SOME ASPECTS OF METAL PROTECTION BY VAPOR PHASE INHIBITORS

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Introduction

Atmospheric corrosion of metals is responsible for an appreciable percentage of total corrosion damage; it has almost come to be accepted as an unavoidable factor to be calculated into the price of new products. Unfortunately, our ore reserves are finite, and such unnecessary waste of resources is becoming increasingly intolerable.

Alloying for corrosion resistance has become extremely expensive so that the need for new economical and reliable corrosion control techniques is generally recognized.

Both classic methods of decreasing the atmospheric attack on metals:

— Covering the metal with a coating and separating the surface from atmosphere

— Alloying for corrosion resistance

have practical as well as economical disadvantages and limitations that retard their further development. Very often these methods are expanded for new applications with calculated sacrifice of economy, effectiveness of protection or performances, mainly because there is a lack of new methods. The discovery of volatile organic compounds capable of controlling corrosion of metals by the means of vapors, made possible a completely new approach to the problem of prevention against atmospheric corrosion—Vapor Phase Inhibitors.

General

The vapor phase inhibitors were originally developed[1] for protection of ferrous metals in tropical environments but soon this became a limitation because compatibility problems with non-ferrous metals arose.[2] Evidently such limitation of usage was a reason for decreased interest although philosophy of VPI's allows many engineering advantages. Recent development[3] is based on synthesis of volatile compounds which would provide satisfactory generality of protection, in other words which would besides ferrous metals, afford anti-corrosion protection to most commonly used non-ferrous metals and alloys.

Basic principles of transport of inhibitor

The transmission of inhibitor by vapors from the emittor onto the metal surface to be protected is the principal advantage of vaporization inhibitors. The inhibitors are crystalline solids whose vapor phase is controlled by the structure of crystal lattice and the character of the atomic bond in the molecule. The protective vapors expand within the enclosed space until the equilibrium determined by their partial vapor pressure is reached.

The higher the vapor pressure, the sooner is the saturation of protected space. For practical applications, it is preferable to use less volatile inhibitors which provide:

— Long-lasting and durable protection over periods of two-three years.

— The protection of breathable enclosures and enclosures where changes of local atmosphere occasionally occur.

Experience has shown that the proper selection of volatile compounds enables controlled and dependable volatilization so that the quantity of inhibitor introduced into the system is determined with the same parameters which determine the thermodynamic level of corrosion reaction. The graphic presentation of this phenomenon is given on diagrams a. and b., Fig. 1.

As it is shown on diagram b. the higher the temperature, the stronger is the general tendency of brass towards corrosion. The volatilization rate of VPI's is in the similar functional dependence upon temperature, so that more inhibitive material is evaporated at higher temperatures (diagram a.). The consideration of this rule leads to the conclusion that VPI's have a property of self-adjustment to the degree of aggressiveness of environment, which explains their effectiveness in relatively wide temperature range.

Electrochemical mechanism of inhibitor action

The volatility of the inhibitors is merely a means of transport. The inhibition process starts when the vapors reach the metal surface and condense on them forming thin film of crystals. In the presence of even minute quantities of moisture, the crystals dissolve and immediately develop strong ionic activity. The result of such activity is evolution of a molecular layer which creates the breakdown of direct contact metal-electrolyte followed with substantial increase of hydrogen over-potential.

The recent development in the field of VPI's represents the synthesis of compounds which can act at the same time as cathodic and anodic inhibitors and have satisfactory volatilization rates. These inhibitors are usually called mixed inhibitors and their main advantage over traditional VPI's is in fact that they are not dangerous if present in insufficient concentrations.

The mixed inhibitors are highly effective and protect metals in low ratios per specific volume of protected space. Such inhibitors are particularly important for applications in salt spray environments, where there are minute portions of activated metallic surface developing anodic type of reaction extremely dependent upon the rate of depolarization of adjacent large cathodic areas.[4] Through the formation of local anode—cathode cells, the whole system is somehow involved in the corrosion process— the only safe way of inhibition is to strongly polarize both cathodic and anodic areas (Fig. 2).

It is certain that during the corrosion process many ions are present which can change the potential of electrochemical reaction enhancing the tendency of metals to be dissolved in electrolyte. The primary function of any inhibitor is to influence the breakdown of such ionic activity on the metal-electrolyte interface. In the case of vapor phase inhibitors, it is achieved by continuous condensation of vapors and evolution into protective double layer. This double layer is electrically charged and it actually represents energy barriers for ions of depolariser to penetrate and to depolarise the metal surface.

Inhibition of pitting corrosion with VPI's

The study of inhibition of pitting corrosion with vapor phase inhibitors showed varying results. Some vapor phase inhibitors were found ineffective but a certain number afforded a high degree of protection even at temperatures over 100^{o}F and 95% RH. Steel was the test material chosen since it is the most widely used construction material.

The continuous monitoring of galvanic current and the potential of evolution of inhibitor indicated that if potential remains constant at rising concentrations of corrodent (e.g. $C1^-$ ions), the protection against pitting is achieved.[5] Therefore, inhibitor A on Table 1 is an ineffective inhibitor, because its potential of evolution is changed at higher concentrations of corrodent. In the same manner, inhibitor B affords protection against pitting because its evolution is not affected at higher concentrations of corrodent:

Table 1

Concentration of $C1^-$, mole/lit	0.2	0.7	1.2
Inhibitor A			
E½ V	0.18	0.10	0.02
I,μa	1.25	1.03	0.87
Inhibitor B			
E½ V	0.311	0.328	0.325
I, μA	3.12	3.26	3.04

It was observed that after the evolution of inhibitor B was completed, the diffusion of dissolved oxygen cannot substantially change the hydrogen overpotential of established layer. Experimental results are in good agreement with theoretical calculations, and they point at two mechanisms of inhibitor's activity:

1. It is not likely that oxygen can drive the reaction:
   $O_2+2H_2O+4e^- \rightarrow 4OH^-$
   when the double layer is evoluted, and to create local differentiations in pH, which are believed to be the cause of pitting corrosion.
2. The tendency of vapor phase inhibitors to act as buffers and to create the uniformity of hydroxyl ion concentration is the second important condition for successful protection against pitting.

Inhibition of galvanic corrosion with VPI's

The galvanic interactions between dissimilar metals have been studied in laboratory humid atmospheres saturated with vapors of volatile corrosion inhibitors. The commonly used VPI's were found to be less effective, probably because of their tendency to act as anodic inhibitors only. Localized attack was concentrated at areas with accidentally higher concentrations of depolariser and at areas where the ohmic resistance between depolarized cathode and adjacent passivated anode was lower than average.

The specially synthesized mixed inhibitors were proved to be effective; weight loss measurements and continuous monitoring of galvanic current showed substantial decrease in intensity when compared to identical experiments but with anodic inhibitors. The SEM investigations showed the double layer of mixed inhibitor evoluted on both cathodic and anodic part of galvanic couple. Even in severe corrosion situations, such as coupling of a small anode to a large cathode, mixed inhibitors were proved to be effective, probably because of their tendency to strongly polarize both cathodic and anodic areas. The hydrogen layer spread over enlarged cathode, although unusually thin, has sufficient polarization to resist combining with oxygen. Accordingly, mixed volatile corrosion inhibitors lower the role of oxygen diffusion as the controlling factor of corrosion reaction, thus providing protection expandable on almost all types of galvanic interactions in atmospheric exposure. In addition, continuous supplies of volatile corrosion inhibitor by condensation of vapors, assure continuous renewal of the protective layer, a very important condition for effective protection against galvanic corrosion.

Effectiveness of VPI's

Of many grounds examined as volatile corrosion inhibitors, a number in varying degrees conferred protection upon ferrous and some to non-ferrous metals (Fig. 3).

It is well known that amines are endowed with highest protective properties to steels. All other compounds are somewhat inferior to the amines. However, their protective properties are still on the high level but they reduce the aggressiveness of amines to non-ferrous metals.

It was discovered that the composition and structure of organic compounds determines their effectiveness in the art of corrosion inhibition. The position of nitro group plays an important role since it is negatively charged and shifts the steady state potential of the metal in the positive direction, inhibiting the anodic ionization reaction. The introduction of carboxylic group into the compound promotes the reduction of the nitro-group and thus increases the oxidizing properties of inhibitor.

Devices — a new approach in VPI's

Vapor phase inhibitors have been used as powders, coated on papers, and incorporated in oils. Neither way accomplishes the main advantage of VPI's, the possibility to control the corrosion of the entire system from one relatively small device: the carrier of powder (Fig.4).

The device as such can be introduced in any type of enclosure where corrosion occurs and will immediately start emitting vapors. There is no limitation on selection of compounds to be integrated into the chemical package of device-carrier. A chemical package usually contains a mixture of vapor phase inhibitors which provides a very important generality of protection. The relatively high partial vapor pressure compounds afford rapid initial protection. The long-lasting durable protection is achieved with low vapor pressure inhibitors, the protection of ferrous metals and alloys with compounds containing a nitro group, the protection of copper and zinc with compounds containing a carboxyl group and protection of aluminum and magnesium with compounds containing CrO_4^{2-}, etc. The chemical package can also contain a volatile fungistat for the control of fungal growth and a volatile buffer for creating the uniformity of concentration of hydroxyl ions.

The usage of device carrier assures unique simplicity of protection. There is no requirement for wrapping the item to be protected as in the case of VPI paper. Furthermore, the process of impregnation of paper usually affects some protective properties of VPI material, and eliminates the possibility of selection of compounds on the basis of best performances; the selection of compounds is made on the basis of solubility in appropriate solvent for impregnation.

Applications

Whereas the conventional methods require the metal parts to be protected with grease, oil, paints, plating or humidity control with silica gel, vapor phase inhibitors obtain the same preventative effect but in one single operation consisting of introduction of a device into the enclosure. Furthermore, vapor phase inhibitors provide positive protection under conditions where the traditional coatings, wraps and silica gel fail or cannot be used.

The vapor phase inhibitors were used for corrosion control in enclosures varying in size from miniature volume of magnesium dry cell or hearing aid to the rudder cavities in mammoth tankers.[6] There is no limitation of usage in relation to the type of atmosphere; the vapor phase inhibitors have been used in tropical environments as well as in local industrial atmospheres with a high percentage of sulfur dioxide. The application of VPI's does not require tightly sealed enclosures, furthermore they perform well in breathable or frequently opened enclosures.

The industrial applications of VPI's cover three main areas:

1. Product Improvements
   Upgrade existing products by adding VPI's in the form of a device-container as a product component. Unlike oils or coatings, VPI's allow the electrical and mechanical parts to operate at 100% efficiency, while still providing corrosion protection. Typical applications include switch boxes, electronic equipment, instruments cases, junction conduits, etc.

2. Packaging, Shipping, Storage
   VPI's are used to protect all types and sizes of metal parts from corrosion without special coatings. The stored parts are ready for immediate use being protected from outside or inside regardless of surrounded conditions. VPI's allow protection of hard-to-service areas and areas

where the physical contacts of stored parts can create galvanic couples.
The typical applications include tool chests, auto and aircraft parts, storage, molds storage, etc.

3. Protection of Standby Equipment
The 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 equipment is operating or on standby.[7] The vapor phase inhibitors can be introduced into the system immediately after the shutdown occurs. The rapid initial protection obtainable with VPI's assures rapid corrosion control which is then prolonged for the whole period of shutdown. Unlike other protectives, VPI's are always ready to use, can be applied immediately, and can be reused.

Summary

The properties of vapor phase inhibitors and their performance records have established their suitability for metallic protection against atmospheric type of corrosion. Accordingly, vapor phase inhibitors are:

1. Easy to Use —
    - The philosophy of VPI's allows corrosion control from one centre which assures unique simplicity of application and savings on labor costs automatically implied.
    - A tightly sealed enclosure or puncture proof containers are unnecessary.
    - Articles stored can be removed, examined and replaced without loss of protection.
    - VPI's afford protection to metal parts continuously during exploitation without affecting their performances.

2. Economical to Apply —
    - VPI's eliminate greasing or coating at the manufacturing stage and de-greasing at the next assembly stage.
    - The economical corrosion control of hard-to-service areas which are usually centres of severest corrosion damage.
    - Lowering the shipping costs because VPI's perform well in humid atmospheres, so that heavy, air tight containers are not needed.
    - Economical vapor phase corrosion control in various enclosures regardless of shape and ranging from very small volumes up to 1000 cu. ft.

3. Effective —
    - Vapor phase inhibitors were successfully used in many corrosive environments, in such atmospheres as tropical with cyclic

condensation of moisture, marine with high salt content, industrial with percentage of SO_2 ranging up to 0.15 (w/v) etc.

- The proper selection of vapor phase inhibitors and integration of selected compounds into chemical package of device container can assure protection to ferrous and non-ferrous metals and alloys.
- The vapor phase inhibitors were proved to be effective in prevention of galvanic corrosion of coupled dissimilar metals exposed to humid atmospheres.
- The temperature controlled volatilization rate assures increased emission of inhibitor on temperature levels at which corrosion rate is generally severe.
- As classes of inhibitors and also because of their vapor phase transmission, they are effective in the fight against pitting corrosion of exposed metals.

References

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INTERNAL LINING OF DESERT PIPELINE

Hemisphere Corrosion Services (Middle East) Ltd. are currently undertaking the internal lining of approximately 100 Kilometers of 30 inch and 20 inch gas pipe in the State of Qatar in the Arabian Gulf. The pipe line when completed will distribute natural gas to the new industrial complexes in Doha.

The contract was won in the face of fierce world wide competition and is said to be the largest of its kind ever let in the Middle East, and is scheduled to be completed in about 26 weeks.

The complexities of the contract involved Hemisphere Corrosion Services (Middle East) in much research and development work, and the design and manufacture of special plant and equipment.

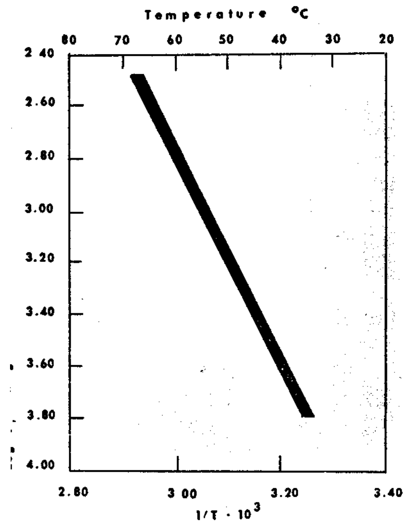
A production line 100 metres long has been built in the desert, and all the pipes are first internally blasted to Swedish Standard Sa 2.5. using rotating headed blast machines. The blast machines are run on tracks and utilize variable speed motors and gear boxes designed by Hemisphere Corrosion specifically for the contract.

Some 50,000 litres of polyamide cured epoxy, manufactured by International Paints Limited is being used on the internal coating of the pipes. Spraying is by means of a remotely controlled spray head which utilizes up to eight spray tips at a time and is withdrawn through the pipe which rotates on rollers at predetermined speeds.

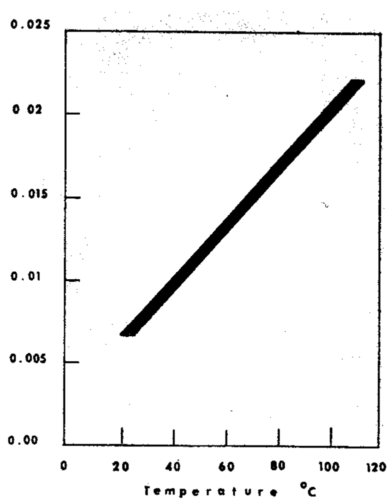
In order to determine the correct machine settings, detailed computer analysis was used programming all the theoretical data and practical constraints relating to speed of rotation and withdrawal, spray tip size, fan width, paint utilization and viscosity. Figures were produced for all the operating conditions which are likely to occur and the results obtained will greatly assist the company in designing plant for future contracts throughout the world.

Hemisphere Corrosion Service (Middle East) Limited are prepared to undertake specialized blasting and lining contracts of all types, and their service includes the design and manufacture of plant and equipment to suit particular needs. They already have established offices in Kuwait and Doha, and during the current year it is intended to expand into other overseas areas. Details: Hemisphere Corrosion Services (Middle East) Limited, Mill House, Locke Road, Liphook, Hampshire.

Figure 1



a. Temperature dependence of partial vapor pressure of typical VPI upon temperature



b. Functional dependence of corrosion rate of 70% Cu, 29% Zn, 1% Sn upon temperature (frequent wetting)

Fig. 2 Qualitative cathodic and anodic polarization curves for steel in absence of inhibitor (control) and in presence of various inhibitors (anodic, cathodic and mixed respectively)

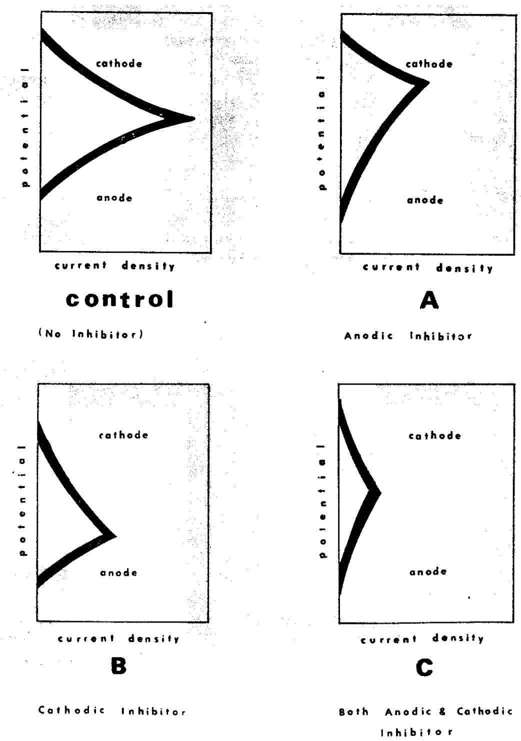


Fig. 3 Effect of VPI's on the corrosion rates of non-ferrous metals. A—Anodic inhibitor. B.— Cathodic inhibitor. C—Both anodic and cathodic. Control—No inhibitor

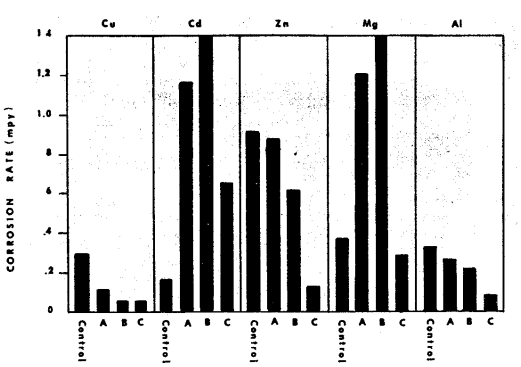


Fig. 4 VPI devices NIC—1, NIC—2, NIC—3 for protection of 1.5, 5 and 40 cu. ft. respectively