

## **Volatile inhibitors of metal corrosion**

### **II. Interaction of systems being protected with the environment and corrosion prevention conditions**

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#### **Abstract**

This paper is a continuation of a series of publications dealing with the protection of metals by volatile corrosion inhibitors (VCIs). It presents a review on the propagation of VCI vapors, VCI distribution in the volume being protected, and specifics of vapor-phase protection of isolated systems and systems interacting with the environment in various ways. The review is supplemented by the authors' own theoretical materials.

**Key words:** *volatile corrosion inhibitors, protection conditions, mathematical models of vapor-phase protection.*

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#### **Introduction**

Previously [1], we considered the first stage of metal vapor-phase protection, namely, VCI vaporization. Depending on conditions, VCI vapors propagate into the space being protected due to diffusion and with gas streams, including convective and other streams [2]. However, it is the ability of inhibitor vapors to undergo spontaneous diffusion that determines the advantages of VCIs over other types of inhibitors and governs some of their specific parameters, such as protection radius ( $l_{pr}$ ), passivation time, *etc.* [3, 4].

The purpose of this publication is to analyze data concerning VCI vapor diffusion, inhibitor distribution in the space being protected, as well as specifics of vapor-phase protection of isolated systems and systems interacting with the environment.

#### **Propagation of VCI vapors and simulation of protection in isolated systems**

Though the role of diffusion in vapor-phase protection of metals is obvious and the mathematical tools for its description had been developed long before VCIs appeared, the first attempts to create a mathematical model of their action were made at the end of the 1980s [3, 4]. They were based on a simple idea: protection of a metal item requires that its surface be reached by an amount of a VCI sufficient for corrosion prevention before corrosion can damage the item. Ideally, mathematical simulation of this condition had to

determine an analytical relationship between the volatility of a compound and its inhibiting properties expressed in an understandable, easily measurable form, on the one hand, and efficiency in vapor-phase protection, on the other hand. This would allow a targeted selection of VCIs.

Persiantseva and Polteva [4] suggested to consider the mass of an inhibitor irreversibly adsorbed on a metal as the critical mass ( $m$ ) of the VCI ensuring metal preservation. Then the authors considered one-dimensional nonsteady-state diffusion in order to estimate the times of vapor-phase passivation of metals by various VCIs. Their study did not much simplify the search for new VCIs. The calculations were performed by numerical methods, while the amount of a VCI irreversibly adsorbed on a metal is hardly an easily measurable amount.

A more successful series of studies was performed by Agres and Altsybeeva [3, 5–9] who analyzed the quasi-steady-state evaporation of a VCI droplet inside a metal sphere coated with a water film. This model assumed that a minimum protective inhibitor concentration ( $C_{pr}$ ) should be created in the surface electrolyte as a prerequisite for metal corrosion prevention.

The analytical solution of the problem:

$$\lambda l_{pr} = \{Dp^0 / [C_{sat} \ln(1 - C_{pr} / C_{sat})]\}^{1/2} \quad (1)$$

defines the relationship between the VCI efficiency expressed through  $l_{pr}$ , its saturated vapor pressure ( $p^0$ ), diffusion coefficient in air ( $D$ ), solubility ( $C_{sat}$ ) and protective properties under conditions (temperature, test duration, thickness of the moisture film adsorbed on the metal, geometrical characteristics of the VCI source, *etc.*) determining the  $\lambda$  coefficient.

The validity of the main theoretical conclusions made in these studies was checked for VCIs with  $C_{sat} \gg C_{pr}$ . In this case, equation (1) becomes simpler:

$$\lambda l_{pr} = (Dp^0 / C_{pr})^{1/2}. \quad (2)$$

The  $D$  value of inhibitors was estimated using the semiempirical relationship:

$$DM^{2/3} = 1.7, \quad (3)$$

whose constants were determined from the  $\lg D - \lg M$  relationship for a wide range of organic compounds.

Despite its numerous assumptions, the model rather accurately describes the metal protection conditions in nearly isolated systems. The calculated and experimental data on the efficiency of various VCIs and its dependence on temperature ( $T$ ) and  $P$  are in reasonable agreement.

The most important achievement of the authors [3, 5–9] is that they distinguished  $p^0$ ,  $C_{sat}$ ,  $D$  in the air, and  $C_{pr}$  in the surface electrolyte as the main physicochemical characteristics determining the efficiency of a VCI in sealed systems. Analysis of the

possible ranges of their variation [10, 11] suggests that  $p^0$ ,  $C_{\text{sat}}$  and  $C_{\text{pr}}$  are most important for direct creation of VCIs; the latter parameter is most important if aqueous solutions of VCIs are used for vapor-phase protection.

On the other hand, the regularities of metal protection with VCIs established for a sealed space should be used with care for real systems. Attempts [5] to attribute the low efficiency of VCIs under conditions of frequent renewal of the water film on the metal due to  $T$  oscillations merely to diffusion processes do not seem adequate. Under these conditions, inhibitor vapors propagate, to a considerable extent, by convective flows.

It is only in rare cases that mass exchange can also be neglected in practice. According to the conclusions made in [3, 5–9], other conditions being equal, the efficiency of VCIs increases with an increase in  $p^0$ . However, it is known that highly volatile inhibitors fail to provide long lasting protection since they quickly evaporate from incompletely sealed systems [12–14]. According to the conclusions made in these studies, it is the mass exchange between the system and the environment rather than the processes analyzed in [6] that determines the amount of a VCI to be placed in a system ( $W$ ).

It must be acknowledged that the model of VCI action presented in [3, 5–9] is not versatile and is only valid in the absence of mass exchange and heat exchange between the system being protected and the environment.

These conditions are rather similar to the conditions used to preserve metal items. General practice [2, 12, 15] is that, after an article and VCI sources have been sealed, the system is kept for some time at a constant temperature in order to allow the inhibitor vapors to reach the surface. This initial period of joint exposure of the metal and VCI is well described by equations (1, 2). Here  $l_{\text{pr}}$  can be considered as the main criterion of VCI efficiency, and the recommendations on the arrangement of VCI emitters developed in [3, 5–9] actually improve the quality of protection.

### **Corrosion initiation by mass exchange in systems protected by VCIs**

Analysis [3, 5–9] suggests: if a VCI concentration ( $C_{\text{inh}}$ ) exceeding the protective concentration is created in the surface electrolyte on the metal within time  $t$  shorter than that required for corrosion damage of the metal, the system will remain corrosion-inactive for any amount of time, provided that there are no exchange interactions with the environment. The role of mass and heat transfer in the initiation of corrosion in such systems is probably that they merely decrease the surface concentration,  $C_{\text{inh}}$ , below  $C_{\text{pr}}$ . Inhibitor evaporation is often believed to be the possible reason of this phenomenon [12–14, 16]. Its regularities are determined by the diffusion of VCI vapors, so the main measures for the prolongation of metal protection in incompletely sealed systems involve the use of not-too-volatile chemicals ( $p^0 < 10^{-1}$  mmHg), selection of isolating materials with low permeability for VCI vapors, and increasing the amount of the VCI placed in the system.

However, corrosion initiation in incompletely sealed systems may also result from a decrease in the surface concentration and an increase in  $C_{pr}$  due to diffusion of water and other corrosive environment components into the system.

Ref. [2] is among the few papers where the effect of water diffusion into a system on the duration of metal protection with VCIs is analyzed. A study of aqueous solutions of VCIs allowed Golyanitskii to find that a certain critical  $C_{inh}$  exists below which VCIs lose the capability to provide vapor-phase protection. Apparently, if the relative humidity of outside air exceeds the relative humidity above a solution with a critical  $C_{inh}$ , gradual dilution of the solution with atmospheric moisture will result in corrosion initiation, even if the inhibitor is not evaporated from the space being protected.

Incompletely sealed systems are most complex for mathematical simulation. However, analysis of even the simplest models suggests that the rate of water diffusion into the space being protected can appreciably exceed the inhibitor evaporation rate and determine the kinetics of VCI dilution in the system and, in some cases, the protection period.

One of such models involves a small space incorporating a VCI ( $N_{inh}^0$  is the number of moles of the inhibitor placed into the space) and a metal. The space is exposed to an environment with a constant temperature and humidity and is separated from it by a material that has low permeability for water and inhibitor vapors. Here the mass exchange with the environment is limited by diffusion through the barrier material, while the contents of the system are in a quasi-equilibrium state.

If the vapor pressure ( $p$ ) of the VCI at the outer surface of the barrier film equals 0 and the VCI is a water-miscible liquid, its mass exchange with the environment is described by the following equations:

$$dN_{H_2O} / dt = D_{H_2O} S (p_{H_2O}^0 - p_{H_2O}) / RTl_0; \quad (4)$$

$$dN_{inh} / dt = D_{inh} S p_{inh} / RTl_0, \quad (5)$$

where  $N$  is the number of moles of the VCI or water, as indicated by the subscript, that have diffused over time  $t$  through a barrier with surface  $S$  and thickness  $l_0$ .

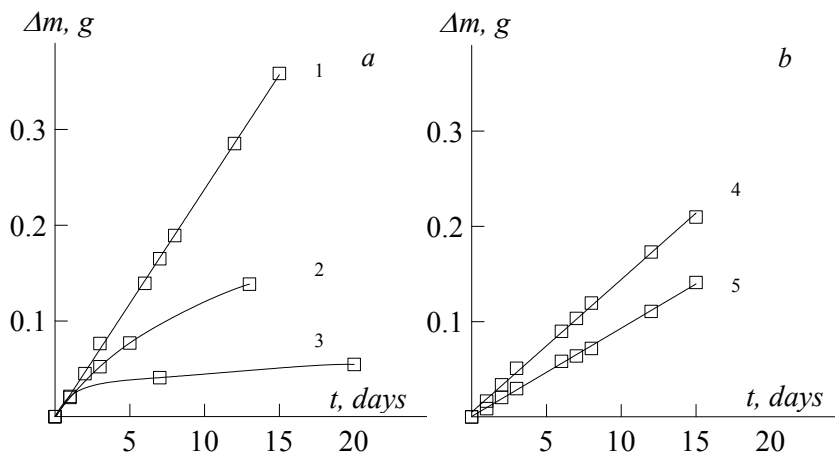
Simultaneous solution of (4) and (5):

$$N_{H_2O} / N_{inh} = D_{H_2O} p_{H_2O}^0 / D_{inh} p_{inh}^0 \quad (6)$$

determines the ratio of water and inhibitor that penetrated through the barrier in the same amount of time. Calculation shows that in the case of mass exchange *via* through pores and carrier material damages, the  $N_{H_2O} / N_{inh}$  ratio can be up to  $10^5$  for low volatile inhibitors.

Thus, both the decrease in  $C_{inh}$  and the time  $t$  during which the condition  $C_{inh} > C_{pr}$  ensures protection of the system from corrosion are often determined by the rate of water ingress into the system that exceeds the VCI evaporation rate.

This conclusion is indirectly confirmed by success in combined protection (VCI together with desiccants) of metals in practice [15, 17] and directly confirmed by tests where cells with a weighed portion of an inhibitor and a calibrated hole in the cap were exposed above a large volume of water (Fig. 1). Mass exchange was accompanied by a mass increase for all the VCIs studied.



**Fig. 1.** Plot of mass ( $m$ ) variation of a cell containing monoethanolamine, dimethylaminoethanol, ethyldiethanolamine, benzylamine, or aniline on exposure time ( $t$ ) under 100% humidity conditions.

All the above raises some doubts about the validity of the popular technique for estimation of the suitability of VCI emitters based on the total inhibitor content in the carrier without consideration for water. Obviously, unlike  $C_{inh}$ , this value incompletely reflects the capability of an emitter for vapor-phase protection.

### Corrosion initiation by heat exchange and specifics of vapor-phase protection in sealed systems

The mechanisms of corrosion initiation by heat exchange in VCI protected systems have been studied in more detail, though the majority of users just state that conditions of abundant moisture condensation created due to temperature variations adversely affect vapor-phase protection [2, 5, 18].

A deeper analysis of this problem is related to the protection of heat-power equipment with solutions of volatile neutralizing amines [19–21]. These studies deal with the search for bases capable of pH control and formation of solutions with near-unity distribution coefficient of the compound between the gas and liquid phases. Spatially separated heating and/or cooling of a system containing a solution of this type is not accompanied by redistribution of the compound in it. The amine concentrations both in the heated solution and in its condensed vapors will not decrease in time and these solutions will maintain a constant pH value.

This concept was developed in [22, 23] where the mechanisms of corrosion initiation by heat exchange in systems protected with VCIs were considered in detail. The authors showed that heat exchange processes that create a temperature gradient on the metal result in water and VCI redistribution in the surface electrolyte similar to distillation of solutions. Evaporation is intensified on heated areas. Since the vapors are enriched in the more volatile component of the mixture, its concentration in the latter will decrease. If  $p_{\text{inh}}^0 > p_{\text{H}_2\text{O}}^0$ , a decrease in  $C_{\text{inh}}$  below  $C_{\text{pr}}$  will result in formation of a corrosion area after some time  $t$ . Conversely, the surface electrolyte is enriched in the volatile component on cooled surfaces where vapor condensation is intensified. This effect can initiate corrosion at  $p_{\text{inh}}^0 < p_{\text{H}_2\text{O}}^0$ .

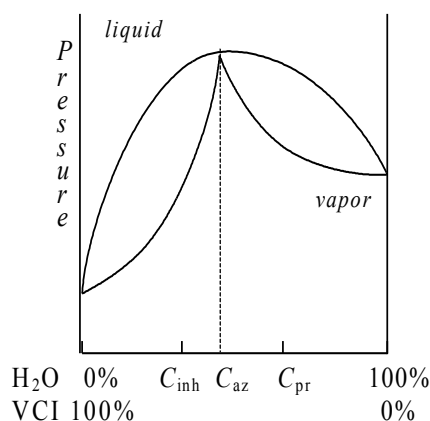
A number of ways to prevent corrosion that is initiated by this mechanism were noted in [22, 23]. One of these involves the use of VCIs that are irreversibly adsorbed on a metal and have a protective residual effect. If a temperature difference on the metal appears occasionally and afterwards the system comes to a near-equilibrium state, this residual effect can protect the article. However, this way does not guarantee that the article will remain protected. However good the VCI's residual effect, a heat-transfer mode initiating corrosion may exist.

Yet another possibility of vapor-phase metal protection under heat-transfer conditions is to use VCIs with  $p^0$  and vaporization enthalpy ( $\Delta H_v$ ) values equivalent to those of water. In such case, the composition of the surface electrolyte is identical to that of the vapor above it. Evaporation and condensation cannot change  $C_{\text{inh}}$  and cause corrosion. As a matter of fact, this way was considered in [19-21]. However, ideal matching of  $p^0$  and  $\Delta H_v$  only occurs in the case of optical isomers, and it is practically impossible to find a VCI that satisfies this condition.

The third, principally new and most promising way for metal protection by VCIs under heat transfer conditions is to use inhibitors that form azeotropic mixtures with water. If one uses such doses of VCIs that are azeotropic with water that their equilibrium concentration ( $C_{\text{inh}}$ ) in the surface electrolyte exceeds the  $C_{\text{az}}$ , no heat-transfer mode initiating corrosion can be found at  $C_{\text{az}} > C_{\text{pr}}$  in the entire possible temperature range of the environment. In fact, irrespective of whether azeotropism is characterized by a maximum (Fig. 2) or a minimum on the “composition – pressure” diagram, a surface electrolyte that meets the condition

$$C_{\text{inh}} > C_{\text{az}} > C_{\text{prot}} \quad (7)$$

can be distilled into the pure VCI and a VCI solution with a concentration of  $C_{\text{az}}$ . If  $C_{\text{az}} > C_{\text{prot}}$ , corrosion initiation is impossible.



**Fig. 2.** “Composition – vapor pressure” diagram for “water – VCI” binary mixtures with an azeotropic point.

The conclusions made in [22, 23] do not imply that a hermetically sealed item cannot be protected from corrosion under particular heat transfer conditions with a VCI that is not azeotropic or does not meet conditions (7). However, the validity of conditions (7) in the entire possible temperature range ensures that the VCI will prevent metal corrosion initiated by heat exchange.

## Conclusions

1. In order to protect a metal in a sealed space above aqueous VCI solutions, it is necessary that an inhibitor concentration preventing corrosion be formed in the surface electrolyte in time  $t$  smaller than the time required to form a corrosion damage area.
2. In incompletely sealed spaces, the surface concentration of the inhibitor ( $C_{inh}$ ) decreases and corrosion is initiated due to VCI evaporation from the system and diffusion of corrosive environment components, including water, into the system. The latter process often determines the duration of vapor-phase metal protection.
3. Heat exchange causes inhibitor redistribution in VCI-protected sealed systems and initiates metal corrosion if the  $C_{inh}$  in the film decreases below the protective concentration. Under these conditions, efficient metal protection is achieved by VCIs that form azeotropic mixtures with water in doses ensuring an equilibrium value of  $C_{inh}$  in the surface electrolyte exceeding the  $C_{az}$ , if  $C_{az} > C_{pr}$  in the entire possible temperature range.

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