

# Volatile Corrosion Inhibitors Find a New Home

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**Developed originally to protect the insides of ships' hulls, these compounds now help to cut corrosion in a number of CPI services that involve enclosed atmospheres.**

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□The direct cost of atmospheric corrosion in metals and alloys has been pegged at \$5 billion annually. \*One tool that has recently gained favor in the chemical processing industries for combating such damage is the volatile corrosion inhibitor.

VCI's condition air or other gaseous environments with trace amounts of inhibitive material to achieve the protective effect. Classic methods of protection involve either changing the composition of an alloy, or covering the metal with a protective coating. In some instances, these measures may prove impractical due to cost, limited accessibility or risk of contamination.

Examples of applications where VCI's have been used include instrumentation and control-room equipment, vapor spaces above the liquids, condensers and boilers during shutdown and standby, vessels and other equipment during storage and shipping and inventories of warehoused metal objects.

For VCI's to be suited for use in the chemical process industries, they must be cheap and easy to apply, durable, nontoxic and nonpolluting.

Chief advantages of these inhibitors are procedural and economic. It is unnecessary to prepare the metal surface prior to using VCI's,

since their vapors can penetrate to remote areas of an enclosure. The nearly indiscriminating nature of some newly developed formulas to protect dissimilar metals and to perform in severe environments reduces the need for a rigidly planned maintenance schedule.

## HOW THEY WORK

VCI's generally come as solids, for convenience in handling. Volatility is simply a means of transport. Protective vapors disseminate within an enclosed space until equilibrium-determined by the partial vapor pressure-is reached. The inhibiting process starts when the vapors contact the metal surface and condense to form a thin film of microcrystals. In the presence of even minute quantities of moisture, the crystals dissolve and develop strong ionic activity.

The result of such activity is adsorption of protective ions onto metal surfaces, with the concurrent formation of a molecular film that fosters breakdown of contact between the metal and an electrolyte. The presence of an invisible monomolecular film does not alter any of the important properties of the metal, even in precise electronic applications, where properties such as conductivity, magnetic permittivity or dimensional tolerances are critical, and where even minute deviations could cause malfunctioning.

Too high a vapor pressure will cause the inhibitor to be released to such an extent that a protective concentration cannot be maintained. On the other hand, a low-vapor-pressure inhibitor is not used up as quickly and can thus assure more-durable protection, but more time is needed for a protective vapor concentration. This raises the risk of corrosion during the

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nitrites and amine carboxylates is limited to a range of pH about 5.5 to 8.5. On the acid side, the volatile acid constituent is present in the vapor in excess and dissolves in the condensate on the metal surface to give it an even lower pH; with nitrous or short-chain organic acids, rusting may actually accelerate under such circumstances. At above pH 8.5, without buffering, the acid remains nonvolatile as an anion.

Observed reduction of the *cathodic* reaction stems from a decrease in oxygen concentration caused by formation of an adsorption film that constitutes a diffusion barrier for oxygen. Strong inhibition of the *anodic* reaction results from the inhibitor's having two acceptor-donor adsorption centers that form a chemical bond between the metal and the inhibitor. Adsorption of these compounds changes the energy state of metallic ions on the surface, diminishing the tendency of metal to ionize and dissolve. In addition to preventing general attack on ferrous and nonferrous metals, mixed VCIs are found to be effective in preventing galvanic corrosion of coupled metals, pitting and, in some cases, stress corrosion and hydrogen embrittlement.

#### APPLICATIONS

Vapor-phase inhibitors have been used for corrosion control in enclosures varying in size from the miniature volume of a hearing aid to the cavities and void spaces in mammoth tankers. There is little or no limitation of usage in relation to the type of atmosphere, and the compounds have found use in local industrial atmospheres containing sulfur dioxide, chlorine or hydrogen sulfide. Enclosures need not be tightly sealed, and the compounds have been used in breathable or periodically opened enclosures. CPI applications fall into three main areas:

1. *Product improvements.* The inhibitors may be installed as a product component in the form of cartridge, tablet or powder. Typical applications include switch boxes, junction conduits, process control equipment, computers, fire-control electrical equipment, and instrumentation.
2. *Packaging, shipping, storage.* VCIs are used to protect all types and sizes of equipment, including pumps, motors, valves, process control devices, commutators, molds, piping and tanks.
3. *Protection of standby equipment.* Corrosion control of equipment is as important during shutdown as it is during operating periods. The same conditions of oxygen, water and low pH initiate

corrosion whether the equipment is operating or on standby. VCIs can be applied immediately, and protected equipment can be put into operation without elaborate preparation or degreasing.

#### COMMON PRACTICE

For larger equipment such as tanks, boilers and condensers, these chemicals are applied in bulk powder form. Once the inhibitor is introduced into the enclosure, it vaporizes. The protective film is continuously renewed as the compound vaporizes and vapors condense. Any accidental breakdown of the film is instantaneously repaired by recondensation. Application requires relatively simple, commercially available equipment. Once misting is completed, the enclosure is sealed and no additional measures, such as dehumidification, oxygen scavenging, etc., are needed for the entire period of protection. In certain instances, where it is possible to seal the enclosure airtight, it has proved convenient to apply the inhibitor by first evacuating the enclosure and then repressurizing and allowing the powder to be drawn in.

The quantity of inhibitor needed to protect a given volume can be determined in accordance with the following empirical formula:

$$Q = 0.0277VC$$

Where Q = total quantity of VCI powder, oz; V = volume of the enclosure to be protected, ft<sup>3</sup>, and C = confidence factor (2 to 3).

Assuming a nominal volume of 1,000 ft<sup>3</sup> and a confidence factor of 3, we can demonstrate that VCIs are attractive from a cost standpoint.

$$Q = 0.0288 \times 1,000 \times 3 = 86.4 \text{ oz.} \\ = 5.4 \text{ lb}$$

$$\frac{Q}{1,000} = 0.0054 \text{ lb/ft}^3 \text{ or } 0.0027 \text{ lb/yr}$$

This translates to a cost per unit of volume per year that is nominally \$0.01 per cubic foot per year. The protection of smaller enclosures, such as for electrical and electronic equipment, can be achieved by using one or more VCI devices, or tablets. The devices' chemical package usually contains a mixture of inhibitors, and can also contain a volatile fungistat for the control of fungal growth, and a volatile buffer for

creating a uniform pH on exposed metallic surfaces. Because of the various shapes and sizes of the enclosures, and the varying conditions of storage, it is often difficult to determine the exact number of VCI devices necessary. Typical devices can protect a 1 – 40 ft<sup>3</sup> volume for a nominal duration of two years.

For vapor to fully protect an enclosure, a protective concentration must be reached over a period that is typically shorter than 48 h. The actual number of devices necessary to achieve saturation of vapors in a specific period of time, and to maintain that saturation over two years' time, is conventionally given with the following equation:

$$N = (k_a) (k_p) (k_s) (k_o)$$

Where N = number of devices needed to protect a given volume under specific conditions; k<sub>a</sub> = factor expressing the corrosiveness of the environment; k<sub>p</sub> = factor expressing frequency of opening, or breathability of the enclosure; k<sub>s</sub> = factor expressing the shape of the enclosure; and N<sub>o</sub> = number of VCI devices based on nominal volume of protection.

For example, to protect an electrical box with exterior dimensions of 6 ft x 5 ft x 1.33 ft (40 ft<sup>3</sup>) located on the gulf Coast, which is expected to be opened for inspection and servicing approximately twice a week, the following number of VCI devices are required for protection:

$$N = (k_a = 1.2) \times (k_p = 1.3) \times (k_s = 1.1) \times (N_o = 1) = 1.716$$

or two devices whose nominal capacity is 40 ft<sup>3</sup> for a period of two years.

## **TOXICITY**

It is believed that VCIs based on certain amine/fatty-acid complexes do not represent an undue risk to health in their intended market. The transfer rate of a corrosion inhibitor to exposed surfaces by vaporization

and condensation should be far below the minimum levels at which physiological effects in humans and test animals have been detected.

## References

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## The Author

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*A member of the Natl. Assn. Of Corrosion Engineers, he has published a number of technical articles and has presented talks at international corrosion conferences. He is chairman of NACE Task Force T-3A-4 on volatile corrosion inhibitors. He holds patents pertaining to inhibitors and protective coatings.*