

Review

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Technological applications of volatile corrosion inhibitors

<https://doi.org/10.1515/corrrev-2017-0102>

Received September 1, 2017; accepted November 20, 2017

Abstract: The objective of this review is to create a body of knowledge on the theoretical and practical aspects of corrosion inhibition to prevent and/or to eliminate corrosion in natural environments such as water, air, and acids and in industrial facilities such as oil, natural gas, concrete, paints and coatings, electronics, and military equipment. Corrosion inhibitors (CIs) and volatile corrosion inhibitors (VCIs) are applied in diverse forms such as powders, pellets, aqueous, or solvent solutions and in impregnated papers; closed in pouches and sachets; and added to coatings. Natural CIs are extracted by water or organic solvents from suitable plants. They represent the advanced trends of corrosion management based on green chemistry.

Keywords: corrosion; corrosion inhibitors; environments; industries.

1 Introduction

Inhibition, in general, is a process aimed to restrain an activity in natural and industrial areas. In medicine, inhibitors arrest the action of an organ or a tissue in the human body, e.g. they bind to enzymes to decrease activity. Recommendations for the application of norms of inhibition are recorded in psychology manuals to improve human behavior. In water, scale inhibitors maintain salts in solution to avert deposits of mineral scale. In this work,

inhibitors used to prevent, avoid, or mitigate corrosion processes and events are reviewed.

Corrosion and pollution are pernicious problems that affect environment quality, industrial efficiency, and infrastructure assets (Raichev et al., 2009; Hummel, 2014). Many pervasive pollutants produced by power stations burning fossil fuels accelerate corrosion, and corrosion products such as rust, oxides, and salts pollute bodies of water (Raichev et al., 2009; Valdez et al. 2012).

The aim of this review is to build a body of knowledge on the theoretical and practical aspects of corrosion inhibition, useful for the selection of VCIs to prevent and to eliminate corrosion in natural environments and industrial facilities.

The economic and social relevance of the corrosion management and control industry is evident in the activities of diverse international and national professional associations and R&D institutions dealing with all aspects of corrosion science, engineering, and technology such as the World Corrosion Organization (WCO), NACE International the Worldwide Corrosion Authority, with its central office at the USA; the European Federation of Corrosion (EFC), CEBELCOR, Centre Belge d'Etude de la Corrosion; and many national organizations operating in industrial and developing countries. In the annual NACE conferences, the subject of CI is widely treated. For instance, in the 2016 Conference, technical symposium research on corrosion inhibition by volatile corrosion inhibitors (VCIs), on corrosion control in oil and gas production with inhibitors, on coatings containing inhibitors, and on inhibitors for water reuse systems was presented. Furthermore, the importance of the dissemination of corrosion information is demonstrated by the numerous journals published in several languages. It is worthwhile to note that one journal is jointly dedicated to corrosion and scale inhibition. In this collection of *Corrosion* journals, it is appropriate to include the NACE International Corrosion Press, a newsletter that presents information on corrosion events and their curative treatment and offers solutions to current corrosion problems. Every 5 years, European Symposium on Corrosion Inhibitors is held at Ferrara, Italy, organized by the European Federation of Corrosion.

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2 Volatile corrosion inhibitors

This review presents VCI as an economical and useful tool to control corrosion in environments such as water, air, soil, acids, and road deicing; in industrial facilities such as oil, natural gas (NG), chemicals, concrete, and electronics; and in marine and prolonged protection of military equipment.

The use of VCI or vapor phase corrosion inhibitors (VPCI) has rapidly expanded in the last decades; in particular, a special type called VPCI was also designed as VCIs. VCIs slow the rate of corrosion reactions when added in relatively small amount to a corroding system. Corrosion inhibitors are classified into the following categories:

- anodic inhibitors, which retard the anodic corrosion reaction by forming passive films;
- cathodic inhibitors, which suppress cathodic reaction, such as reduction of dissolved oxygen (DO);
- mixed inhibitors, which interact with both anodic and cathodic reactions; and
- adsorption inhibitors such as amines, oils, and waxes, adsorbed on the steel surface forming a thin protective film and preventing metal dissolution.

VCIs contain organic and inorganic chemical compounds able to vaporize and condense in the presence of moisture-forming thin films on metallic surfaces. The development of these thin films and how the metallurgical and microstructural aspects of steel play a role in the corrosion mechanism are described in learned publications (Raja et al., 2003; Bastidas et al., 2005).

Sometimes, VCIs are impregnated in plastic bags and cover films or kraft wrapping paper, closed in pouches and sachets, or utilized in the form of powders or pellets. Kraft paper is made from chemical pulp that was produced through kraft process, a sulfate process that converts wood into pulp; this is the most widely used process. The process differs from normal paper production, for the solution used to convert wood into wood pulp consists of water, sodium hydroxide, and sodium sulfide. In addition, VCIs are also formulated in liquid aqueous or oil solutions, which can be sprayed over the metallic surfaces to protect. Some corrosion mechanisms focus on the thermodynamics and kinetics of the protection provided by the VCIs. The electrochemical nature of most corrosion processes requires similar mechanisms for the VCI performance during the corrosion inhibition. Ions or heteroatoms such as oxygen (O), sulfur (S), or nitrogen (N) contained in organic molecules such as amines, aldehydes, alcohols, carboxylic acids, and thiols among others and even π bonds enhance the adsorption

of protective films on the metallic surfaces (Subramanian et al., 2000). Volatilization capability of the inhibitor substance is one of the most important factors for an efficient corrosion inhibition. Volatile chemicals such as morpholine and hydrazine are added into boilers and transported by steam where they neutralize carbon dioxide or increase the pH rising alkaline value to protect condenser pipes from corrosion. In closed spaces, volatile cyclic amine salts are used as VCIs, as their vapor condenses and hydrolyzes with the moisture, releasing protective ions that interact with the metal surface (Roberge, 1999).

VCIs volatilize into the air and inhibit corrosion on metallic materials and metal-based products, particularly during shipment and storage. They are cost-effective and help conserve resources, then they are incorporated into packaging materials (McConnell, 2008).

The corrosion rates of reactive metals, e.g. Fe, are decreased by a modification of their surface with the mentioned organic molecules. This is the useful function of adsorbed VCIs. Their inhibition efficiency (IE) might reach 98% including degradable, non-toxic, natural VCI. The era of green VCI has already started (Costa & Marcus, 2015).

Types of VCIs include nitrite of amines, amine carboxylates, heterocyclic compounds (thiazole, triazole, pyrrole, mercaptans, imidazoline, etc.), carboxylic acid esters, amines, acetylenic alcohols, and the mixtures or reaction products of these substances. Currently, the use of certain amines and nitrites has been prohibited by environmental and health regulations, as they can form nitrosamines, which can produce cancer. Figure 1 shows the structures of some typical VCIs.

VCI is a modern and economical technology for the reduction of corrosion. Its importance is evident by the patents gathered in a recently published review (Inzunza et al., 2013).

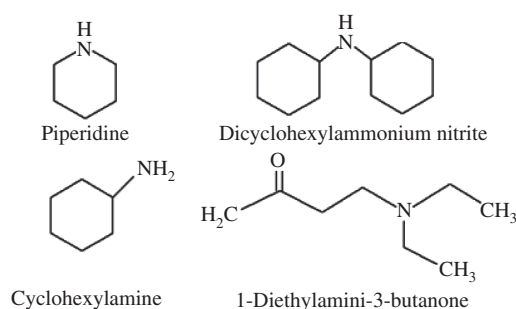


Figure 1: Chemical compounds used for the production of volatile corrosion inhibitors.

3 Green corrosion inhibitors

The advanced field of green chemistry, also known as sustainable chemistry, involves the design of chemical products and processes that reduce or eliminate the generation and use of hazardous substances as by-products. Sastri deals in his book “Green corrosion inhibitors: theory and practice” with CI adsorption on metal surface and its corrosion inhibition mechanism in different media: acid, neutral, and alkaline. The book presents guidelines for testing the toxicity, biodegradation, and bioaccumulation of CIs; standards for their environmental testing; and models to use in industrial practice. Sastri calls the environment-friendly CIs “green” but toxic CIs are termed “gray”. An additional classification of CIs considers them as hard, soft, and borderline (Sastri, 2011).

Sharma has published an advanced book entitled “Green corrosion chemistry and engineering: opportunities and challenges” addressing the conflicts of societies and economies associated with corrosion problems and their real solutions and presenting an up-to-date overview of the progress in corrosion chemistry and engineering but emphasizing the aspects of “green” chemistry. Green chemistry technologies provide numerous benefits: safer products, depressed waste, saving critical resources such as water and energy, and improved chemical manufacture.

Two primordial chapters – “New era of eco-friendly corrosion inhibitors” and “Green corrosion inhibitors status in developing countries” – are devoted to the fundamentals and application of CIs. The author deals with the diverse types of CIs such as anodic, cathodic, and mixed inhibitors; VCI; and precipitation inhibitors. Natural products mainly extracted from vegetables are considered green CIs. Sharma describes recent research and progress in these CIs and their uses in developing countries. Corrosion inhibition processes and CI practical utilization are the core and the essence of this book. Furthermore, the book promotes the research for newer inhibitors for diverse applications (Sharma, 2012). Sastri has focused his book on green VCIs covering all aspects of basic principles and their modern application, with a full range of topics on the environment and industries as presented in this detailed review. He presents two types of green VCIs: based on amino acids and those extracted from natural plants. Other VCIs are produced to combat atmospheric corrosion (Sastri, 2011).

Petroleum-based VCIs are replaced by VCIs obtained by extraction with solvents derived from vegetables such as soy and canola oils. These VCIs are biodegradable, contributing to maintain a healthy environment (Kharshan & Cracauer, 2011).

Eco-friendly VCIs, also known as “green” CIs, devoid of toxic components and biodegradable, are extracted from plants and presented in a large, learned paper (Kesavan et al., 2012).

Another group of non-toxic and biodegradable VCIs has been proven effective in controlling the corrosion of steel, stainless steels, iron, aluminum and its alloys, copper, and steel in concrete structures. This report provided a focused definition of sustainable development (Sharma et al., 2008).

VCI packaging in the worldwide market trend includes recycled Kraft paper, which is reprocessed after use and has biodegradable and non-toxic properties.

4 Applications of volatile corrosion inhibitors

4.1 Atmospheric corrosion

Carbon steel is the main material employed for the fabrication of equipment that should be manufactured, transported, and stored under aggressive atmospheric conditions in tropical, arid, sandy, rainy, and humid regions.

Subramanian et al. (2000, 2002) report on the examination of the atmospheric corrosion resistance of steel, copper, and brass machinery supported by the application of octylamine, a VCI that has antibacterial properties. When equipment processes are wrapped with octylamine impregnated kraft paper, the corrosion IE is 80% for all three metals.

A special VCI is produced by impregnation of 20% amino-carboxylate CI (ACCI) into kraft paper, obtained by applying a particular process for production of pulp paper. Experiments were carried out to assess the effectiveness of kraft paper, wrapping them around polished steel plates and placing them in a humidity chamber with 100% humidity level during 5 days. Amino-carboxylate of 5% has the best effect on corrosion protection (Valdez et al., 2017).

Kumar tested the efficiency of four VCIs regarding carbon steel under different atmospheric conditions at 40°C under high relative humidity containing 3.0% NaCl. IE was in the following order: n-capryli acid > n-butyric acid > 2-amino benzothiazole > N,N-dimethyl propylene urea (Kumar et al., 2013).

Temporary protection of carbon steel surfaces during transport and storage was achieved by applying a VCI, bio-piperidinium-menthol-urea (BPMU). Atomic force

microscopy (AFM) examination showed that the interaction between the steel surfaces and VCIs generated an adsorption protective film (Zhang et al., 2006).

Thermally stable VCIs absorbed on porous inorganic substrates, such as zeolites and diatomaceous earth, provided protection against corrosion during transport and storage. The VCIs studied were dicyclohexylammonium p-nitrobenzoate and phosphate. These VCIs reduce the corrosion rate (Estevao & Nascimiento, 2001).

4.2 Water supply

Fresh water comes from rain and snow. It is gathered in lakes and rivers, which are the sources of potable water for human consumption. They contain total dissolved solids (TDS) including chlorides, sulfates, and phosphates. Water is conveyed by pipelines made mainly of carbon steel, which suffer from corrosion. Water quality and its influence on human health depend on the pipeline performance and whether it is free from corrosion, scaling, and fouling. CIs are applied in sectors of the water industry such as cooling waters in power stations, desalination plants, potabilization plants, waste water reuse facilities, pollutants and microorganisms removal, and after sanitation and disinfection operations.

The CIs applied in several industrial cooling water systems are shown in Table 1 (Sastri, 2011, Garcia et al., 2013).

4.3 Acid corrosion inhibition

A great variety of acids, sulfuric, nitric, hydrochloric, hydrofluoric, phosphoric, acetic, sulfamic, citric, and

formic, are broadly applied in environments and industries: water purification, fertilizers production, mines excavation, mineral leaching, food production and processing, metals cleaning and pickling and acidizing petroleum wells and refineries distillation, fracturing of shale gas matrix, and more (Schorr & Valdez, 2016). The acids undergo ionic dissociation in water forming hydronium ion and an anion:



The acids attack carbon steel:



Well-acidizing procedures are required in the oil, gas, and geothermal drilling industry to improve productivity. HCl is employed at various concentrations (depending on the reservoir characteristics) leading to acidic corrosion of steel, thus effective CIs are employed such as acetylenic and propargyl alcohols. Surfactant chemicals are added to assist in the formation of protective adsorbed films (Jackson, 2016).

HCl and H_3PO_3 are the main acids selected for pickling of steel equipment such as body cars in the automotive industry. The CIs used are mixtures of nitrogen-bearing organic compounds, acetylenic alcohols, and sulfur containing organic molecules. Commercial CIs were available and dissolved in water or organic solvents (Sastri, 2011).

An innovative research describes the use of Schiff base compounds as CI for carbon steel in acid media. Quantum chemical calculations were conducted to determine the relationship between IE and the molecular structure of the CI. The Schiff base molecules were adsorbed on the steel surface providing corrosion resistance (Ju et al., 2017; Jw et al., 2017).

Table 1: Corrosion inhibitors for cooling waters.

Cooling water	Corrosion inhibitors
Engine coolants	– Molybdate – Molybdate with nitrite; molybdate, arsenite, or arsenate and benzotriazole along with borate/phosphate/amine – Nitrite, nitrate, phosphate, borate, silicate, benzoate, aminophosphonate, phosphinopolycarboxylate, polyacrylate, hydroxybenzoate, phthalate, adipate, benzotriazole, tolytriazole, mercapto-benzothiazole, and triethanolamine are combined with molybdate. In glycol, 0.1–0.6 wt% of molybdate is used.
Closed recirculating cooling water	– 200 ppm sodium molybdate with 100 ppm of sodium nitrite – 50 ppm molybdate, 50 ppm phosphate, 2 ppm Zn^{2+} – 40 ppm sodium molybdate + 40 ppm sodium silicate – 2-phosphonobutane-1,2,4-tricarboxylic acid and Polyvinylpyrrolidone
Cooling water of steam plant boiler waters	– Molybdate with an aluminum salt and thiourea – Mild steel corrosion inhibition in boilers by a mixture of sodium molybdate, sodium citrate, manganese sulfate, polymaleic acid, and morpholine – Protection of mild steel in hard water boilers by sodium molybdate and sodium nitrite

The corrosivity of industrial phosphoric acid (PA) solutions of different concentrations depends on the chloride and the fluoride contents and the conditions of their use. Various investigators have proposed to employ organic compounds as CI to protect steel equipment in PA solutions, as follows: acid extracts of piper guanines, by Oguzie (2012); piperidine derivatives, by Ousslim (2014); N-containing organic compounds, by Zarrouk (2013); and benzotriumehtyl ammonium iodide, by Li et al. (2011). Full details are given in their articles listed in the references previously mentioned.

4.4 Corrosion inhibitors extracted from vegetables

In the past, people living around jungles and forests discovered and extracted active biomaterials from trees and shrubs and used them to prevent and cure diseases and to relieve pain, improving the quality of their lives. Nowadays, the pharmaceutical enterprises, with their sophisticated chemical laboratories, synthesize their drugs and remedies, sometimes similarly to natural medicines.

Following the actual trend of “green” chemistry, natural CIs are extracted from suitable plants, mixed, and applied in corrosion control industry. Numerous commercial vegetables, e.g. tobacco, are involved in the production of these novel CIs.

The tobacco industry comprises many products: dried tobacco leaves, stems, dust, liquid extracts. The use as CIs is based in their addition to steel coating, to increase their ability to protect against corrosion. Many countries grow tobacco; the residues are considered for anticorrosion activity (Von, 2008).

Inulin is an extract from the roots of the chicory plant, used as a particulate CI mixed with an aqueous acid solution; the fluid is introduced into a well or supplied to a pipeline. The particle size of inulin is in the range of that of powder. It may be suspended in liquid for ease of handling, e.g. water or oil, depending on its application. The concentration range of inulin is from 0.01% wt/vol to 5% wt/vol of the aqueous acid solution (Choudary et al., 2012).

Laboratory investigations were performed to assess the use of aqueous and ethanolic extracts from plants encountered in the arid regions of the State of Baja California, denominated as Creosote bush (*Larrea Tridentata*) and *Pachycormus discolor*, in HCl solutions. The inhibition action of ethanol extract of the Creosote bush in HCl aqueous was evaluated and found to be effective on carbon steel surfaces. HCl is employed for pickling and also in removing carbonate scales from steel surfaces (Inzunza et al., 2013; Inzunza, 2014).

4.5 Electronics industry

The worldwide electronics semiconductor industry produces microelectronics devices essential for the manufacture of digitally controlled televisions, telephony, radio, transmission equipment, instruments, vehicles, aircraft, and watercraft.

Advanced sensors and actuators are installed in autonomous vehicles, robotics, smart homes, machines, instruments, satellites, etc. Today, there is no human activity, industrial production, energy generation, water supply, transportation and communication, infrastructure maintenance, health care, or economy management that is not provided with electronic equipment.

Many metals and alloys, silver, copper, gold, aluminum, are applied in the fabrication of these devices. The indoor environment of manufacturing plants requires the control of conditioned air by the use of EPA filters to avoid penetration of corrosive pollutants. VCI sprays, emitters, or impregnated plastic and paper films are employed to protect against corrosion. The main pollutant is hydrogen sulfide (H_2S), which tarnishes silver devices, producing silver sulfide and altering the electronic behavior of the components. The combined use of chemical filters and VCIs improved the corrosion protection of copper and silver components in microchips manufactured at clean room conditions in a semiconductor plant.

The use of filters to trap chemicals in a TV manufacturing plant located in Mexicali, Mexico, was not enough to avoid the inlet of H_2S , which raised concentration above the 100 ppb causing corrosion on silver surfaces. To control this silver corrosion, VCI Vappro (Vapour-phase-protection) 870 (Magna International Pte Ltd., Singapore) (trade name), was sprayed on silver electronic devices. The VCI product prevents corrosion in silver components, which retain their electronic properties and the ability for wave soldering process (Valdez et al., 2003, 2012).

Chemical mechanical polishing (CMP), also called planarization, is applied to remove materials from the surfaces of microelectronic device wafer. Several patents are available on CMP, which contain mixed CI and colloidal silica. Other CIs based on sarcosine are utilized to protect printed circuit boards (Saji, 2010).

4.6 Petroleum industry

Petroleum is a mixture of hydrocarbons, extracted together with water, salts, and gases from wells. Water contains corrosive agents: CO_2 , H_2S organic acids, chlorides, and sulfates. Wells with H_2S are called sour wells, and sweet wells

are those with CO_2 (Sastri, 2011). The petroleum industry consists of a complex system of operations, starting with crude oil extraction from wells, onshore and offshore; its conveyance by pipelines to treatment plants; and its refining to produce many oil derivatives such as gas, gasoline, kerosene, naphta, and asphalt (Garcia, 2015).

The applied CI includes organic compounds containing nitrogen, such as aliphatic salty acid derivatives, imidazoles, and quaternary ammonium compounds.

Oil refineries apply fractional distillation to produce diverse derivatives, with gasoline as the most valuable. Wet corrosion is controlled by applying passivating, neutralizing, and adsorption types of VCI. During oil refining, corrosion augments due to the formation of HCl , H_2S , CO_2 , and O_2 . The acids are neutralized by the addition of alkali to reach a pH level of 7.0–7.5 (Saji, 2010; Inzunza et al., 2013).

Gasoline contaminated with water causes corrosion in transport systems and motor vehicles, which is treated with VCIs formulated with esters of carboxylic or phosphoric acid, following the regulation in accordance with NACE TM-01-72 and ASTM D6651 (Sastri, 2011).

Corrosion control of the carbon legs of an offshore oil platform was effected using VCI as powder, contained in a string of closed pouches, suspended in hangers in the space adjacent to the legs (Al-Sayed et al., 2014).

Crude oil is transported from the producing countries to the consuming countries in petroleum steel tankers. They are cheaper and more efficient than submarine pipelines. In their trip back, the tanker holds are filled with seawater to provide adequate stability. A VCI, VAPPRO 844 (trade name), is added to seawater as powder, which is converted into a colloidal suspension of nanoparticles dispersed in the water and adsorbed on the steel surface, forming a thin, protective film (Cheng et al., 2016).

4.7 Natural gas industry

NG is a source of energy for industrial, residential, commercial, and electrical applications; it is also a source of raw material for the polymers and plastic industry. The sectors of the NG industry are drilling, production, storage, transportation, and distribution; all suffer from corrosion. NG is extracted from land and marine wells, containing salty and briny water and corrosive gases, H_2S and CO_2 (Schorr et al., 2006).

The main engineering materials for construction of NG industry facilities are steel and concrete; for ports, wells, pipelines, marine platform, liquefied NG regasification plants and storage plants. Corrosion control is

managed by applying technical processes for selection or corrosion-resistant material for equipment and facilities construction, protective paints and coatings, cathodic protection, and VCI. Many types of CIs are used: anodic, cathodic, film forming, scavengers for annihilation of H_2S or oxygen (Valdez et al., 2015).

Multicomponent mixtures of CI and amine carboxylates based VCIs are mixtures of inhibitors employed in NG depending on the characteristics of the NG systems, water content, and operation temperature (Sastri, 2011; Inzunza et al., 2013; Garcia, 2015).

The formation of black powder, constituted by corrosion powders, iron sulfides, iron oxides, and iron carbonates produced by corrosion attack of H_2S , CO_2 , and O_2 in wet NG, has been detected in NG pipelines. Application of a combination of VCIs, more effective dehydration, and process control contributed to the solution of this problem (Olabisi, 2017).

4.8 Concrete corrosion

Concrete is a composite material, useful for structures in ports, airports, roads, bridges, stadia, etc. It is made of a mixture of water, portland cement, sand, and mineral aggregates. Steel reinforced concrete is generally very durable; nevertheless, concrete infrastructure, in particular, in marine environments, can undergo visible damage due to penetration of seawater, reaching the steel reinforcement. Concrete structures require expensive maintenance programs, which include cathodic protection, paints and coatings; therefore, CIs and VCIs are considered appropriate protection alternatives. Accordingly, VCIs are inserted into concrete structures, either during construction or after their finishing. Preferred VCIs are amine carboxylates cyclohexylamine nitrites, benzonates, and carbonates (Inzunza et al., 2013).

Calcium nitrite is a widely used VCI in concrete as it provides protection in the presence of chlorides; it does not affect the properties of concrete and is available for commercial utilization. $\text{Ca}(\text{NO}_2)_2$ promotes the formation of a protective oxide film on the steel rods. Although nitrites have a good performance as VCIs, their use is regulated by environmental laws and VCI formulations must be designed nitrite-free. Other CIs that have been found effective are benzoates, molybdates, borates, amines, and esters (Sastri, 2011).

During harsh winters in the northeastern states of USA and the north European countries, plentiful snow falls on roads and highways, freezing into ice. Salts and chemicals are spread on the snow to decrease the freezing

temperature, to prevent freeze-thaw cycles, and to avoid road accidents. These corrosive, deicing chloride salts damage the road steel reinforced concrete and corrode the metallic parts of cars and trucks bodies. Corrosion inhibitors, artificial and natural (extracted from vegetables), are added to the deicing products to prevent, avoid, and/or mitigate corrosion (Augst et al. 2016). The deicers, NaCl, CaCl₂, MgCl₂, have an environmental impact as they might leach into the soil; become toxic to humans, animals, and plants; and reach water bodies. VCIs produced by Magna International Singapore have been evaluated to know about their performance in inhibiting corrosion when used as deicing salts. The behavior of these VCIs has been studied in laboratory-simulated tests of road deicing conditions (Salinas et al., 2017).

4.9 Military equipment

The combat fields of modern wars, including the struggle against global terrorism, are localized in diverse, harsh regions: tropical, desert, arctic, marine and urban, with varied weather conditions, which adversely affect the corrosion resistance of the equipment, weapons, and vehicles involved. A significant development for corrosion control in the military services is the establishment of a central institution to serve the US Armed Forces. The US Department of Defense Office of Corrosion Policy and Oversight maintains a Web site, CorrDefense.org, which features contents on corrosion and corrosion control of military facilities, equipment, and weapons with the active participation of NACE International and the support of the North Atlantic Treaty Organization and the National Aeronautical and Space Administration (Corrdefense Electronic Magazine, US Department of Defense, 2002).

Parts of the equipment are kept in closed paper or polymeric envelopes and films or in cardboard boxes or wrapped with cotton canvas, well impregnated with a VCI. Sometimes, the parts are also sprayed with a VCI, depending on their size and shape. For long-term storage of vehicles and weapons, polyethylene, vinyl, and canvas tarps wetted with a VCI are used as covers, which also provide protection from ultraviolet radiation, humidity, rain, snow, dust, and mold. The covers are easy to install, are resistant to climate factors, and are durable (Cheng et al., 2016).

VCIs act by slow ions release mechanisms interacting with humidity, within a sealed airspace, vaporizing volatile anticorrosive compounds, which are deposited on the metal surface in ionic form. If the container is opened and reclosed, the inhibitor continues protecting the military equipment (Miksic et al., 2004; Bastidas et al., 2005).

4.10 Coatings, paints, and films

Coatings and paints applied on a metal surface form a barrier that impedes the access and action of the environment corrosive factors and are old tools for anticorrosion protection. Today, CIs are integrated into the coatings and paints or are deposited as a thin protective film. Furthermore, “smart” coatings provided with nanoparticles can release CI on demand and then an electrical or mechanical control signal is applied to the coatings. Such coatings are utilized in the aircraft industry, where CIs and the conversion coatings are able to detect pitting corrosion initiation. Organic-inorganic hybrid composites are employed in this methodology (Saji, 2010).

VAPPRO VBCI 830 (a trade name) is impregnated in a mineral stone paper that is utilized and settled on the metal surface. The mineral paper contains a mixture of CaCO₃, SiO₂ powder, and VCI. Unlike pulp-based paper, this stone paper is UV-resistant and antistatic. It combines corrosion protection and packaging (Magna International, 2016).

VCIs form adsorption layers of different thickness for the protection of high-precision tools in electronic, radio, and electronic equipment, where some VCIs form nanosized layers. Copper is the most important material in those industries due to its high electrical and thermal conductivity. To inhibit copper corrosion, benzotriazole and heterocyclic derivative molecules were used and their performance was based on the formation of an insoluble film on the copper surface (Andreev & Kuznetsov, 2005; Dehaghani, 2016).

Certain VCIs generate passivation films on steel, in particular, those able to vaporize and react with the steel surface. This mechanism was investigated by polarization electrochemical methods and electrochemical impedance spectroscopy (EIS). Figure 2 illustrates the formation of a protective film that contains VCI molecules, closed with a paper film that carries VCI, too. Carboxylates, amines, and azoles form a protective film in neutral and alkaline solution. The passivation mechanism strongly depends on the pH solution (Rammelt et al., 2009).

5 Evaluation of VCI performance

The VCI performance is evaluated following practices and standard methods to determine vapor inhibitor ability (VIA). The most commonly used is 4031 described in the federal standard FED-STD-101. Some practices applied to evaluate VIA are based on the above-mentioned method like the NACE TM0208-2013 or the German test method

Table 2: Test methods for evaluation of VCI performance.

Test method	Specimens materials	Cleaning	Test chambers	Control chamber	Test solution Glycerin/water	Saturation period (h)	Heating time	Condensation time (h)	Cycles	Evaluation
FED-STD-101 Test Method 4031	Carbon steel QQ-S-698 condition 5	Described	3	1	26% by volume of glycerin in water	20 h (at $22 \pm 3^\circ\text{C}$)	–	3 at room temperature, add cold test solution at 4.4°C	1	Visual
NACE TM0208-2013	Carbon steel UNS G10100 (or UNS G10180) or cooper ASTM B15210	FED-STD-101 Test Method 4031	3	1	26% by volume of glycerin in water	20 h (at $22 \pm 3^\circ\text{C}$)	5–20 s in warm bath water at $50 \pm 2^\circ\text{C}$	3 at room temperature after add cold test solution at $0-2^\circ\text{C}$	1	Visual
German Test Method TL 8135-002	Carbon steel DIN EN 10025	Described	3	1	26% by volume of glycerin in water, DIN 50008-1	20 ± 0.5 h (at $23 \pm 2^\circ\text{C}$) without test solution. Test solution is added to the flask and stored for 2 h 10 m.	The set is kept for 2 h 10 m in a heating chamber at $40 \pm 1^\circ\text{C}$.	Not applicable	1	NACE TM0208-2013
BSI* IEC 68-2-30:1980	–	–	–	–	–	–	40 or 55°C for 12 h	$25 \pm 3^\circ\text{C}$ for 12 h at 95% RH	2, 6, 12, 21, 56 for 40°C . 1, 2, 6 for 55°C .	–

BSI, British Standards Institute; DIN, Deutsches Institut für Normung/German Institute for Standardization; – indicates that results are not available.

TL 8135-002 (German Federal Armed Forces, 1980; British Standards Institution Procedures, 1999; Department of Defense, 2002; NACE International, 2013). There are many reports in the literature that can be applied for VCI performance evaluation techniques (Table 2).

All the tests were similar and performed according to the steps described as follows:

- Preparation of the metal specimens requires grinding by hand or machine. This preparation must yield polished test surfaces with highly reproducibility of the final finishing.
- Specimen cleaning process is performed following the recommendations of test 4031; each sample must be immersed in a tank or container of hot mineral spirits followed by immersion in methanol, allowed to dry in clean air, and then stored in a desiccator until ready to use.
- The test solution consists of a glycerin/water solution with a mass ratio of 1:2.

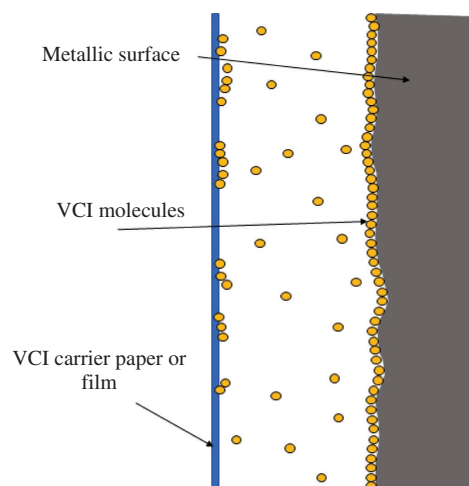


Figure 2: Protection mechanism of VCI.



Figure 3: Experimental set-up to evaluate VIA.

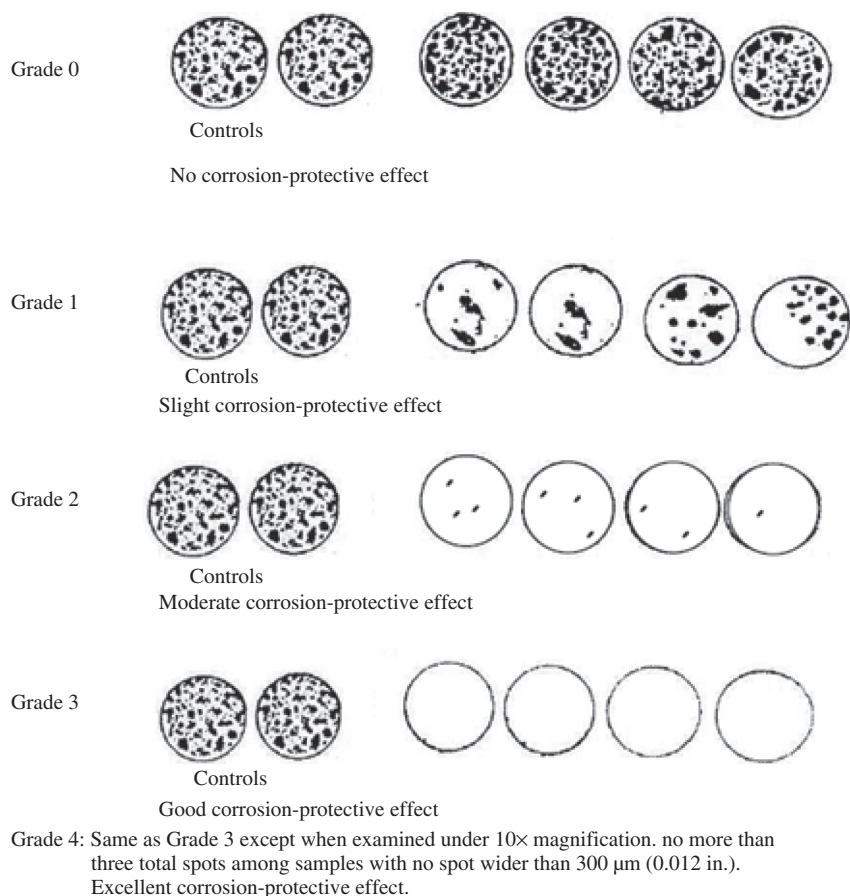


Figure 4: Visual patterns for rating the group of specimens according to NACE TM0208-2013.

- Set-up of chamber for VCI materials includes the use of glass jars or Erlenmeyer flask depending on the selected test method (Figure 3).
- VCI and moisture saturation period is one of the most important factors to be taken into consideration. During this time, the relative humidity (%RH) should increase to saturation of the closed container.
- Heating is sometimes required according to the procedure selected to perform the test. Some standards require rising of the temperature chamber.
- Condensation: after the saturation period, the temperature of the specimen is diminished to condense water on its surface and to form a CI film.
- Conditioning of specimens is the time in which the RH should increase and stabilize at a level greater than or equal to 90%.
- Visual observation: after the specimen-conditioning period has elapsed, condensation of water should be visible and corrosion should have occurred on the control specimens.

- Rating: Assign a numeral rating or grade to each metal specimen exposed in the test in accordance with the method selected. Visual patterns for rating the specimens according to NACE TM0208-2013 are displayed in Figure 4.

6 Conclusions

The actual expansion of the economic, social, and military activities worldwide leads to the proliferation of corrosion phenomena and events, which should be combated.

Practical procedures that minimize or eliminate corrosion involve the selection of corrosion-resistant construction materials, application of coatings and linings, cathodic protection, and application of VCIs.

VCIs are broadly utilized for corrosion control in natural environments such as the atmosphere, water, soil, road-deicing, and industrial plants and facilities:

electronics, petroleum, natural gas, concrete, coatings, and military equipment.

In the last decades, the use of “green” VCIs, which include natural vegetables extracted into aqueous and solvents solution, is expanding. They belong to the novel field of “green” chemistry.

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Bionotes



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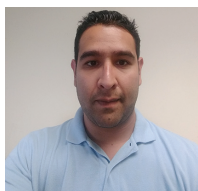


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Graphical abstract

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Technological applications of volatile corrosion inhibitors

<https://doi.org/10.1515/correv-2017-0102>
Corros Rev 2018; x(x): xxx–xxx

Review: Information on the technological applications of vapour corrosion inhibitors is presented.

Keywords: corrosion; corrosion inhibitors; environments; industries.

