

# VAPOR PHASE CORROSION INHIBITORS FOR NAVY APPLICATIONS

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## **ABSTRACT**

Vapor Phase Corrosion Inhibitors (VCIs) are chemical compounds having significant vapor pressures that allow vaporization of the molecules and subsequent adsorption of these on metallic surfaces. The advantage of these vapor phase corrosion inhibitors is that the vaporized molecules can reach hard-to-reach areas commonly found in electronic enclosures, between two metal flanges and similar other systems. In order to be used effectively, the VCIs must be compatible with the metals to be protected and the environment, be economical for the operation, be easily applied and must have greatest desired effect in protecting the metallic surfaces from atmospheric corrosion. Several commercially available VCIs have been investigated on aluminum, steel and aluminum/steel (Al/steel) galvanic couple exposed to simulated marine environment using potentiodynamic slow scans. The inhibitor efficiencies calculated from electrochemical data are presented. The systems reach a steady state after 48 hours of exposure of the metal to VCI vapors. The most efficient VCIs were screened for toxicity before recommending them for selected ship-board applications in the U.S. Navy.

Keywords: inhibitors, vapor phase corrosion inhibitors, volatile corrosion inhibitors, atmospheric corrosion, potentiodynamic scans

## INTRODUCTION

Although practical applications of vapor phase corrosion inhibitors also known as volatile corrosion inhibitors (VCI), became common only in recent years, it was a practice in Sweden in the 19th Century to place camphor in a gun case to protect it from corrosion<sup>1</sup>. Corrosion is an electrochemical phenomena resulting from the individual or combined action of oxygen moisture and atmospheric pollutants with metals and alloys<sup>2</sup>. Acid rain, hydrogen sulfide, chlorides, temperature and high humidity will also accelerate corrosion. Classical methods of protecting metals and alloys from atmospheric attack include (a) using paints and coatings and (b) alloying the metal to increase its resistance to corrosion. An effective and relatively inexpensive method of controlling corrosion in closed systems or environments is through the use of vapor phase corrosion inhibitors. In the case of precise scientific instruments, electrical and electronic equipments, VCIs offer a definite advantage over classical methods of protection. A VCI is a chemical substance which when added in small concentrations to an environment, effectively checks, decreases or prevents the reaction of the metal with the environment<sup>3</sup>. A VCI can be defined as an individual chemical or combination of chemicals (mostly organic) having high vapor pressure that can prevent atmospheric corrosion of metallic materials. According to Miksic and Miller, "volatile corrosion inhibitors are secondary electrolyte layer inhibitors that possess appreciable saturated vapor pressure under atmospheric conditions, thus allowing vapor-phase transport of the inhibitive substance."<sup>4</sup> Based on this definition, compounds that inhibit corrosion by only adjusting the pH of the electrolyte, e.g., volatile neutralizing amines, should not necessarily be classified as VCIs. Two review papers, one by Floor<sup>2</sup> and the other by Miksic<sup>5</sup> provide a very good overview on the classification/nomenclature, mechanism and nature of adsorbed films of VCIs. However, the exact mechanism of how VCIs work is still not completely known nor is the specific type of bonding between the metal surface and the VCIs. In the current work, several commercially available VCIs were investigated on steel, aluminum and steel-aluminum couples in simulated marine atmospheric conditions with the objective of finding out their efficiencies in protecting the metallic substrates. Some VCIs were also installed in selected systems on a Navy ship and were monitored for almost two years.

## VCI ACTION MECHANISM

By definition, a VCI must be a volatile compound or a mixture of such compounds. It must be capable of forming a relatively stable bond at the metal interface, thus producing a protective layer that limits the penetration of corroding species<sup>6,7</sup>. According to Balezin<sup>6</sup> 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.

The mechanism of inhibition as illustrated by Balezin is shown in Figure 1. Two functional groups are attached to the nucleus RO: R1 is responsible for the adsorption of the inhibitor on the metal's surface. R2 gives the thickness and impenetrable nature to the protective inhibitive layer.

Vapor pressure is a critical parameter in determining the effectiveness of a VCI. A VCI reaches the metal surface that it must protect through the vapor phase. This transport mechanism requires the VCI to possess an optimum vapor pressure. Too low a vapor pressure, e.g., on the order of  $10^{-6}$  Torr at room temperature, leads to slow establishment of a protective layer which may result in insufficient corrosion protection. Furthermore, if the space that houses the equipment and the VCI is not sealed, sufficient inhibitor concentration may not be reached. On the other hand, if the vapor pressure is too high (approximately 0.1 Torr at ambient conditions), VCI's effectiveness will be limited to a short time period, as its consumption rate will be high. Therefore, the VCI must not have too high or too low vapor pressure, but some optimum vapor pressure. Both the corrosion rate of a metal and the volatilization rate of a VCI are a function of temperature. Because of this similar temperature dependent nature, the available vapor phase concentration of a VCI may adjust to the aggressiveness of the environment<sup>7,8</sup>.

## EXPERIMENTAL

### Materials

Six commercially available VCIs have been investigated.\*\* A brief manufacturer's description of VCIs considered for the study are given in Table 1. The metallic substrates used for testing were aluminum alloy 6061-T6, hot rolled steel and galvanic couples of both.

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\*\* The six VCIs are: VCI 105, VCI 110, VCI 237, COR-PAC and 1-MUL obtained from Cortec Corporation and ACF 50 obtained from Corrosion Technologies Inc. They are referred to in this paper as: VCI A, VCI B, VCI C, VCI D, VCI E, and VCI F respectively.

### Method of Study

The metal samples were polished to 600 grit size, washed with distilled water, followed by acetone wash, and finally air dried at room temperature. The polished metal sample was suspended inside an enclosure of approximately 12"x12"x12" size and was exposed to each VCI for different periods of time: 6, 12, 18, 24, 48 and 72 hours. After each interval, the VCI coated metal sample inside the enclosure was carefully transferred to a three electrode corrosion cell where a high humidity electrolyte spray, created by

bubbling air through 3.5 weight % NaCl completely filled the flask. This was done to simulate a topside environment on a ship where some of the systems such as junction boxes and electrical boxes are subjected to a combination of marine atmospheric exposure and occasional seawater spray. The VCI coated sample was immersed in the electrolyte only during the potentiodynamic scan. When the equilibrium was reached, the potentiodynamic scan was performed. The purpose of this was to determine the optimum time needed to saturate the metal surface with VCI molecules to achieve adequate corrosion protection. The sample was made the working electrode by screwing it to a stainless steel rod. A slow potentiodynamic scan at a rate of 1 mV/sec was obtained using carbon-carbon counter electrodes placed in the electrolyte solution and a standard calomel reference electrode placed close to the working electrode. An EG & G potentiostat, PARC 273 and 352 Softcorr software were used to collect potentiodynamic scan data and the plots generated in such scans. A metal sample was reused by polishing each time to 600 grit size before using it for another test with a different VCI.

## RESULTS AND DISCUSSION

According to Miksic<sup>5</sup>, attempts to develop a reliable laboratory experiment that would provide usable information on the behavior of volatile corrosion inhibitors have been only partially successful. Electrochemical techniques have been used to study the performance of several water soluble corrosion inhibitors. However, such electrochemical study is scanty with regard to assessing the performance of VCIs. The attempts to correlate the electrochemical measurements in a volume of electrolyte with actual atmospheric conditions occurring beneath thin films of electrolyte have been unsuccessful due to drastic changes in electrochemical behavior of metals under these two conditions<sup>5</sup>. It appears that for the first time an electrochemical study of VCIs has been performed under conditions that is approximately intermediate between total immersion in electrolyte and total marine atmospheric exposure - a condition that is experienced on top-side of a ship. For example, slow potentiodynamic scans for Al 6061, hot rolled steel and Al/steel galvanic couple with and without the presence of VCI F are shown in Figures 2-4. After 72 hours of exposure to inhibitor VCI F,  $E_{corr}$  for aluminum alloy (Figure 2) shifted to a more positive direction, while such an effect was minimal for steel (Figure 3). This shows that VCI F is better suited to protect aluminum alloys than steel. For Al/steel galvanic couple, however, the protection offered by VCI F is quite high (77.3%) only slightly lower than that provided for protecting aluminum alloy (82.8%). A small shift in  $E_{corr}$  towards positive potential demonstrates this behavior as shown in Figure 4. Additionally, lower corrosion currents were recorded for Al and Al/steel galvanic couple in presence of VCI F. This reflects higher inhibitor efficiencies.

The inhibitor efficiencies (IE) were calculated using the relationship:

$$IE \% = ((i - i_{vci}) / i) \times 100$$

where  $i$  is the corrosion current density in the absence of a VCI and  $i_{vci}$  is that in the presence a VCI. In general, the VCI efficiency increased as a function of exposure time of

the metal to VCI atmosphere. Exceptions to this trend were shown by the behavior of VCI D and VCI E for which the efficiencies decreased after 48 hours of exposure of the metal to the VCI atmosphere. The maximum efficiencies are reached at different durations of exposure for different VCIs. This may be attributed to differences in vapor pressures, physical forms and chemistries etc. between VCIs. Low efficiencies for VCI D and VCI E after 72 hours of exposure of Al 6061 indicate that these VCIs are not intended for protecting aluminum in a severe environment such as a salt fog atmosphere. Based on inhibitor efficiencies calculated from potentiodynamic scans on aluminum 6061 samples exposed to VCI atmospheres for 72 hours, the following order was obtained:

VCI: VCI F> VCI A> VCI C> VCI B  
 IE%: 82.8 78.9 68.4 25.9

The two top performers for protecting 6061 aluminum alloy are VCI F and VCI A. According to the manufacture's brochure<sup>9</sup>, VCI F is an ultra-thin compound with the consistency of 10 weight oil. It meets MIL-C-81309D, Type III (Class 1 and 2) and is specially intended as anti-corrosion material for aircraft. According to Cortec Corporation<sup>10</sup> both VCI A and VCI B are dual action (desiccant/VCI protection) breathable devices intended for multi-metal protection in electronic enclosure types of environments. It is not clear at this time why VCI B did not perform as well as VCI A though according to the manufacturer, both contain similar chemical ingredients but differ in the volume they protect. It is possible that the membrane on VCI A device allows better permeation than the foam on VCI B. Recently, this foam device has been replaced with a device covered with a membrane. VCI C is a corrosion-inhibiting spray that provides a dry, ultrathin, protective film that is intended for use on electronic equipment and components that are in enclosed environments<sup>10</sup>. It must be mentioned that all VCIs considered in this study should offer better corrosion protection if the environment is not as aggressive as simulated in the current work. In reality, the VCI emitters and sprays are intended for controlling atmospheric corrosion and the results obtained here are for the worst conditions.

By performing a similar analysis of the results obtained for steel, the efficiency order of VCIs is:

VCI: VCI F> VCI B> VCI E> VCI C  
 IE%: 71.6 59.1 40.3 29.3

It is interesting to note that after 72 hours of exposure of the Al/steel galvanic couples to VCI atmospheres, VCI B, VCI C and VCI F were the top performers. Excluding VCI E which showed very low efficiency, the order of VCIs according to their efficiencies for providing corrosion protection for Al/steel galvanic couples would be:

VCI: VCI B> VCI C> VCI F> VCI D> VCI A  
 IE%: 95.1 92.1 77.3 65.3 38.0

It is not clear that why VCI B and VCI C show higher efficiency in protecting the Al/steel galvanic couple compared to their performance on aluminum alloy or steel. A possible explanation could be that the VCI molecules are adsorbed well and are in sufficient concentration in the crevice formed by two metallic components. The efficiency of VCI F in protecting the galvanic couple is higher than that for protecting steel, but lower than that for protecting aluminum alloy. These results indicate that VCI F is better suited for protecting aluminum alloys than for steel.

### Shipboard Test

It is important that any chemical and/or chemical device intended for use on ships should be non-toxic and be free from any vapors or fumes that are likely to cause health concerns. Selected VCIs were evaluated by Fourier Transform Infrared Spectroscopy/Thermogravimetric Analysis (FTIR/TGA). The details of this work will be reported in a later publication. VCI A and VCI B were found to contain no toxic chemicals and were selected for shipboard testing. These were installed inside an enclosed cabinet containing a rack full of diodes and other electrical components on a ship where corrosion of diodes was reported.

Installation of VCI A and VCI B devices in such cabinets has controlled the corrosion of diodes. Though VCIs cannot eliminate corrosion that has already taken place, they have helped in not allowing corrosion to continue. By doing so, VCIs are helping to increase the life of such electrical cabinets.

### SUMMARY

1. VCI A, VCI B, VCI C (spray) and VCI F (spray) have been found to show high inhibitor efficiencies in controlling corrosion of Al 6061 and Al/steel galvanic couples in simulated marine environment.
2. VCI A, VCI B, and VCI F showed moderate inhibitor efficiency in controlling corrosion of 4340 steel while VCI C showed low efficiency in protecting steel in simulated marine environment.
3. Inhibitor efficiency is dependent on the type of metal/alloy, the type of environment, air-tightness of cabinets/enclosures in which they are placed, concentration and temperature fluctuations.
4. Ship board tests showed that VCIs are suitable and efficient in controlling atmospheric corrosion in closed systems such as electrical cabinets. Since VCI efficiency is not universal, specific testing and screening is suggested.

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#### REFERENCES

1. Lund, L., "Practical uses of Vapor Phase Inhibitors," Proc. Third European Symposium on Corrosion Inhibitors, Ferrara, Italy, pp. 875-879, 1970.
2. Fodor, G. E., "Inhibition of Vapor-Phase Corrosion- A Review," Report No. BFLRF-209, Southwest Research Institute, San Antonio, TX, September 1985.
3. Riggs, Olen L. Jr. (Nathan, C. C. Ed), Corrosion Inhibitors, NACE, 1973.
4. B. A. Miksic, R. H. Miller, European Symposium on Corrosion Inhibitors, 5th Proceedings, 107th Manifestation of the European Federation on Corrosion, pp. 217-236, September 1980.
5. B. A. Miksic, "Use of Vapor Phase Inhibitors for Corrosion Protection of Metal Products," 11-16-1, NACE Symposium Proc., 1983.
6. S. A. Balezin, Comptes Rendus de 2eme European Symposium Sur les Inhibiteurs de Corrosion, Ann. Univ., Ferrara, Italy, N. S., 1966.
7. I. L. Rosenfeld, V. P. Persiantseva and M. N. Polteva, Inhibitors (Houston, TX: National Association of Corrosion Engineers) pp. 606-609, 1972.
8. B. A. Miksic, Chem. Eng., pp. 115-118, September 26, 1977.
9. Technical Brochure on ACF 50 from Corrosion Technologies, Inc., Dallas, TX.
10. Technical Brochure, "Environmentally Safe VCI Technology," Cortec Corporation, St. Paul, MN, 1993.

TABLE 1  
VENDOR'S DATA ON VCIs

VCI I. D.	Description of VCI
VCI A <sup>10</sup>	Breathable membrane, plastic cartridge filled with nitrite-free VCI for multi-metal protection. Protects 5 Cu ft. of enclosed space.
VCI B <sup>10</sup>	Breathable, open-cell foam emitter, nitrite free for multi-metal protection. Protects 10 Cu ft. of enclosed space.
VCI C <sup>10</sup>	Corrosion-inhibiting spray for use in electronic enclosures; does not alter electrical resistance, magnetic or thermal properties.
VCI D <sup>10</sup>	All purpose VCI tablets for multi-metal protection. Nitrite-free and non-polluting.
VCI E <sup>10</sup>	Breathable membrane filled with multi-metal VCI E. For applications where powder contamination is not acceptable.
VCI F <sup>9</sup>	Anti-corrosion light weight oil spray for aircraft; meets MIL-C-81309D Type III (Class 1 and 2).

Figure 1. The Mechanism of Corrosion Inhibition, Balezin<sup>6</sup>

Figure 2. Slow Potentiodynamic Scans of Aluminum 6061-T6 in 3.5% NaCl with and without VCI F

Figure 3. Slow Potentiodynamic Scans of hot rolled steel in 3.5% NaCl with and without VCI F



Figure 4. Slow Potentiodynamic Scans of Al/Steel Galvanic Couple in 3.5% NaCl with and without VCI F