury-mercurous chloride) reference electrode, and a gas inlet/outlet purge tube. The experiments were monitored and the polarization resistance data collected by a microprocessor-controlled EG&G PAR Model 350 Corrosion Measurement System⁸.

The experimental procedure used for the polarization resistance experiments was a modification of the ASTM-G5 standard⁹. After measuring the exposed surface area of the sample in order to convert the current measurements to current density measurements, the sample was immersed in the electrolyte and the reference electrode bridge tube tip was placed within 5 mm of the sample surface. After an additional hour of gas purging, the gas purge was terminated and the sample was allowed to come to equilibrium for one hour.

The potentiodynamic scan was started at 25 mV cathodic to the sample's corrosion potential, which was measured at the end of its one hour equilibrium period, and continued at a scan rate of 0.167 mV/sec. The current required to maintain the sample at its controlled potentials was measured every 0.5 mV throughout the linear scan. The 50 mV scan was completed at 25 mV anodic to the sample's equilibrium corrosion potential.

At the completion of each experiment the data were stored on digital tape by the EG&G PAR Model 355 Tape Storage Module and then transferred through the EG&G PAR Model 350 Corrosion Measurement System to the DREA DEC 20 computer through the use of a Fortran program, <Staal>C11A20¹⁰. The polarization resistance data were analyzed by the method of nonlinear least squares using a Pascal computer program, CORROS¹¹.

CORROS simultaneously calculates the corrosion potential, the anodic and cathodic Tafel constants, the polarization resistance and the corrosion current density from polarization resistance data obtained from the mixed potential region around the corrosion potential. The program's basic routine is a nonlinear least squares fit of the data. The output includes the corrosion parameters, their standard deviations, and the relative root mean squared error of the fitted data.

Replicate experiments were conducted for each set of solution conditions to enable calculation of mean corrosion current densities and standard deviations.

3. RESULTS

The results of the tests carried out on the copper sample are not reported here because the corrosion rates measured were inseparably low in

both uninhibited and inhibited solutions of 10% ethylene glycol in water.

The mean corrosion current densities and standard deviations for mild steel in aerated and deaerated solutions are listed in Tables II and III respectively. The effect of inhibitor concentration on mild steel in both aerated and deaerated solutions of 10% by volume ethylene glycol in distilled water are shown in Figures 1 and 2 respectively.

Figure 1 shows that the corrosion current density of mild steel in the aerated solution was reduced by additions of borate ion, by additions of nitrite ion and especially by additions of CSW311 which contains both borate and nitrite ions. The corrosion current density of mild steel in an aerated solution containing CSW311 at the manufacturer's recommended concentration of 1500 ppm nitrite ion, was at a minimum and higher concentrations showed no further decrease in corrosion current density. These results show that the combined effect of nitrite ion and borate ion in the same solution, as is the case with a solution of CSW311, provided the lowest corrosion current density which would indicate that such a solution would provide the most effective corrosion prevention.

Figure 2 shows that the corrosion current density of mild steel in the deaerated solutions was also reduced by additions of both borate and nitrite ions, and again to minimum values by the addition of CSW311. The corrosion current density of mild steel in deaerated, uninhibited solutions is very high (41.28 nA/cm^2) in comparison with that in deaerated solutions inhibited with either borate ion or CSW311 which contains both borate and nitrite ions. Treatment with nitrite ion alone was expected to provide better corrosion prevention than the results would indicate and this could be associated with the lack of alkalinity in these solutions. Alkalinity is provided by borate ion and appears to be the surest way to reduce corrosion in deaerated solutions.

The effect of residual phosphate ion concentration on the inhibiting power of CSW311 at the manufacturers's recommended concentration is shown in Figure 3. It was found that phosphate ion concentrations up to 400 ppm did not significantly increase the corrosion current density of mild steel in either aerated or deaerated solutions. It should be noted that the corrosion current densities observed in this part of the study range from a maximum of 4.89 nA/cm^2 for 400 ppm PO_4^{-3} in aerated solutions of CSW311 (1500 ppm NO_2^-) to a minimum of 1.23 nA/cm^2 for 400 ppm PO_4^{-3} in deaerated solutions of CSW311 (1500 ppm NO_2^-). These values are in the same range as the corrosion current density for inhibited solutions containing no PO_4^{-3} (ie. 1 to 5 nA/cm^2).

4. DISCUSSION

The corrosion current density measurements indicate that CSW311 is indeed an effective corrosion inhibitor for mild steel in both aerated and deaerated distilled water solutions containing 10% by volume ethylene glycol. The results show that CSW311 is consistently more effective than the nitrite ion alone, in both the aerated and deaerated solutions. This indicates that borate ion must be present in order for nitrite ion to be an effective inhibitor. The results also show that CSW311 is significantly more effective than the borate ion alone in the aerated solution. The measurements show, however, that the borate ion alone is as effective in inhibiting corrosion in the deaerated solution as the CSW311. This suggests that borate ion is able to provide an independent anodic inhibiting action in the deaerated solution but not in the aerated solution.

It should be stressed that the corrosion current densities reported here are those associated with a freshly polished metal surface which has been exposed to a clean environment for a relatively short period of time. These values would increase if the environment was made more corrosive by the addition of common salts found in hard water². An inhibitor will still effectively reduce the corrosion current density of mild steel, even in corrosive water. If a corroded or unclean metal surface was exposed to the inhibited environment, its corrosion current density would again be effectively reduced.

Corrosion current density measurements made after a metal sample has been exposed for a longer period of time are predictably lower than those after a one or two hour exposure. Most exposed metal surfaces form protective films of corrosion products which reduce the corrosion current density. The corrosion products on some metals in certain environments would be unstable and nonadherent. It is predicted, however, that CSW311 would effectively reduce the formation of corrosion products. In doing so, the accumulation of iron oxide deposits in the DDH 280 Class ships' hydronic water system would also be reduced.

The manufacturer's recommended concentration of 1500 ppm nitrite ion appears to be a sufficiently safe concentration in order to maintain an inhibited aerated environment. A reduction to 500 ppm nitrite ion would result in corrosion current densities only half those in an uninhibited environment. CSW311 is effective over a broader range of concentrations in deaerated solutions. It is as effective at 350 ppm nitrite ion as it is at 1500 ppm nitrite ion when there is no oxygen present. CSW311 concentrations higher than those recommended are not dangerous but are also unnecessary.

The presence of residual phosphate ion up to concentrations of 400 ppm does not significantly reduce the effectiveness of CSW311 as an inhibitor for mild steel.

If all of the mild steel components were removed from the DDH 280

Class ships' hydronic system and high quality makeup water was continuously used, an inhibitor package would not be necessary. Copper base alloys, of which the entire system should be fabricated, will not corrode in relatively clean solutions of 10% by volume ethylene glycol in water unless the ethylene glycol has broken down because of extended use.

5. CONCLUSIONS

Polarization resistance measurements resulting in corrosion current density measurements have shown that CSW311 is an effective corrosion inhibitor for mild steel in both aerated and deaerated solutions of 10% ethylene glycol in distilled water.

Table I Nitrite ion analysis

Nitrite Ion Concentration (ppm) Prepared	Nitrite Ion Concentration (ppm) UV Method	Nitrite Ion Concentration (ppm) Test Kit
314 628 1257	316 645 1290	300 560 1200

Table II Corrosion current density measurements for mild steel
in aerated ethylene glycol solutions

<u>Inhibitor</u>	<u>Conc.</u> <u>ppm</u>	<u>I_{corr}</u> <u>(nA/cm²)</u>
none	0	62.55 ± 12.88
NO ₂ ⁻ from	500	23.19 ± 4.90
CSW311	1500	4.21 ± 1.62
	2500	3.96 ± 0.35
NO ₂ ⁻ from	500	23.26 ± 6.48
NaNO ₂	1500	36.89 ± 2.45
	2500	43.15 ± 3.77
B ₄ O ₇ ⁻² from	300	35.42 ± 0.71
Na ₂ B ₄ O ₇	600	47.15 ± 0.95
	1000	35.84 ± 2.76
PO ₄ ⁻³	100	1.26 ± 0.20
+ 1500 ppm	200	3.37 ± 0.95
NO ₂ ⁻ from	400	4.89 ± 0.51
CSW311		

NO₂⁻ = nitrite ion
B₄O₇⁻² = borate ion
PO₄⁻³ = phosphate ion

Table III

Corrosion current density measurements for mild steel
in deaerated ethylene glycol solutions

<u>Inhibitor</u>	<u>Conc.</u> <u>ppm</u>	<u>I_{corr}</u> <u>(nA/cm²)</u>
none	0	41.28 ± 6.89
NO ₂ ⁻ from	333	2.73 ± 0.35
CSW311	1000	3.23 ± 0.70
	1667	2.27 ± 0.55
	2500	2.32 ± 0.30
NO ₂ ⁻ from	500	21.86 ± 4.14
NaNO ₂	1500	31.06 ± 1.17
	2500	21.22 ± 1.36
B ₄ O ₇ ⁻² from	300	4.96 ± 0.27
Na ₂ B ₄ O ₇	600	2.57 ± 0.44
	1000	2.77 ± 0.14
PO ₄ ⁻³	100	2.76 ± 0.01
+ 1500 ppm	200	2.03 ± 0.14
NO ₂ ⁻ from	400	1.23 ± 0.13
CSW311		

NO₂⁻ = nitrite ion
 B₄O₇⁻² = borate ion
 PO₄⁻³ = phosphate ion

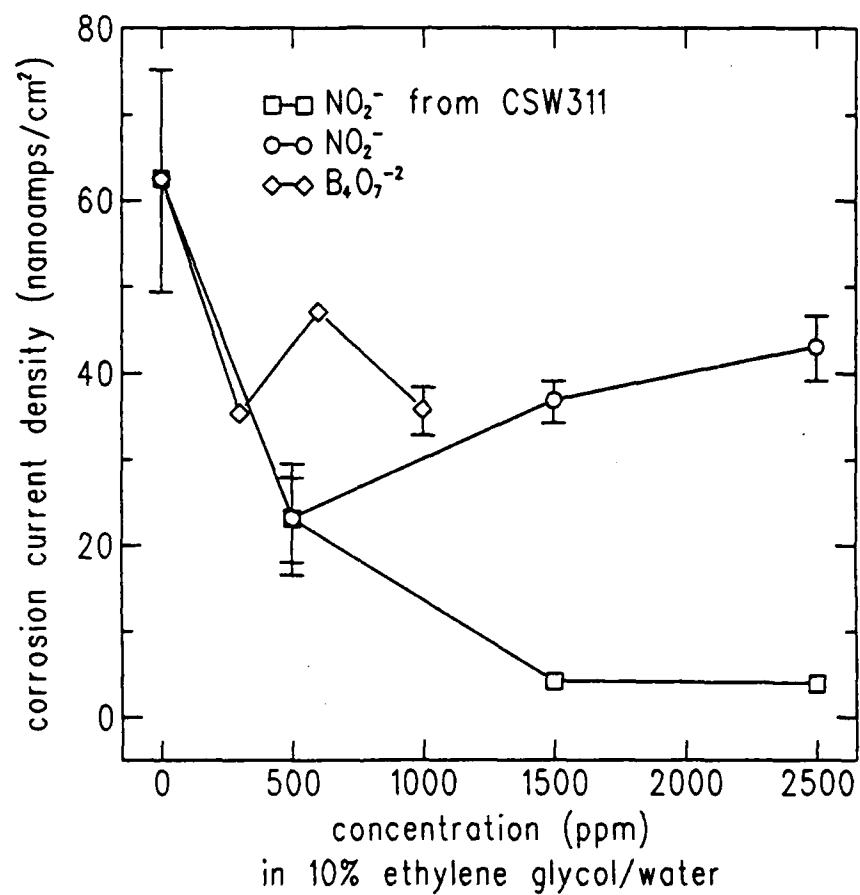


Figure 1 Effect of inhibitor concentration on corrosion current density of mild steel in aerated solutions of 10% ethylene glycol in water

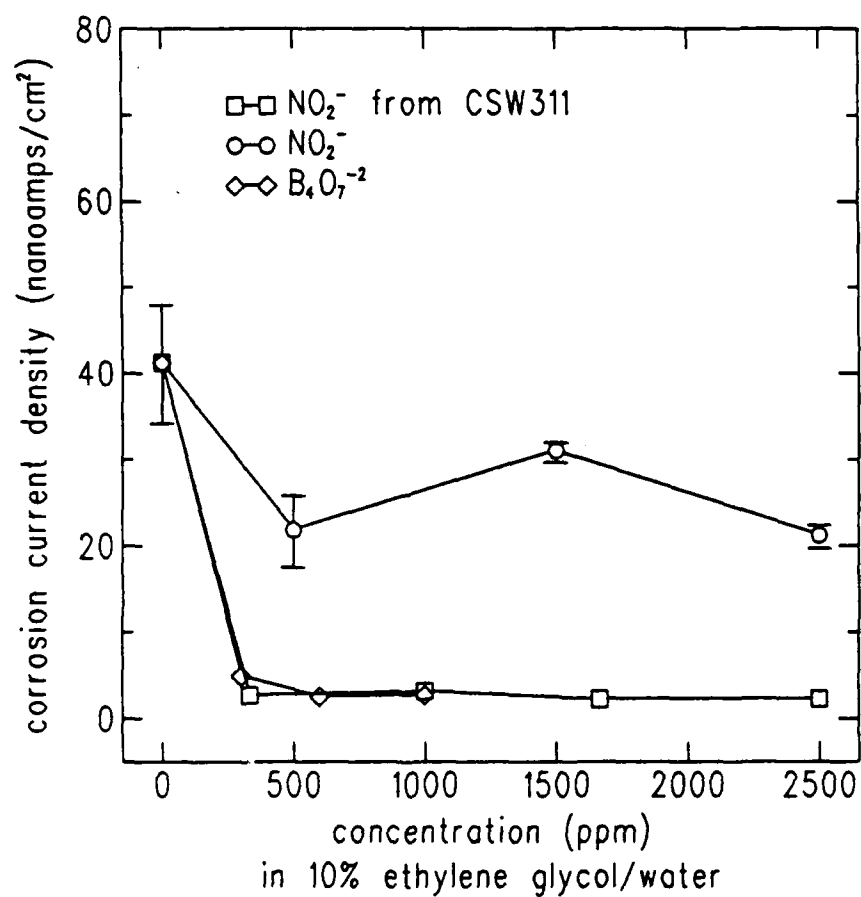


Figure 2 Effect of inhibitor concentration on corrosion current density of mild steel in deaerated solutions of 10% ethylene glycol in water

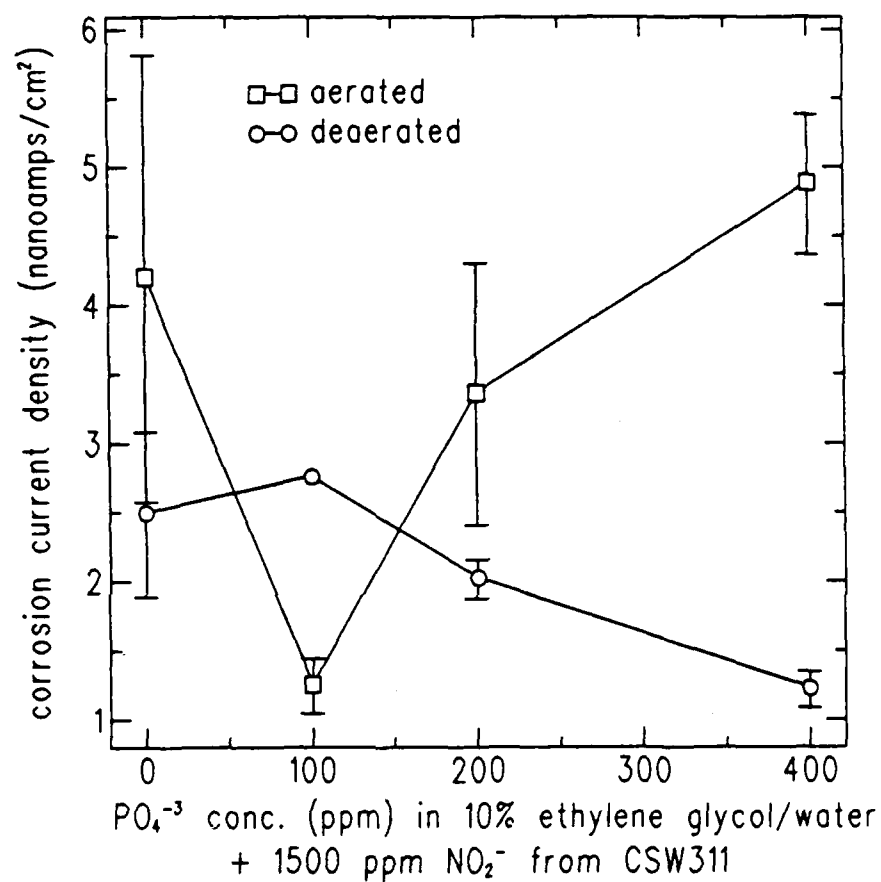


Figure 3 Effect of residual phosphate ion concentration on corrosion current density of mild steel in aerated and deaerated solutions of CSW311 providing 1500 ppm nitrite ion in a solution of 10% ethylene glycol in water

REFERENCES

1. Kemmer, F.N., "The NALCO Water Handbook", McGraw-Hill Book Company, New York, p. 38-8, 1979.
2. Betz Laboratories, "Betz Handbook of Industrial Water Conditioning", 6th Edition, Betz, Trevose, Pennsylvania, p. 238, 1962.
3. "Corrosion Basics, An Introduction", National Association of Corrosion Engineers, Houston, Texas, p. 127, 1984.
4. Howe, L.C., "Application of Inhibitors in Automobiles and Their Environment", Corrosion Inhibitors, edited by C.C. Nathan, National Association of Corrosion Engineers, Houston, Texas, p. 173, 1973.
5. Betz Laboratories, "Betz Handbook of Industrial Water Conditioning", 6th Edition, Betz, Trevose, Pennsylvania, p. 259, 1962.
6. Uhlig, H.H., "Corrosion and Corrosion Control", John Wiley & Sons, Inc., New York, p. 257, 1971.
7. Schaschl, E., "Methods of Evaluation and Testing of Corrosion Inhibitors", Corrosion Inhibitors, edited by C.C. Nathan, National Association of Corrosion Engineers, Houston, Texas, p. 28, 1973.
8. Peterson, W.M. and Siegeman, Howard, "A Microprocessor-Based Corrosion Measurement Sytem", Electrochemical Corrosion Testing, ASTM STP 727, Florian Mansfeld and Ugo Bertocci, editors, American Society for Testing and Materials, p. 390, 1981.
9. 1983 Annual Book of ASTM Standards, Section 3: Metals Test Methods and Analytical Procedures, Volume 03.02: Metal Corrosion, Erosion, and Wear, G5-82, American Society for Testing and Materials, Philadelphia, PA., p. 122, 1983.
10. Staal, P.R., Defence Research Establishment Atlantic, informal communication.
11. Hanham, C.M. and Gallagher, P.J., "CORROS: A Computer Program for Analyzing Polarization Resistance Data", Defence Research Establishment Atlantic Technical Communication 86/303, April 1986.

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13. ABSTRACT The air conditioning system on Canadian Forces Ships utilizes air conditioning plants that produce hydronic water and a network of pipes, fittings and pumps that distribute the water to fan coil units throughout the ship. Hydronic water is a 90:10 mixture of fresh water and ethylene glycol which is chilled to 4.4°C by the air conditioning plants and used for cooling, or heated to 60°C by hot water converters and used for heating. A hydronic water system is designed to be fabricated from copper or copper alloy components in order to minimize corrosion. As a result of an investigation of the plugging of hydronic system strainers and small orifices with hydrated iron oxide, which resulted in a reduction of the effectiveness of the air conditioning system, some parts of the system have been found to be fabricated from mild steel. Corrosion of steel parts produces hydrated iron oxide deposits and sludges, and additional corrosion control of these parts in either oxygen rich or oxygen deficient hydronic water environments is necessary. This report describes the results of some corrosion rate measurements that were conducted using the polarization resistance technique, to evaluate the effectiveness of various chemical inhibitor combinations and concentrations for corrosion control of steel components in oxygen rich and oxygen deficient hydronic water.		

KEY WORDS

corrosion
 inhibitors
 ethylene glycol
 polarization resistance

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