

CORROSION INHIBITION IN NAVAL VESSELS

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ABSTRACT

This paper documents a limited literature review on the past, current and proposed use of corrosion inhibitors in naval vessels. A brief discussion of the type of corrosion inhibitors used, mechanisms of corrosion protection and practical methodology of evaluating corrosion inhibitors is given. Wherever, possible, examples of the systems protected by corrosion inhibitors are cited.

Keywords: corrosion inhibitors, marine corrosion, naval vessels, corrosion inhibition mechanisms, vapor phase corrosion inhibitors.

INTRODUCTION

Information about inhibitors, in general, is scattered throughout the corrosion literature. In the past two decades, separate symposia and conferences have been held on inhibitors and inhibition technology. It is not surprising that papers and reports on the use of inhibitors in the Navy is scanty. This review paper is an attempt to summarize such work.

According to Norman E. Hamner,¹ the definition of inhibitor favored by the National Association of Corrosion Engineers (NACE) is: a substance which retards corrosion when added to an environment in small concentrations. It is well established that inhibitors function in one or more ways to control corrosion: by adsorption of a thin film onto the surface of a corroding material, by inducing the formation of a thick corrosion product, or by changing the characteristics of the environment resulting in

reduced aggressiveness.² These mechanisms cover most of the observed effects and form the basis for experimental work leading to research, development and engineering applications of inhibitors.

Organic Corrosion Inhibitors

H. R. Baker and W. A. Zisman³ of the Naval Research Laboratory (NRL) published in 1951 a report on liquid and vapor corrosion inhibitors. Their research on polar-type rust inhibitors for steel in non-aqueous fluids revealed that both soaps and amine-acid complexes acted as rust inhibitors in oils through the release of organic acids which had been held by association. They have shown that most effective rust-inhibiting additives are those which remain in the oil in the most highly dispersed colloidal condition and which release those which organic acids having the greatest ability to inhibit rusting of steel. The most effective acids are those which react with the iron surface to form soaps in situ. Baker and Zisman did not find any evidence showing these soaps to be the same as soaps made in bulk and then added to the oil. In addition to reviewing the work of several other researchers on inhibitors, they pointed out that both amines and soaps can associate with carboxylic acids and thus can be used in oils to neutralize acids, act as peptizers or coupling agents, and deterge acidic and insoluble oxidation products. Contrary to some claims in the literature, Baker and Zisman³ found no reason to believe that rust inhibitors adsorb as polymolecular films on steel. Postwar experiences in various laboratories showed the unsuitability of humidity cabinets for corrosion testing. They instead recommended the use of NRL fog cabinet⁴ and the static water-drop test method utilized by Hoar and Smith⁵ and McCue and Blanc⁶ for research and control. They recommended these for Naval specifications.

Baker and Zisman³ also reviewed the work done in the area of vapor corrosion inhibitors and observed that during the first years of World War II the equipment losses due to poor packaging for overseas shipment were appalling. In order to adequately protect war equipment exposed to rough handling and a wide range of climatic conditions, many improved packaging materials and techniques were developed. Among these, the application of the substituted ammonium nitrites^{7,8,9} as vapor phase corrosion inhibitors gained considerable prominence. The earliest tests were conducted at NRL using diisopropyl ammonium nitrite to inhibit corrosion of the interiors of rocket bodies¹⁰ and in developing aqueous hydraulic fluids which were inhibited against both liquid and vapor phase corrosion.¹¹ It was shown by Temple and Wolfe^{12,13} that diisopropyl ammonium nitrite and also diisobutyl and dicyclohexyl ammonium nitrite could be prepared by a method which allowed manufacture of the crystalline product. In another investigation, Baker¹⁴ described a variety of applications and limitations in packaging due to attack on some non-ferrous metals.

Baker and Zisman³ stated that the three nitrite compounds, diisopropyl, diisobutyl and dicyclohexyl ammonium nitrite, sublime readily at room temperature and inhibit rusting by adsorbing onto exposed metal surface to form a protective film. A hydrophobic monolayer is formed, on top of which there may deposit a loosely adhering layer of

crystalline inhibitor. The hydrophobic film had a contact angle of 55° for the diisopropyl and 50° for the dicyclohexyl ammonium nitrite at 20°C. The hydrophobic property is attributed to the polar-nonpolar structure of the substituted ammonium nitrite molecule. Because of the low molecular weight of the hydrocarbon portion of the organic nitrite molecule, prolonged contact with bulk water will result in dissolution or desorption of the protective film and allow corrosion of the substrate. Film desorption and solubility of the inhibitor in water lead to limited vapor-phase inhibition under conditions of extreme humidity. Recent developments suggest the use of a mixture of two or more corrosion inhibitors to provide corrosion protection in such extreme humidity conditions.

Several commercially available vapor phase corrosion inhibitors (VCIs) were evaluated using potentiodynamic polarization technique to determine their efficiency in controlling corrosion of 6061-T6 aluminum alloy, hot rolled steel 4340 and galvanic couples of both in 3.5 weight % NaCl.¹⁵ The successful VCIs were subjected to toxicity evaluation before considering them for shipboard application. Two VCI emitter products (VCI A and VCI B) and an aerosol inhibitor spray (VCI C) were found to be non-toxic and suitable for shipboard application. The VCI emitters containing amine carboxylates were designed to protect multi metals or parts within an enclosure where there is no ventilation. When installed, VCI emitters release a vapor and wherever moisture is present the VCI vapors deposit on metal surface and form a monomolecular film. This film protects the metals from further corrosion. With additional moisture entering the enclosure, the VCI will quickly reform and thus provide continuous protection. VCI C is a similar vapor phase corrosion inhibitor dissolved in a volatile solvent base. The author installed these VCIs on a Navy ship for controlling corrosion of diodes in an electronic cabinet. The details of the ship tests and results obtained will be reported in a separate publication. Based on positive results of the tests in controlling corrosion for nearly two years, these VCIs were recommended for similar applications on other ships.¹⁶

Mora and Bastidas¹⁷ studied the influence of NaCl contamination on efficiency of volatile corrosion inhibitors. They performed corrosion tests at room temperature using mild steel and zinc coupons contaminated with six levels of sodium chloride (0,10,20,50,75 and 100 mg/m²/day) at three levels of humidities (60, 80 and 100%) in the presence and absence of dicyclohexylamine, decylamine and one commercial product. The NaCl contamination levels studied had no effect on the inhibiting efficiency of dicyclohexylamine and decylamine. The inhibition efficiency was 40% higher for mild steel than for zinc. Weight loss measurements indicated that these inhibitors can be used as volatile corrosion inhibitors for mild steel and zinc in the presence of NaCl.

Mechanism of Inhibition

According to Balezin¹⁸ every corrosion inhibitor, including volatile ones, should: a) be capable of establishing a stable bond with the metal surface in a given environment of a certain range of acidity and pressure and b) create an impenetrable layer for corroding ions. No attempt will be made here to provide details of inhibitor mechanisms, as there are several excellent papers on the subject matter in the literature.^{19,20}

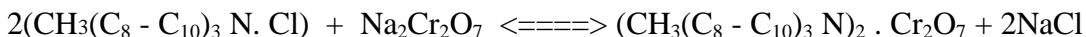
When an aqueous solution of one of the substituted ammonium nitrites is in contact with a clean iron surface, preferential adsorption occurs, and the resulting film prevents the water from attacking the ferrous metal at 100°F. The optimum inhibitor concentration at 100° F has been found to be 0.01% by weight. At higher temperatures, higher inhibitor concentrations would be required. However, if uninhibited water washes the surface of the inhibited steel, it dissolves the adsorbed film allowing corrosion to occur.

The precise mechanism of rust inhibition is not completely understood. The amine alone will inhibit in aqueous solution, but not as effectively as ammonium nitrite; while in the vapor phase, the amine is much less effective. Sodium nitrite is approximately as effective as the ammonium nitrites as a liquid phase inhibitor. Two cooperating properties of the substituted ammonium nitrites make them efficient inhibitors: a) they readily adsorb to form a hydrophobic film which acts as a water barrier, and b) the polar nitrite group in contact with the metal has a passivating action similar to that of sodium nitrite. Paper, cardboard, cloth and other packaging materials can be impregnated with these nitrite compounds and used for equipment storage or shipment. Foster²¹ has described their uses in packaging ordnance materials, and instruments and machinery, respectively. Baker¹⁴ has shown that the substituted ammonium nitrites accelerate the corrosion of zinc, cadmium, magnesium and lead in humid atmospheres only and do not affect these metals in the absence of water.

Microencapsulated Inhibitors

The sudden and catastrophic environmentally related failures of high strength steel and aluminum alloy naval aircraft parts have been considered a major material problem.²² Increasing the strength of the steels also increased their susceptibility to environmental cracking or fatigue failures. To minimize the corrosion processes associated with fatigue cracking, several exploratory studies were carried out at the Naval Air Development Center, Warminster, PA on the feasibility of developing new inhibitors such as quaternary ammonium salts and crown ether complexes, to be applied in situ for arresting the crack propagation.^{23,24} Organic amine chromate salts were also investigated previously as potential inhibitors, and were found to be generally more effective than the common inorganic primer chromates;²⁵ however, instability to heat and/or light has precluded their continued development. Several new compounds, successful in retarding corrosion fatigue and stress corrosion cracking of high strength aerospace materials such as 4340 and 300M steels, 7075-T6 aluminum alloy, are described by Agarwala.²⁶ These materials have been named DNBM, an acronym for a dark brown, highly viscous, 100% solids mixture of quaternary ammonium dichromate, nitrite, borate, and molybdate. The important characteristics of DNBM salts are that they inhibit moisture entry at the crack tip, thereby inhibiting corrosion, they modify the interfacial chemistry such that atomic hydrogen is removed immediately, and they create a chemical barrier (passive film) at the crack surface. The details of development of DNBM materials and formulation of DNBM inhibitors for paint applications via the technique of microencapsulation are given

elsewhere.²⁶ The concept of reversibility of the exchange equilibria and the integrity of the quaternary functionality is shown by the following reaction:²²



In order to prevent direct interaction of DNBM inhibitor with the solvents and uncured polymers of the epoxy system, a suitable microcapsule shell polymer was selected after a good deal of research. The microencapsulated DNBM mixture is held in reserve in the primer coat and released into the area when a damage of the top coat and primer occurs. The shell of the microcapsule must be sufficiently hydrophilic so that when seawater penetrates the primer by diffusion or through cracks, the microcapsules will allow water to pass through, thereby releasing the DNBM inhibitor from the shell. They²⁶ successfully tested the MIL-P-23377 epoxy polyamide primer with DNBM microcapsules, replacing the standard strontium chromate inhibitor.

Inhibitors on Canadian Forces Ships

The air conditioning systems on Canadian Forces Ships utilize 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 either chilled to 4.4° C by the air conditioning plant and used for cooling or heated to 60° C by hot water converters and used for heating. Copper or copper alloy components were used to design the hydronic water system. Some of the parts of the system were made from steel. It was found as a result of an investigation that the plugging of hydronic system strainers and small orifices with hydrated iron oxide resulted in reduction of the effectiveness of the air conditioning system. Corrosion of steel parts produced hydrated iron oxide deposits and sludges, and additional corrosion control of these parts in either oxygen-rich or oxygen-deficient hydronic water environments became necessary.

Hanham et al²⁷ investigated the effect of sodium nitrite (NaNO_2) and sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) independently on copper and steel samples in 10% ethylene glycol and water solution, using polarization resistance and potentiodynamic scan measurements. The effect of their combined corrosion inhibiting effectiveness was studied by adding a proprietary inhibitor package to DDH 280 Class ships' hydronic water system. The inhibitor package was a concentrated aqueous solution containing sodium nitrite, sodium borate decahydrate and mercaptobenzothiazole (MBT). It was found that the corrosion rates for copper were very low in both uninhibited and inhibited solutions of 10% ethylene glycol in water. The results of polarization resistance measurements showed that the proprietary inhibitor package was an effective inhibitor for mild steel in both aerated and deaerated solutions of 10% ethylene glycol in distilled water. The presence of residual phosphate ions up to 400 ppm did not interfere with the effectiveness of the inhibitor for mild steel.

Corrosion Inhibitor Films

James Miller's application for two patents on an effervescent cationic film forming corrosion inhibitor material for use in torpedo launcher tubes was accepted in July 1992.^{28,29} This US Navy owned invention is available for US and foreign licensing. A copy of the patent can be obtained from the Commissioner of Patents, Washington DC 20231. It describes a material and process for providing a corrosion inhibitor cationic film on the exterior aluminum surface of a weapon, when contained in a submarine launch tube. An effervescent tablet containing a corrosion inhibitor material is disposed within the launch tube with the weapon, and upon flooding of the launch tube with seawater, the effervescent tablet releases the corrosion inhibitor material into the water, to form a solution that coats the exposed aluminum surfaces of the weapon with a cation film of the corrosion inhibitor material.

Methods of Investigation

Agarwala and Kennedy, in a patent,³⁰ have described a method and apparatus for measuring corrosion beneath thin films. The aircraft carrier environment is a particularly corrosive one, with sulfur from aircraft-carrier stack gases, combining with sea spray to provide a hostile environment which undermines the structural integrity of naval aircraft. Corrosion of aircraft hydraulic pistons, engine components, and bearings is a serious problem. The corrosion protection of such parts relies greatly on the formation and stability of thin lubricant films, which remain on the metal surfaces after the lubricant drains, and act as barriers to the hostile environment. They showed by their method and apparatus described in their patent, one can quantitatively measure the corrosion-inhibiting ability of thin films of materials, such as lubricants.

SUMMARY

This paper is intended to be an overview of the history of inhibitor studies for naval applications. Available information on specific inhibitors and systems protected is summarized in Table 1. It is clear that for the Navy, use of corrosion inhibitors for corrosion control and prevention is limited. This could possibly be due to the toxicity and environmental implications on the use of some inhibitors. With the development of non-toxic and environmentally-friendly inhibitors, this situation will, hopefully, change. Corrosion inhibition is still an economical solution to overcome some corrosion problems in naval vessels.

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TABLE 1
LIST OF INHIBITORS AND THEIR APPLICATIONS IN THE NAVY

No.	Inhibitors	Applications	Ref.
1.	Soaps and amine acid complexes	General iron and steel surfaces	3
2.	Substituted ammonium nitrites: diisopropyl ammonium nitrite, diisobutyl and dicyclohexyl ammonium nitrite	Rocket body interior Packaging of equipment for storage and shipment	3 14
3.	VCI A VCI B and VCI C- amine carboxylates	Electronic enclosures	15, 16
4.	Dicyclohexylamine and decylamine	Mild steel and zinc	17
5.	Quaternary ammonium dichromate, nitrite, borate and molybdate (DNBM)	To prevent corrosion fatigue and stress corrosion cracking of high strength aerospace materials	26
6.	Sodium nitrite, sodium tetraborate and a commercial mixture of sodium nitrite, borax decahydrate and mercaptobenzothiazole	Copper and steel samples in 10% ethylene glycol and water solution	27
7.	Cationic film forming inhibitors	Torpedo launcher tubes	28, 29