Application experience and new approaches for volatile corrosion inhibitors

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Abstract

The efficiency and service life of a wide range of volatile corrosion inhibitors (VCIs) are summarized and discussed. Important data, related to experiences in application of these VCIs, during last 10 years, is presented. It is shown that in most cases ferrous, non-ferrous, and multimetal VCI films, diffusers, and plastic strips make it possible to achieve a high efficiency of corrosion protection of metal parts and equipment during storage, shipping, and application of a wide range of spare parts and equipment in various industries. The existing and new VCI systems presented in this paper allow us to select the most effective type of metal preservation, based on different application conditions with required service life.

New methods allow for a range of VCI applications to be reliably extended into new areas of applications, which are described. These existing and new technologies increase efficiency and service life and decrease the total cost of corrosion protection in Oil & Gas, Military, Automotive, Electronic, Electrical, and other industrial sectors.

Keywords: *corrosion, inhibitors, films, diffusers, efficiency, service life, metals.*

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Introduction

All industries have corrosion problems in atmosphere environments. In most cases the corrosion damages are unpredictable because they depend on a wide variety of environmental and application conditions (Table 1).

Table 1. Classification of Atmospheric Pollution.

Type of atmosphere	SO_2 (mg/m^3)	Cl^- (mg/m^2·day)
Countryside	<0.015	<0.3
City	0.015–0.200	<1.0
Industrial	0.200–0.500	<1.0
Seaside	<0.015	1.0–20.0
Sea	<0.015	>20.0

Some environments also contain other corrosive components, for example, H_2S and CO_2. Depending on concentration of H_2S, relative humidity (RH), and temperature, the concentration of O_2 can be from 8 to 21%. In most cases the RH is also unpredictable and can change the corrosiveness of the environment dramatically. As shown in Figure 1, at RH less than 50% the corrosion rate in most cases is very low.

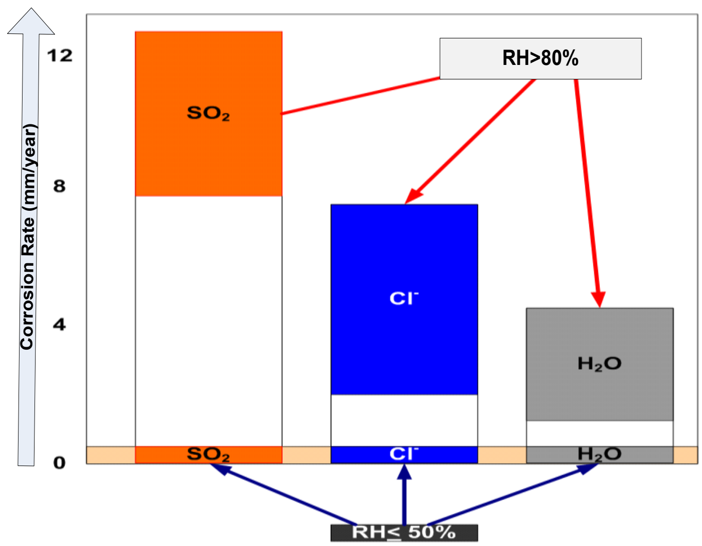


Figure 1. Corrosion rates depend on environment compositions.

But in environments with the same pollutants (composition), corrosion rates can vary widely depending on duration and frequency of changing temperature, pH, properties of corrosion products, *etc.* (Figure 2).

This brief introduction shows how it is difficult to select a corrosion protection (CP) method that will be efficient in all variations of atmosphere/gaseous environments that could happen.

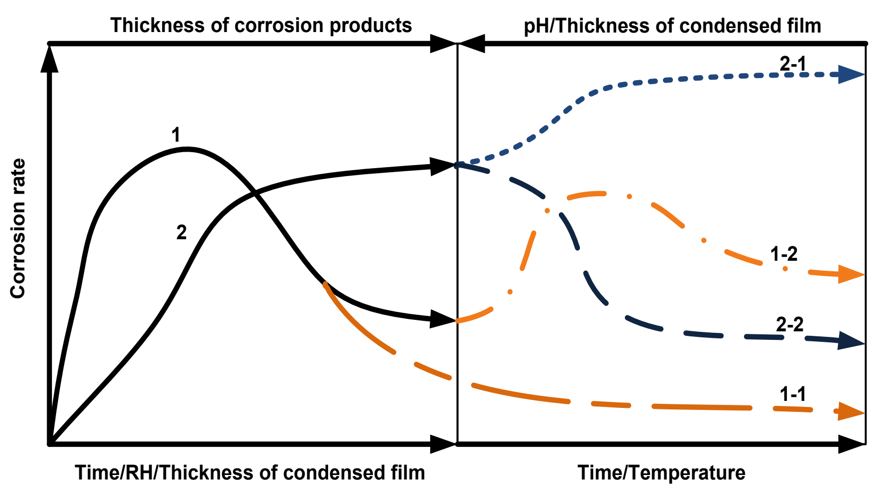


Figure 2. Variations in steel corrosion rates in environments with: *1* - pH>6 (1-1) and pH<6 (1-2); *2* – pH<6 (2-1) and pH>6 (2-2).

A unique CP method in these environments (in these unpredictable situations) is Volatile Corrosion Inhibitors (VCI). When compared with other methods (coatings, dehumidification, vacuum, purging with nitrogen or inert gases, *etc.*), VCI has the following advantages:

1. Allow to achieve the CP by separating ferrous, non-ferrous and multimetal surfaces from the environment by creating a insulating or passivating film, or by decreasing the corrosiveness of environment by using scavenging VCI – environmental conditioners, that removing or decreasing the concentration of the corrosive components in the environment
2. CP can be achieved on inaccessible and invisible surfaces, including in the crevices, where not one of existing methods can be used.
3. The application technology is very simple, the most cost effective, can be used for large and small metal parts and equipment.
4. Can be used in combination with some other CP technologies (coatings, cathodic protection, dehumidification, for example) to increase their efficiency and service life.
5. In most cases exclude the necessity for special cleaning of the metal surfaces before and after using of VCI's.

Thousands of types of VCI compounds are known, but only a fraction of them are acceptably efficient, cost effective, and environmentally-friendly.

VCIs are a class of corrosion inhibiting compounds with a finite vapor pressure (VP). The chemical is delivered through space by the VCI vapor diffusing through the medium and condensing on a metal's surface, creating a protective film. Many types of inorganic VCI compounds exist (for example: nitrite, phosphates, molybdates, *etc.*) that have very low VP. These inhibitors have some advantages (higher service life and more environmentally friendly) and disadvantages (lower radius of protection, corrosion can start before VCI achieves efficiency) compared with traditional VCIs that have high VP.

VCIs are useful in efficient protection systems for ferrous and nonferrous metals. Many of the applications utilize VCI-impregnated polyethylene (PE) packaging, but a variety of other delivery methods have been used. VCIs have unique properties (Figures 3 – 5).

The CP radius depends on the VP of the VCI (Figure 3). The service life of existing VCI systems is in the range of 1 to 5 years, for example. The CP mechanism depends on the VCI compound(s) used and the characteristics of the metal being protected.

With this knowledge and results of laboratory and field tests in different environments, four types of high efficiency VCIs were developed and applied worldwide:

1. Chemicals delivered into a vapor space according to their VP properties
2. Chemicals delivered into a vapor space through association with other "carrier" particles
3. Chemicals acting as scavengers of corrosive contaminants (H_2S, O_2, SO_2) and exclude their permeation into enclosure
4. Chemicals that exhibit both VCI and scavenging effects

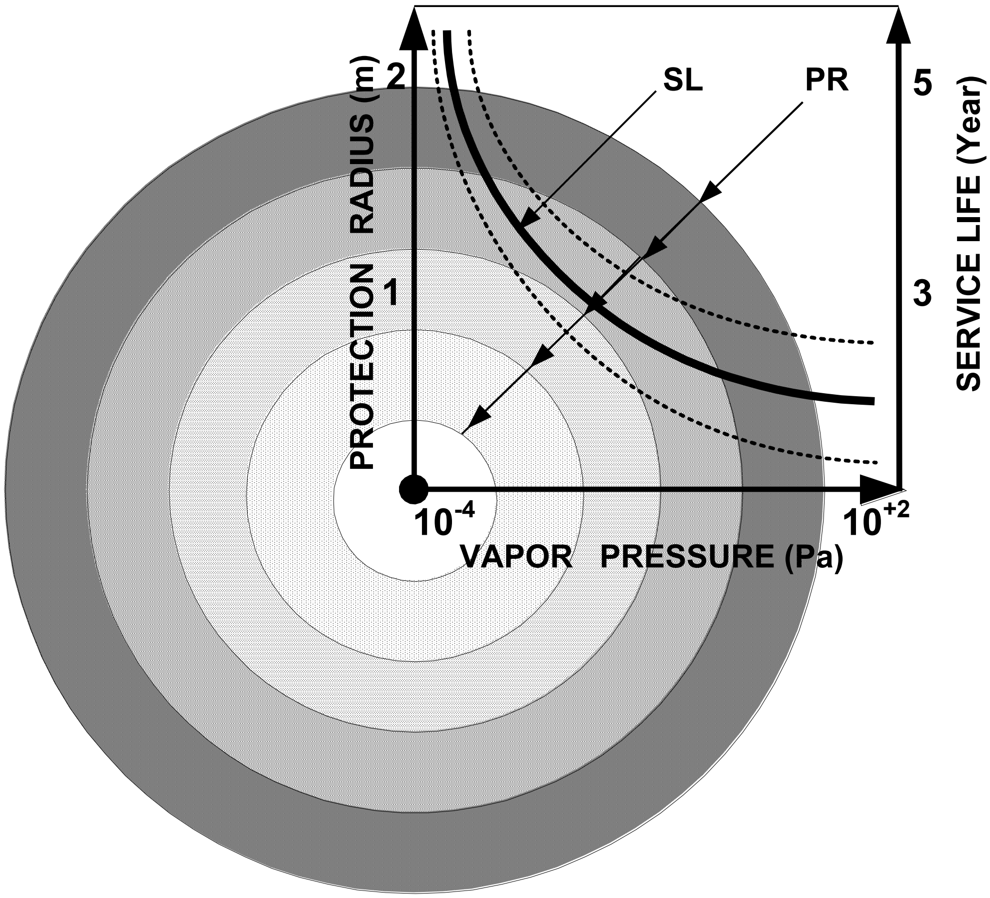


Figure 3. Relationship between corrosion protection radius (PR), service life (SL) and vapor pressure (VP).

Figure 4 shows how different types of inhibitors influence the corrosion process.

When using combinations of different VCIs with low and high VP, high CP efficiency can be achieved that result in significant increases in service life, from 0.6 to 5 years, for example (Figure 5). The VCI with high VP properties starts to provide CP before the corrosion begins. The VCI with low VP properties provides long-term protection, allowing the required service life to be achieved. All above information and world experience were the bases for creating and application VCI technologies that are described below.

Application experiences of existing VCI systems

Combining the information described above with principles of VCI technologies and the sum of our and the world's experiences, we have created many VCI products (Figure 6). Most of these are polymeric films, paper and boxes impregnated with VCI used to make materials for packaging equipment and parts. VCI diffusers are recommended for enclosures and control panels. With the proper application of VCI products, it is now possible to ensure that stored equipment will not undergo serious deterioration. Some of

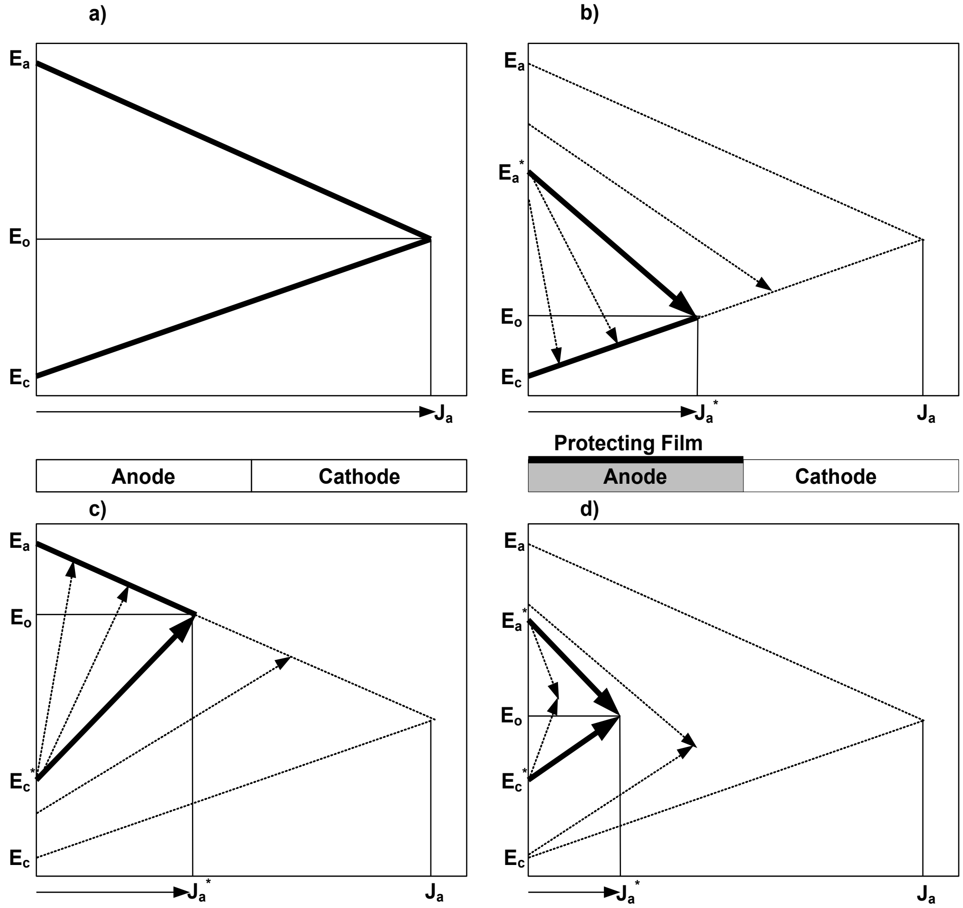


Figure 4. Relationship between corrosion potential (E_0) and current density (J_a) of metals without inhibitor (*a*) and with different types of inhibitors: *b* – anodic, *c* – cathodic, *d* – insulating (or mixed anodic-cathodic). Corrosion rate (CR) is proportional to J_a.

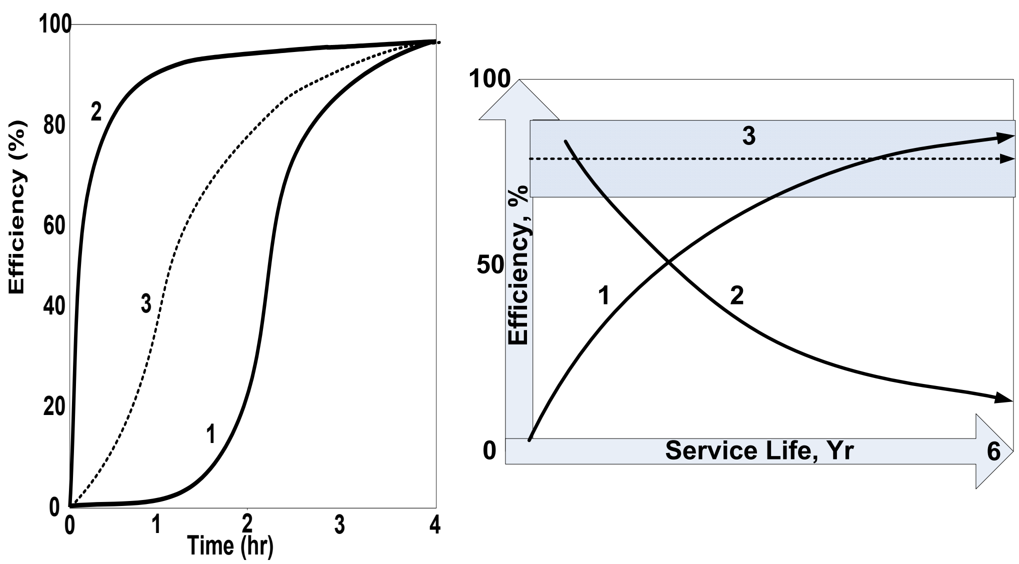


Figure 5. Relationship between efficiency and service life of corrosion protection by using VCIs with low (*1*) and high (*2*) vapor pressure and their combination (*3*).

these products are listed in Table 2. The VCI applications shown in this paper will be useful for most of industries.

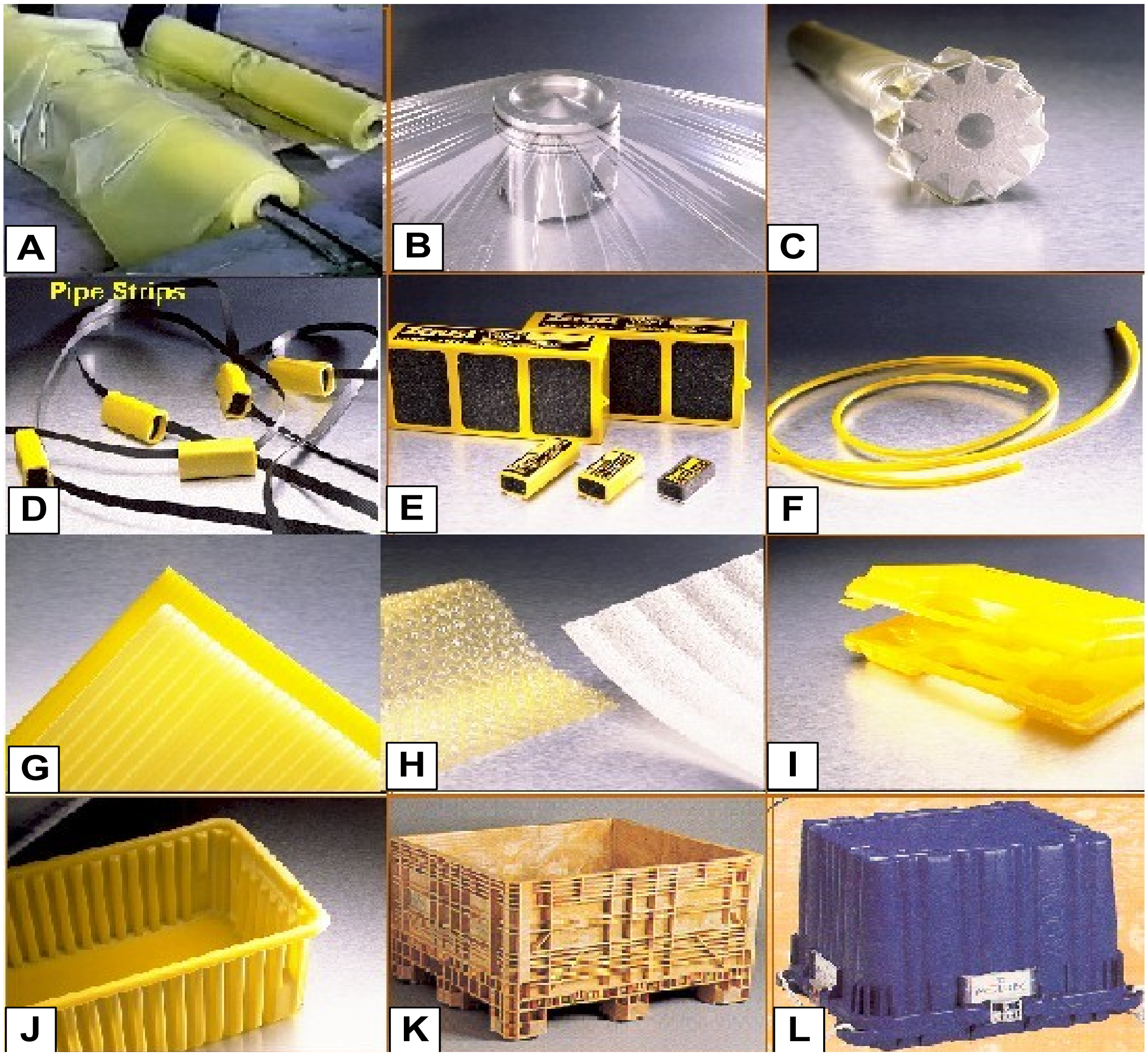
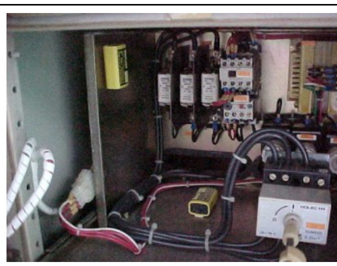
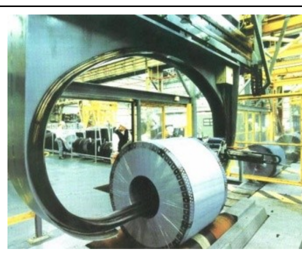


Figure 6. Examples of typical VCI products: A – Film; B – Stretch film; C – Shrink film; D – Strip to protect pipes, tanks, *etc*.; E – Diffusers to protect control panels, equipment, *etc*.; F – Strip to protect pipes; G – Profile board; H – Bubble and foam wraps; I – Injection molded product; J – Dunnage bin; K – Box; L – Box to protect injection molds.

The CP technology depends on the following conditions:

1. the materials, complexity, and size of the equipment,
2. the composition, temperature, and humidity of the environment,
3. the manufacturing technology,
4. the storage, transportation, and application,
5. the required service life and surface quality of the equipment.

Table 2. Examples of VCI application.

Industry – Typical Equipment/Items	
AUTOMOTIVE – Stamping Parts/ Roofs / Doors/ Engines/Components / Crankshafts/ Spare Parts	
 **Engines**	 **Doors**
 Automatic wrapping with VCI	 Skin packaging with VCI
PETROCHEMICAL, REFINERY, *etc.* – Control Panels/ Electrical components	
 Protection of control panel	 Protection of electrical components
STEEL MILL, FOUNDRY, *etc.* – Metal Coils/ Casting Components	
 Automatic wrapping with stretch VCI film	 Engine heads

VCI films are the most widely used technology for the corrosion protection of equipment produced from ferrous, nonferrous, and multimetal alloys. In most cases, components in a clean and dry condition are protected by VCI film.

Packaging films for industrial applications are produced from low- and high-density PE resins and, therefore, resistant to moisture to some degree. Atmospheric moisture will eventually find its way into a film bag. The presence of moisture in a bag can be expected on surface shipments, particularly shipments crossing the equator. Corrosion problems arise when moisture is allowed to enter a VCI bag unimpeded by the film, e.g. through an incorrect closure or a significant hole in the bag. VCI films do not require hermetic sealing. What is required is that the bag be closed such that any air entering the bag must enter through the film, where upon it will be influenced by the VCI in the film. Stapling, taping or folding of the bags is a sufficient closure method. This practice is, however, not always followed. Another instance of an improper closure can occur when shrouds are placed over a part but the shroud is not secured around the part. This permits warm moist air to gain entrance into the shroud, collecting on the surfaces of the part, resulting in severe local corrosion, since the VCI's cannot provide protection in this situation.

Cardboard sheets are often used to separate one row of parts from another in a package. These sheets will absorb moisture in storage and transit and will induce corrosion on the parts surface, which is in contact with the cardboard. The parts surfaces should never be allowed to touch corrugated cardboard, paper, or wood. A sheet of VCI film should be placed between the cardboard surface and the part. A VCI sheet should be placed on the top row of the parts to prevent the cardboard from touching the row of parts immediately below it. Another approach would be to place the cardboard sheet in a flat VCI film bag thereby covering both sides of the cardboard sheet.

Different types of contaminations (dust, oil, fingerprint, *etc.*) increase the danger of corrosion, because the VCI is most effective on the clean metal surfaces.

Many years of application experience of existing inhibiting systems in a wide range of corrosion environments and application conditions (temperature up to 55°C, RH up to 100%, rural, industrial, and sea environments) allow us to recommend the VCI system for CP of metal parts and equipment during storage, shipping, and application in practically all industries. Some examples of existing VCI system applications are shown in Table 2.

Application experiences also demonstrated that too often existing VCI systems are not efficient enough or did not provide the desired service life. There was a need for a system that protects items for longer periods of time than the current VCI methods. These new protection methods should retain many of the advantages of the traditional VCI methods, including self-application of protection and the ability to immediately use the protected item on removal from the protection system.

New approach of VCIs – New corrosion protection systems

As shown above, the CP mechanism depends on the VCI compounds used and the characteristics of the metal being protected. Figure 4 shows how different types of inhibitors can influence the corrosion process. Typically, the corrosion rate depends on the corrosion potential (E_0). Generally, depending on the inhibitor's nature and the metal to be protected, insulating or passivating films can be created on anodic, cathodic, or anodic-cathodic parts of the metal surface. The inhibitors produce changes in corrosion potential and corrosion rate. In some cases, low concentrations of inhibitors can increase the corrosion rate or create dangerous pitting corrosion. The effects depend on many factors such as the metal to be protected and the environmental conditions. In most cases, the best results are achieved by applying insulating or mixed anodic-cathodic inhibitors (Figure 4d). Different types of contaminations (dust, oil, fingerprint, *etc.*) increase the risk and severity of corrosion, because the VCI is most effective on clean metal surfaces. In all cases, the existing VCI system's efficacy and service life depends on temperature, humidity, environmental composition, *etc.* The following is a description of a new and more efficient and much longer service life CP system – the combination of VCI and desiccants.

This understanding allows the best inhibiting systems to be chosen. But, in some cases, for complicated and large metal parts and equipment, the corrosion has different concurrent mechanisms and VCI alone is not sufficient.

The use of desiccants is often used as a CP method. In controlled environments and for periods of time, desiccants are efficient enough and environmentally friendly. But changing temperatures can result in conditions where the moisture level of the desiccant exceeds its saturation point, causing unpredictable condensation. In such situations, desiccants can become a source of moisture and actually increase the possibility of corrosion.

Application experiences show that despite their advantages, both VCIs and desiccants have the following disadvantages:

1. In some environments and in some cases, corrosion can start before the VCI and desiccants begin to work,
2. Efficiency depends on storage and transportation conditions,
3. In many cases, complicated surfaces (equipment with channels, tubes and restricted inner spaces) cannot be protected.

There is a need for a system that provides protection, comparable with current VCI and desiccant methods, of large metal equipment and parts for longer periods of time.

The new methods should retain many of the advantages of the traditional VCI and desiccant systems. These advantages include self-application of protection, as well as immediate use of the protected item upon removal from the protection system.

Additional solutions, described below, can be used to provide enhanced protection when traditional VCI systems are not sufficient.

New Corrosion Protection Method – Two-Layer System

Application Experience

The two-layer systems were created to take advantages of the benefits of both VCI and desiccants (Figure 7).

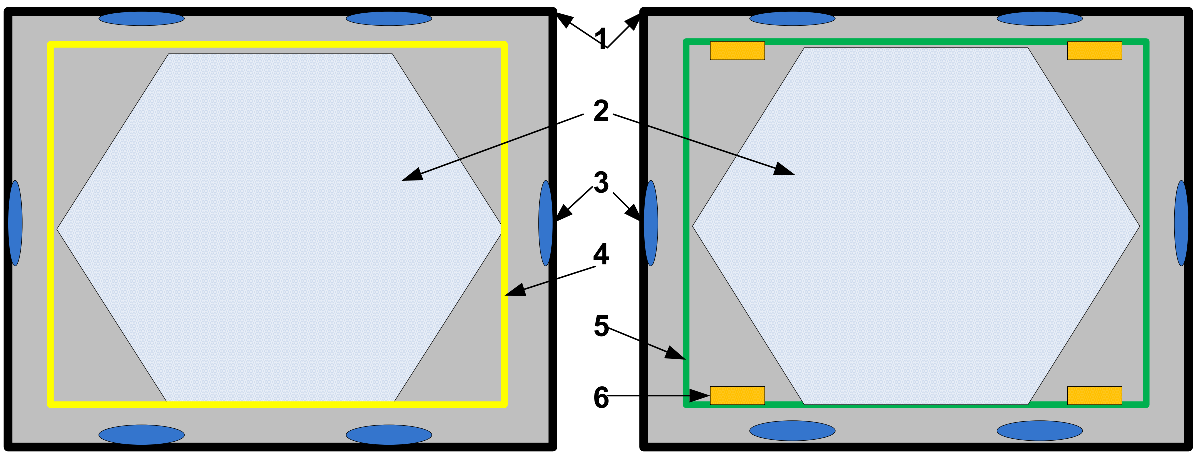


Figure 7. Corrosion protection systems with VCI and desiccant: *1* – barrier, low permeable films or box; *2* – metal part; *3* – desiccant; *4* – VCI film; *5* – desiccant; *6* – Inhibitor (VCI diffusers, devices, powders, *etc*.)

The new two-layer protection systems consists of two enclosures with a combination of desiccant for removing moisture and a VCI system to protect from corrosion when the RH is greater than 50%. The desiccant is placed in the space between the enclosures. VCI is introduced either as part of the inner layer film or as a VCI-containing device placed inside the inner film layer. The desiccant can be easily replaced with minimal disturbance to the protection system.

These systems have the following advantages:

1. The external layer reduces, or eliminates, the introduction of new moisture into the enclosure from the external environment
2. The desiccant absorbs moisture from the space between the layers
3. Because the inner VCI film layer is somewhat permeable, moisture inside this layer passes through this film to the dryer space between the layers and is absorbed by the desiccant. The desiccant works as a pump and pulls the moisture from inside the inner layer.

This process:

1. Decreases the RH by as much as 30%
2. Extends the service life of the system
3. Virtually eliminates the possibility of corrosion inside the VCI layer, even in the most aggressive environments containing Cl^-, SO_2, and H_2S.

This is a two part protection system:

1. The first part excludes the possibility of corrosion by decreasing the RH to less than 50% (See Figure 1).
2. The second step provides CP by VCIs that function only when the RH increases to more than 50%.

To achieve the required service life it is only necessary to periodically renew/replace the desiccant between the layers.

The above summary is the result of numerous experiments performed to understand the efficiency and advantages and to finalize the form of these new CP systems.

The basic results, using carbon steel as the metal substrate, are summarized in Figures 8 and 9 and Tables 3 and 4.

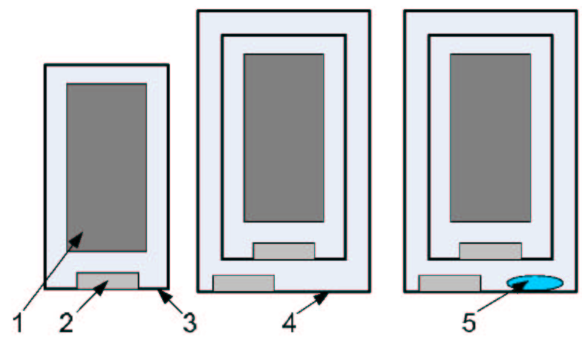


Figure 8. Schematic illustration of testing systems: *1* – metal test specimens; *2* – RH dataloggers; *3* – polyethylene film (either with or without VCI); *4* – low permeable or barrier film; 5 – desiccant.

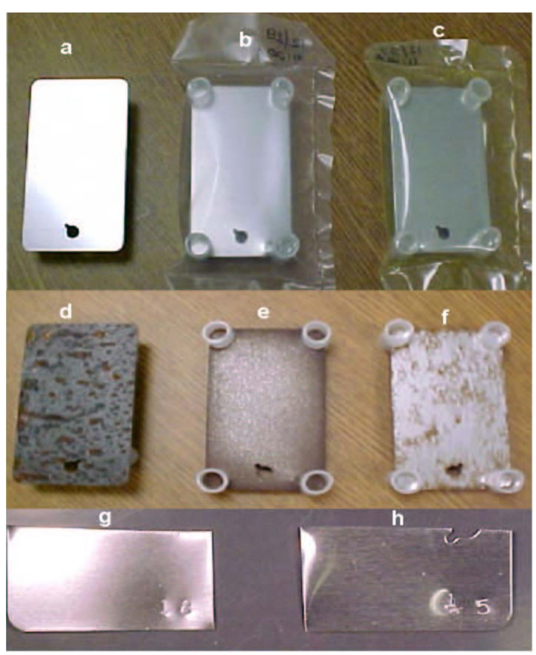


Figure 9. Steel specimens before (*a*–*c*) and after (*d*–*h*) testing: *a*, *d* – unprotected; *b*, *e* – plain PE film; *c*, *f* – VCI film; *g*, *h* – two-layer system.

Table 3. Test specifications and procedures.

#	Test specifications	Test procedure	# of Cycles (Duration, h)
1	Humidity – temperature chamber IEC 68-2-30 (DIN EN60068-2-30)	24-h cycle: 6 h at 25°C, 98% RH 3 h transition from 25°C to 55°C, 95% RH 9 h at 55°C, 93% RH 3 h transition from 55°C to 25°C, 98% RH 3 h at 25°C, 98% RH	14 (336)
2	Tri-gas chamber ASTM G85-98	3-h cycle (98-100% RH): 0.5 h salt spray 0.5 h SO_2 flow of 25 $cm^3/min \cdot m^3$ 2 h soak	80 (240)
3	Tri-Gas Assembly* placed in the humidity – temperature chamber	12-h cycle: 6 h at 25°C 6 h at 50°C Contaminants*: Sodium chloride (NaCl) Sulfur dioxide (SO_2) Hydrogen sulfide (H_2S) RH = 98–100%	60 (720)

*In the assembly, the following aqueous solutions were used to create the indicated environment: 5% NaCl, 1% H_2SO_3, and 0.2% $(NH_4)_2S$.

Table 4. Testing results of efficiency of existing and new corrosion protection (CP) methods.

Test procedure (see Table 3)	CP Method			Time for corrosion to begin, h	Protection efficiency* (%)	RH (%)		
	L1	L2	Desiccant between layers			Chamber	Inside inner layer	Between layers
# 1	VCI	–	–	<48	97	93–98	70–80	–
	VCI	BPE	+	No	100		15–30	10–25
	VCI	BFA	+	No	100		10–30	10–20
# 2	–	–	–	<2	0	95–100	–	–
	PE	–	–	<20	0		–	–
	VCI	–	–	<48	60		–	–
	VCI	BPE	+	No	100		15–30	10–25
	VCI	BFA	+	No	100		10–30	10–20
# 3	VCI	–	–	<20	60	95–100	–	90–95
	VCI	BPE	–	<100	90		90–99	90–99
	VCI	BPE	+	No	100		10–20	12–20

*Protection Efficiency – % of surface area without corrosion products.

List of Acronyms: L1 – inner or single layer, L2 – outer layer, PE – polyethylene film, BPE – barrier polyethylene film, BFA – barrier polymeric film laminated with aluminum foil (12μ).

Thickness of films (μ): PE and VCI – 100, BPE and BFA – 200.

Application Areas and Experience

The new two-layer system provides increased CP of carbon steel, extended service life, and extended range of applications. Similar experiments were carried out using stainless steel, aluminum, copper, and silver.

For the last eight years, the two-layer system has been applied in many situations where existing VCI systems could not be recommended. Some of the experiences received from applications in the most aggressive environments is described below.

The high efficiency two-layer system is used during shipments from India to different countries (Figures 10, 11). The storage and shipping environments are extremely aggressive: RH up to 100%, temperatures from +40°C to –20°C, sea atmospheres, and industrial environments. For most of these equipments, only the two-layer system is efficient and cost effective. The photos clearly show the high quality of the metal parts and equipment when opened after arriving at the destination customer's plant (Figure 10).

Figure 10. Application experience in India. Protected equipment and quality of crankshafts, engine blocks and equipment after shipping

Prior to introduction of the two-layer system, two very big suppliers in India had up to 50% of shipments rejected because of corrosion. For the last 2–4 years, after introduction of the two-layer system, no rejections were seen (Figure 11).

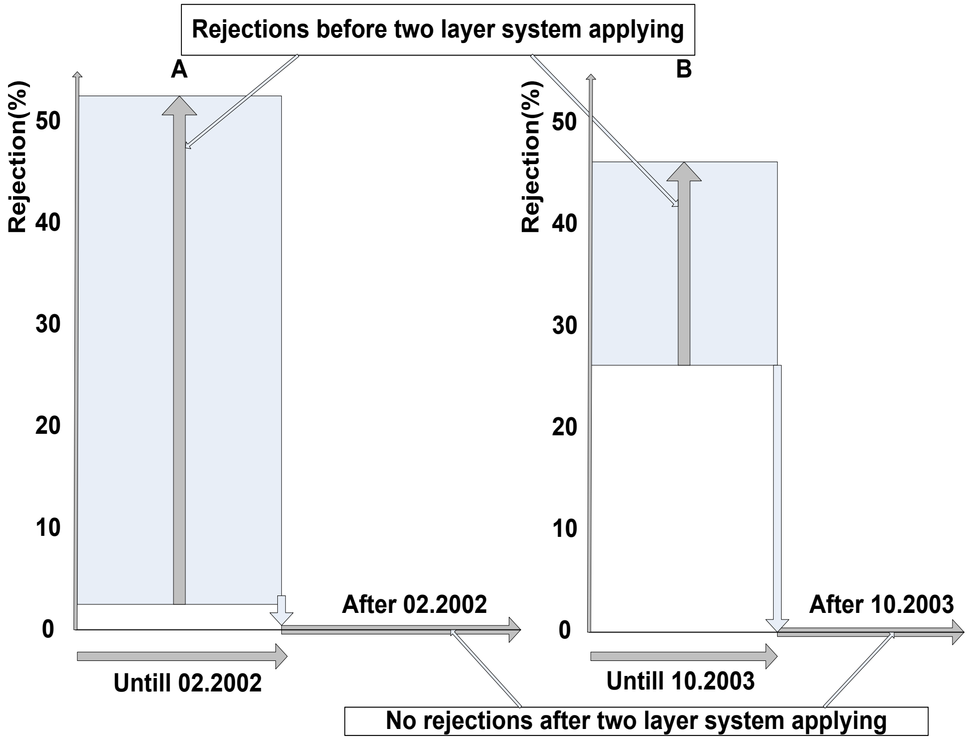


Figure 11. Rejection/rework at delivery customer end due to corrosion before and after suppliers in India applied the two-layer system.

These application experiences allow us to create designs for two-layer systems specifically for application conditions and customers' requirements. The two-layer system allows us to expand the potential for VCI applications to situations that have not been approached before.

According to the results, the new two-layer system can be recommended in many cases. Some potential application areas are shown in Figure 12.

Conclusions

1. VCIs are highly efficient and in many cases provide a unique CP method for critical equipment in corrosive environments.
2. The VCI technology offers attractive cost/performance benefits for customers in almost all industries.
3. The traditional VCI system cannot protect all objects efficiently for long periods of time.
4. The new methods (Two-layer systems) offer a means of protecting valuable metallic and nonmetallic objects.
5. Protection with the two-layer system is effected using a combination of VCI and desiccants.
6. Large equipment or valuable objects, which cannot be allowed to deteriorate, can be preserved for any required service life, for example 10 to 50 years. It only requires periodic replacement of desiccant.

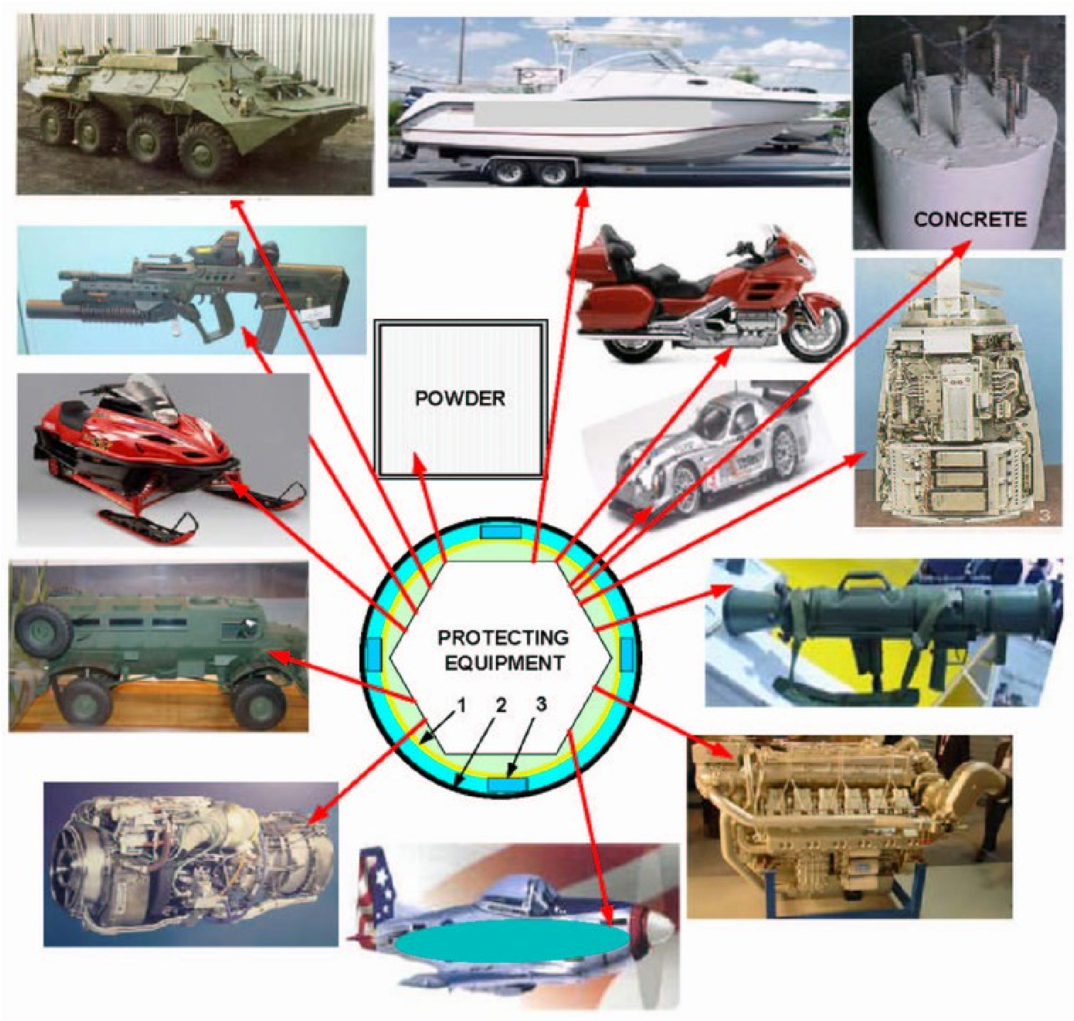


Figure 12. Examples of two layer system application areas.

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