Vappro VBCIs the Future Trends of Volatile Corrosion Inhibitors-VCIs

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Abstract

The demand for green and environmentally friendly products is on the rise. Millennials are consenting to spend more for products that are environmentally friendly [1], just over the period of one year, they are inclined to pay more for products and services from companies promoting green and environmentally friendly products have increased from 55% in 2014 to 72% in 2015 [2].

In view of the awareness of the millennials, the Paris climatic Treaty of 2015 and global governmental policy on green technology, this article projects the future demands for environmentally friendly Vapour Bio Corrosion Inhibitors (VBCIs) over the traditional inorganic hazardous Volatile Corrosion Inhibitors (VCIs) and its transportability exhaustible carrier materials such as mineral oils, hydrocarbon solvents, papers and Polyethylene films etc. It also covers the different types of Corrosion Inhibitor, Chemical Compound Structure of Vappro VBCI Organic Inhibitors, how Vappro VBCI works, the Criteria and Processes used for the development of VBCI Inhibitors including the Selection of Inhibitors, Environmentally Friendly Carriers used for the transportability of Vappro VBCIs, Test Materials Used, its Vapor Inhibition Ability (VIA) and the adsorption corrosion inhibitor mechanism. The present paper consciously restricts itself mainly to organic corrosion inhibitors and its green carriers.

Keywords
Environmentally Friendly VCI Carriers, VBCI- Vappro Bio Corrosion Inhibitors, Corrosion, Organics Inhibitors, VCIs, Nitrites, Inorganic Inhibitors and Vapor Inhibition Ability (VIA).

Introduction
“Businesses are in a unique position to capitalize on the environmental anxieties of millennials”. Accordingly to a study carried out in 2015 study by The Nielsen Company suggests that “the millennials are willing to spend more for products that are environmentally friendly”[1].
Just over the period of one year, millennials are consenting to pay more for products and services from companies promoting green and environmentally friendly products that have positive environmental impact and social change increased from 55% in 2014 to 72% in 2015 [2]. Although seen by some as a niche minority [3], environmental conscious consumers are now a major concern and opportunity for marketing departments across the country. Such an expeditious amplification in green-responsive customers has propelled a grow of companies executing green application at the United States Patent and Trademark Office [4]. Between 2006 and 2007, filings for eco-friendly logo or design doubled. The stores in U.S , offered 73% more green products in 2010 in comparison to 2009 [5]. Hence, even if a business owner does not accept the threat of climate change is certain, businesses should nevertheless invest in eco-friendly practices so they may advertise and sell to green-minded customers [6].

Businesses captivate green-minded customers by advertising their products environmental friendliness. This places them in a position to sell to a demographic whose buying power will increase with age. Although surrounded by environmental ads and political discussion on the environment, consumers do not typically understand the real meaning behind environmental advertisements [7]. Terms like “sustainable”, “carbon neutral”, and “compostable” leave consumers guessing about the real environmental impact of the products they see [8]. This also creates an incentive for companies to “greenwash” their products with false, deceptive, or unsubstantiated eco-friendly claims [9]. The Federal Trade Commission (FTC) is the leading organization in consumer protection in the United States, to safe guard consumers from fraudulent promotion used by companies to promote, and profit from, self-advertise environmental initiatives.

At the Paris climate conference (COP21) in December 2015, 195 countries adopted the first-ever universal, legally binding global climate deal. The agreement sets out a global action plan to put the world on track to avoid dangerous climate change by limiting global warming to well below 2°C. [10]

After the Paris Climatic Treaty in 2015, the new awareness of the millennials, the demand for Vappro VBCI Environmentally Friendly Vappro Bio Corrosion Inhibitors (VBCIs) over the conventional Volatile Corrosion Inhibitors (VCIs) has seen a marked increase over the last few years. The demand trend comes mainly from oil & gas, marine and shipping industries globally, the said industries are the most affected by corrosion causing a constant struggle against it.

Corrosion is a naturally occurring phenomenon commonly defined as the deterioration of a material (usually a metal) that results from a chemical or electrochemical reaction with its environment [11].

Corrosion Inhibitor would be more practical and achievable than complete elimination. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment, for example, formation of oxides, diffusion of metal cations into the coating matrix, local pH changes, and electrochemical potential.

Corrosion Inhibitors

A corrosion inhibitor is a chemical compound, which when added to an environment in small concentration (aqueous solution, oil, fuels, atmosphere) reduces the corrosion rate of a metal exposed to that environment [12]. There are several types of corrosion inhibitors namely; cathodic corrosion inhibitors, anodic corrosion inhibitors, adsorption corrosion inhibitors and volatile corrosion inhibitors (VCI)

Cathodic Corrosion Inhibitors

Cathodic corrosion inhibitors reduce the corrosion rate at the cathode due to retarding cathodic reactions [13]. A cathodic inhibitor causes formation of insoluble compounds precipitating on the cathodic sites in form of a barrier film. The effective cathode area is one of the Factors of galvanic corrosion therefore its reduction results in decrease of corrosion rate. The following compounds are used as cathodic inhibitors: Zinc salts (zinc hydroxide, zinc phosphate); Calcium salts (calcium carbonate, calcium phosphate); Magnesium salts; and Polyphosphates.

Anodic Corrosion Inhibitors

Anodic corrosion inhibitors reduce the corrosion rate due to retarding anodic reactions by forming a protective layer of oxide film on the surface of metal, causing resistance to corrosion [14]. An anodic inhibitor shifts the equilibrium of the corrosion process to the passivation zone, causing formation of a thin invisible passivation oxide film on the anodic sites. Anodic inhibitors are also known as passivator. Anodic inhibitors have a serious disadvantage: at low concentrations they cause increase of corrosion rate therefore it is important to avoid decrease of the inhibitor content.

Adsorption corrosion inhibitors

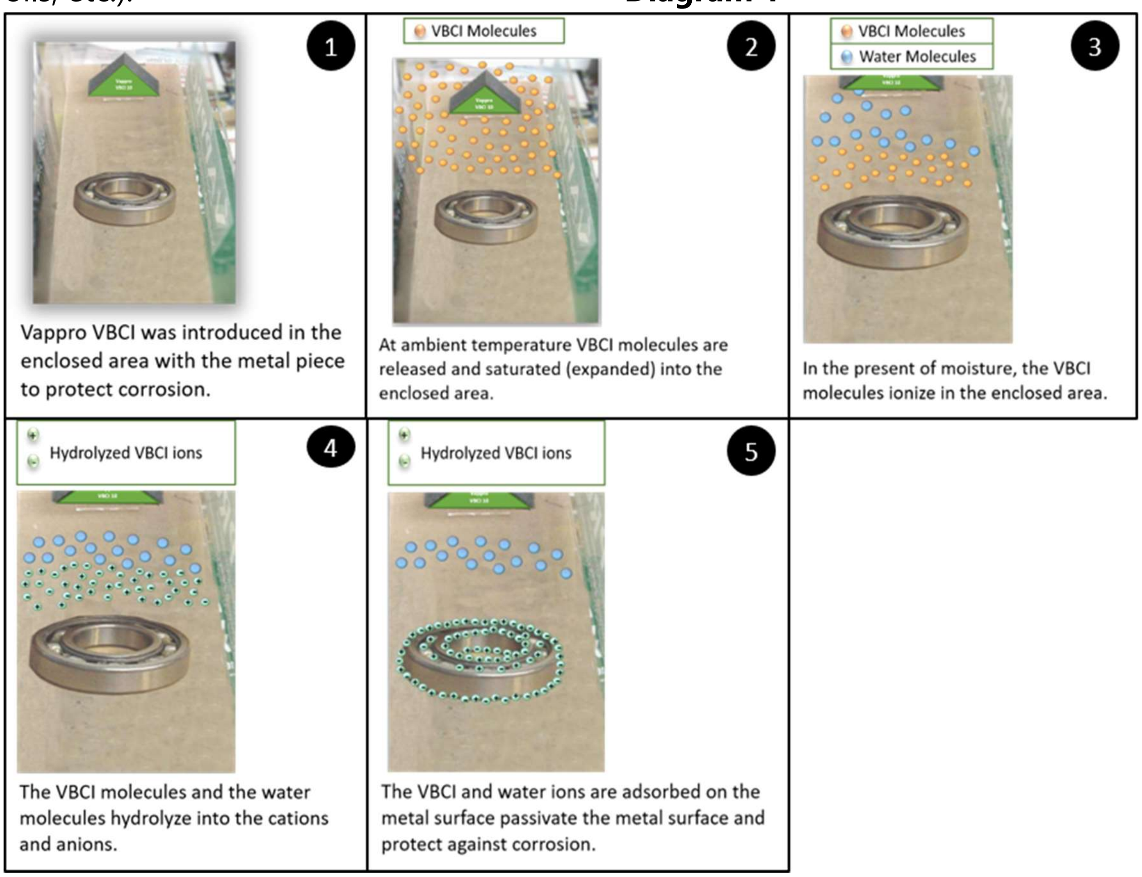
Adsorption inhibitors reduce the corrosion rate due to Polarization of the metal by extremely thin layer of their molecules adsorbed on the surface [15].

Decrease of the effective surface area results in reduction of the corrosion rate. Adsorption inhibitors are substances (mainly organic) capable to form chemisorbed bonds with surface metals atoms. The following compounds are used as adsorption inhibitors: Amines ($R-NH_2$); Carboxyls (R-COOH); Thiourea (NH_2CSNH_2); Phosphonates ($R-PO_3H_2$); Benzoate ($C_6H_5COO^-$); Antimony trichloride ($SbCl_3$).

Vappro VBCIs (Bio based corrosion inhibitors)

Vappro VBCIs reduce corrosion in closed spaces (enclosures- see diagram 1). The VBCI compound is emitted (vaporized) by the material enclosing the space. The vapors condense on the metal surface in form of microscopic molecules, which hydrolyze into ions in the moisture film present on the surface. The ions of the dissolved VCI displace water molecules from the metal surface and form monomolecular invisible protection film reducing the corrosion rate. Volatile corrosion inhibitors may be added to various package materials: polymer film (e.g. low density polyethylene), paper, foam, powder, oils, etc.).

Diagram 1



Vappro VBCI uses environmentally carriers and adsorption inhibitors to reduce the corrosion rate via polarization of the metal by forming a thin monomolecular layer of their molecules on the metal surface. Hence, decreasing the electrochemical activity of the effective surface area results in reduction of the corrosion rate. Adsorption inhibitors are substances (mainly organic) capable to form chemisorbed bonds with surface metal atoms. Vappro VBCI uses the following compounds as adsorption inhibitors: Amines ($R-NH_2$); Carboxyls (R-COOH); Thiourea (NH_2CSNH_2); Phosphonates ($R-PO_3H_2$); Benzoate ($C_6H_5COO^-$); Antimony trichloride ($SbCl_3$).

Many traditional VCI manufacturers developed a wide range anti-corrosion product to combat said problem, many times at the expense of damaging the environment and the safety of the users by using non-biodegradable carriers and exhaustible materials such plastics and paper.

Governments and industry around the world are realizing that environmentally friendly chemicals and its' carriers are important to the general well-being of users and it is important to replace the toxic chemicals to humans and environment with non-or less toxic chemicals.

Environmentally friendly corrosion inhibitors and its carriers prevent or reduce the use of chemicals that are hazardous to the environment or human beings.
Plastics and Paper are common materials used in packaging both for Industrial and consumer markets. About 300 million tons of plastic is produced globally each year. Only about 10 percent of that is recycled. Of the plastic that is simply trashed, an estimated seven million tons ends up in the sea each year [16].

Plastic waste is one of many types of wastes that take too long to decompose. Normally, plastic items can take up to 1000 years to decompose in landfills. But plastic bags we use in our everyday life take 10-1000 years to decompose, while plastic bottles can take 450 years or more [16].

Petroleum-based VCI plastics film such as HDPE and LDPE don't decompose the same way organic material does. This kind of decomposition requires sunlight, not bacteria. When UV rays strike plastic, they break the bonds holding the long molecular chain together. If exposed to ultra violet light, these bags have been estimated to break down in as little as 500 years with a conservative average time of 1000 years. If there is no exposure to a light source, say at the bottom of a landfill, the plastic may remain intact indefinitely [17].

World consumption of paper has grown 400 percent in the last 40 years. Now nearly 4 billion trees or 35 percent of the total trees cut around the world are used in paper industries on every continent. That equates to about 2.47 million trees cut down every day [18].

Globally, many Volatile Corrosion Inhibitors (VCIs) manufacturers are using exhaustible materials such as Kraft Paper, Mineral Based Oils, Hydrocarbon Solvents and non-biodegradable polyethylene resins LDPE and LLDPE, HDPE Polyethylene film as carriers for their products.

In support of the Paris Climatic Treaty, environmental and resources sustainability, Magna International together with Autonomous University of Baja California (UABC) search for ways and means to use environmentally friendly sustainable carriers such as Mineral Stone Paper, water-soluble PVA (Poly Vinyl Alcohol) $[-CH_2CHOH-]_n$ and organic corrosion inhibitors for its range of VBCI (Vapor Bio Corrosion Inhibitor) Products.

The use of biodegradable environmentally friendly organic corrosion inhibitors and its sustainable resources are one of the best options of protecting metals and its alloys against corrosion as they do not contain heavy metals and essentially non-hazardous. In addition to being environmentally friendly and ecologically acceptable, Vappro VBCI products both organic and plant-based products are inexpensive, readily available and renewable. Vappro VBCI is a new class of VCIs, it has been developed in harmony with the concern for the environment. While these chemicals offer excellent protection to metal surfaces, they have a very low impact on the environment and promote the use of sustainable resources.

What are sustainable Resources?

The ability to be sustained, supported, upheld, the quality of not being harmful to the environment or depleting natural resources, and thereby supporting long-term ecological balance [22].

Investigations have been carried out by Magna International and UABC on the corrosion inhibiting abilities of tannins, alkaloids, organic, amino acids, and amine carboxylate. compound.

Organic Corrosion Inhibitors

Vappro VBCI organic inhibitors are a large class of chemical compound in which one or more atoms of carbon are covalently linked to atoms of other elements, most commonly hydrogen, oxygen, or nitrogen. (see diagram 2)

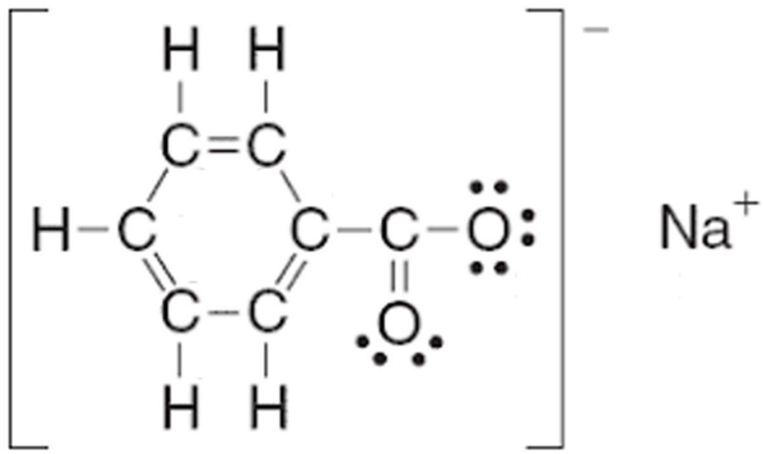


Diagram 2

Over the years, considerable efforts have been deployed by Magna International and UABC to find for suitable corrosion inhibitors of organic origin for the purpose of incorporating in various media, be it acid, neutral or alkaline. [18–21]. In acid media, nitrogen-base materials and their derivatives, sulphur-containing compounds, aldehydes, thioaldehydes, acetylenic compounds, and various alkaloids, for example, papaverine, strychnine, quinine, and nicotine are used as inhibitors.

In neutral media, benzoate, nitrite, phosphonate and phosphate act as good inhibitors. Inhibitors decrease or prevent the reaction of the metal with the media. They reduce the corrosion rate by adsorption of ions/molecules onto metal surface, [9] (ii) increasing or decreasing the anodic and/or cathodic reaction, (iii) decreasing the diffusion rate for reactants to the surface of the metal, (iv)decreasing the electrical resistance of the metal surface. (v) inhibitors that are often easy to apply and have in situ application advantage.

Generally, the mechanism of the inhibitor is one or more of three that are cited below: the inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface; the inhibitor leads a formation of a film by oxide protection of the base metal; the inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex

Chemical Compound Structure of Vappro VBCI Organic Inhibitors

Vappro VBCI organic inhibitors used also generally have heteroatoms. O, N, and S are found to have higher basicity and electron density and thus act as corrosion inhibitor. O, N, and S are the active centers for the process of adsorption on the metal surface. The inhibition efficiency should follow the sequence O < N < S.

The use of Vappro VBCI organic inhibitors containing oxygen, sulphur, and especially nitrogen to reduce corrosion attack on steel has been investigated in some detail. The current data show that most organic inhibitors adsorbed on the metal surface by displacing water molecules on the surface and forming an impermeable barrier. Availability of nonbonded (lone pair) and p-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal.

The performance of a VBCI organic inhibitor is related to the chemical structure and physicochemical properties of the compound like functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule. The inhibition could be due to (i) Adsorption of the molecules or its ions on anodic and/or cathodic sites, (ii) increase in cathodic and/or anodic over voltage, and (iii) the formation of a protective barrier film. Some factors that contribute to the action of inhibitors are(i)chain length, (ii)size of the molecule, (iii)bonding, aromatic/conjugate, (iv)strength of bonding to the substrate, (v)cross-linking ability, (vi)solubility in the environment.

The role of inhibitors is to form a barrier of one or several molecular layers against acid attack. This protective action is often associated with chemical and/or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other. Sulphur and/or nitrogen-containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitors. Thiophene, hydrazine derivatives offer special affinity to inhibit corrosion of metals in acid solutions.

Vappro VBCI organic corrosion inhibitors contain polar functions with nitrogen, sulphur, and/or oxygen in the conjugated system exhibits good corrosion inhibiting properties.

Its good inhibitive characteristics derive from the adsorption ability of their molecules, with the polar group acting as the reaction center for the adsorption process. The resulting adsorbed film acts as a barrier that separates the metal from the corrodent, and efficiency of inhibition depends on the mechanical, structural, and chemical characteristics of the adsorption layers formed under particular conditions.

Criteria and Processes used for the development of VBCI Inhibitors

Selection of Inhibitors

Vappro VBCI Inhibitor option starts with the preferred physical properties such as a solid or liquid. Freezing, thaw stability and melting points of the carriers are essentials depending on the areas of application. The rate of degradation and temperature variance is also critical. Compatibility with other additives and solubility peculiarity have to be considered. The check list can be comprehensive, but is imperative because it determines the sphere of feasible inhibitors. It is the prerequisite of the onset of the appraisal of inhibitor for any new system.

The demand in inhibitor appraisal is the method of adoption that simulates the conditions of the real-world system. The fluctuations to be contemplated include temperature, pressure, and velocity as well as metal properties and corrosive environment chemistry.

Deterioration of system due to corrosion are generally localized and associated to micro conditions at the failure site. Sufficient testing must include the most-harsh conditions that can occur in the system and not be limited to macro or moderate conditions.

Test Materials

Test samplings used should be the same metal as that to be protected; as very small differences in metal chemistry can contribute to major differences in inhibitor performance. Inhibitor performance can vary greatly on different metals and thus inhibitor rankings based on one metal are not universal. Much less obvious are differences between the "same" metal.

These nonchemical differences include grain size and orientation, residual stresses, and surface condition. Surface preparation should, to the extent possible, provide a surface comparable to that in the system that is being modelled.

Transportability of Inhibitor

Vappro VBCI corrosion inhibitors are typically characterized by carriers such as oil soluble, water soluble, oil soluble-water dispersible, foam, powder, solvents, etc.

Many commercial corrosion inhibitors, however, are not single compounds but complex mixtures of many compounds, each with its own unique partitioning coefficient. Thus, a commercial corrosion inhibitor has no unique partitioning coefficient but rather one for each of the multiple components**.** Organic inhibitors are generally more soluble in aromatic hydrocarbons than aliphatic ones and more soluble in long chain aliphatics than short chain ones. The result is that partition coefficients must be measured for each "oil" of interest.

Once the transportability of inhibitor is ascertained, the finished product of Vappro VBCI will be subjected to Vapor Inhibition Ability (VIA) Test using German VIA Test Method TL 81305-002. The said test is herein described below:

German VIA Test 81305-002 [23] [24].

A test sample with a high degree of sensitivity to corrosion through condensation water is packed together with a VCI auxiliary packing material in a vessel, which is then tightly closed. Condensation is then forced on the surface of the test sample. By means of a blank trial – that is, a trial structure of the same type, but without VCI auxiliary packing material – it is determined whether the conditions of the trial are sufficient to cause corrosion to appear on the unprotected test sample.

Test object

Unalloyed, solid construction steel.

Test Sample

6 x (25 x 150mm) VCI Film (Thickness= 3 mils)

4 x Test sample of unalloyed, 16mm diameter solid construction steel S235JRG2 DIN EN 10025 (material number 1.0038)

Test solution

10 ml freshly prepared glycerin/water mixture with a density of 1.076 g/cm^3 at (23±2) °C, which is intended to produce approximately 90% Relative Humidity in the jar.

Test Equipment and Material

For each test, 4 test sets are necessary. A test set consists of the following parts

(1) Test Jar, 1 L, wide-necked.

(2) Rubber stopper, 54 mm Æ, with longitudinal through hole

(3) Test sample of unalloyed, solid construction steel

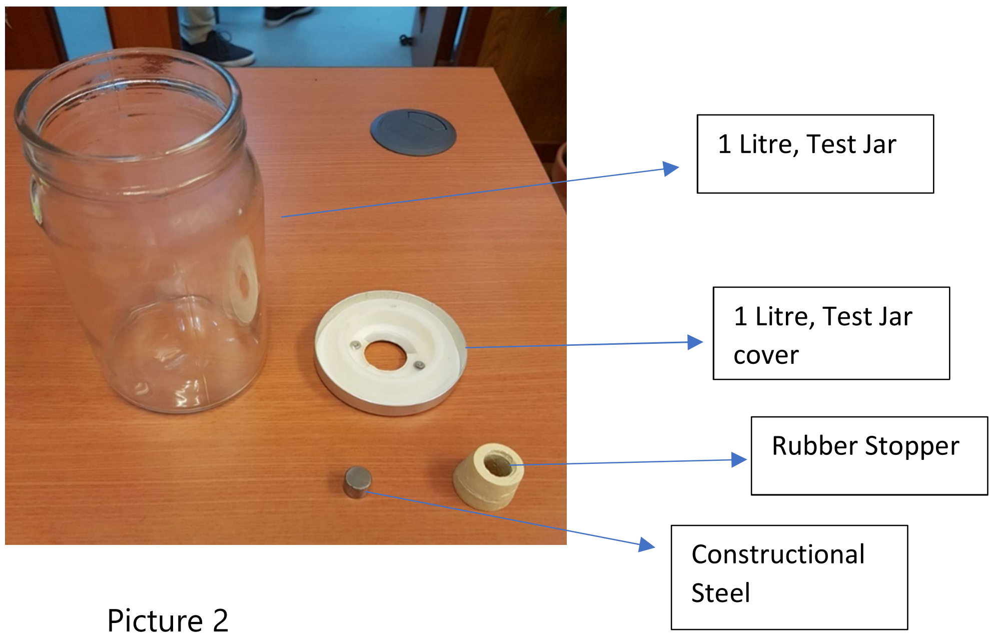
(4) 10 ml freshly prepared glycerin/water mixture with a density of 1.076 g/cm3 at (23± 2) °C (glycerin/water mass ratio about 1:2)

(5) Ethanol

Procedure of the test

Four test objects were polished with 320 grit abrasive paper to remove all the grit and rust. Rinsed with ethanol and dried them.
Polished test object was inserted in the rubber stopper. Please see below pictures.

Picture 1



Picture 2

Test Procedure

The experiment commenced at 1530 hrs, 5 Oct 2016 and concluded at 1630 hrs, 6 Oct 2016.
Phase 1 (1530 hrs, 5 Oct 2016 to 1130 hrs, 6 Oct 2016):
1 control sample for comparison, 3 samples with Vappro VCI Film for 20 hours

1. Wash and dry glass jars
2. Sand all steel samples
3. Attach 2 pieces of Vappro VCI Film onto 3 lids using scotch tape
4. Attach steel samples to rubber stopper with white tape and ensure firm seal
5. Assemble lid, stopper and jar
6. Seal the jar using clean wrap
7. Jars are stored for 20 hours, allowing VCI to coat steel samples

Phase 2 (1130 hrs to 1330 hrs, 6 Oct 2016):

Introduction of glycerine/water mixture to accelerate corrosion for 2 hours

1. Mix 20ml of glycerine into 40ml of water (1:2 ratio)
2. Unseal jars one by one
3. Pour 10ml of glycerine water mixture
4. Reseal jars
5. Store for 2hours

Phase 3 (1330 hrs to 1630 hrs, 6 Oct 2016):

Accelerated corrosion by forced-air heating chamber, 50°C for 3 hours

Materials:

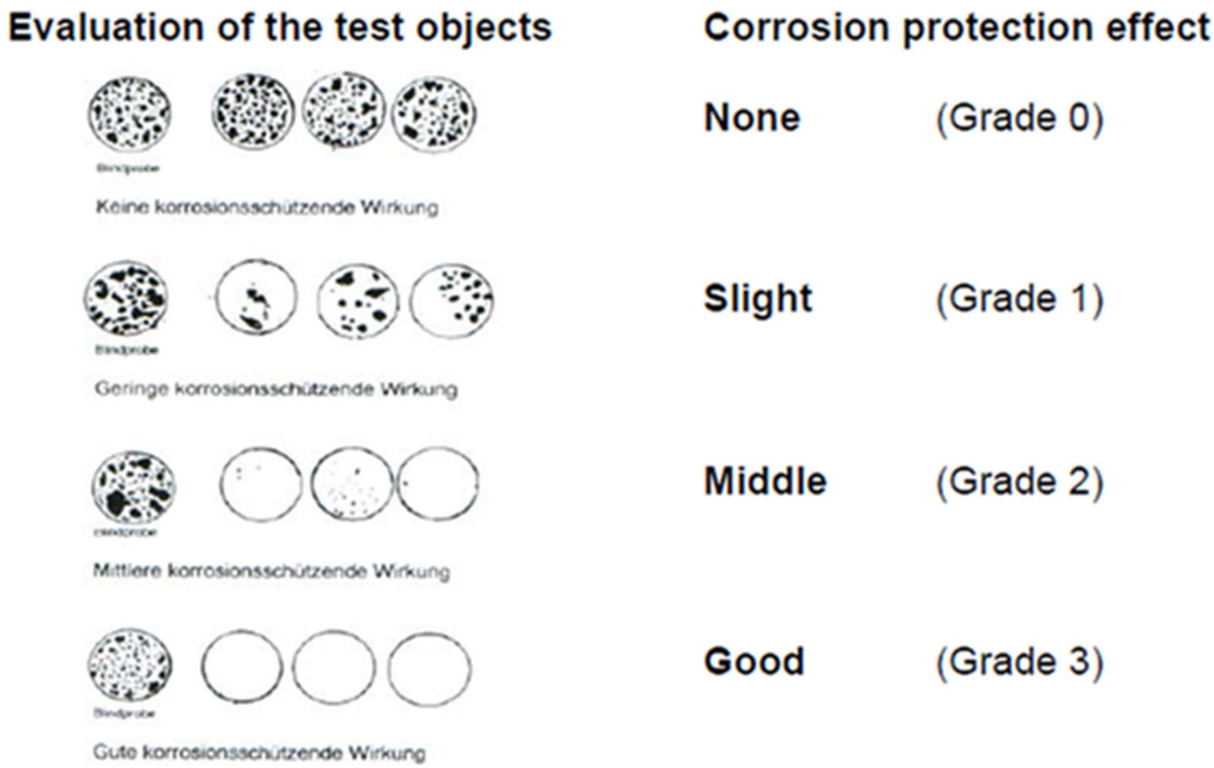
Samples:

1. 6 x (25 x 150mm) VCI Film (Thickness= 0.05mm)
2. 4 x Test sample of unalloyed, 16mm diameter solid construction steel S235JRG2 DIN EN 10025 (material number 1.0038)

Hardware (4 Sets of):

1. 1L glass jar with lid
2. Rubber Stopper
3. 10 milliliters freshly prepared glycerin/water mixture with a density of 1.076 g/cm^3 at (23 ± 2)°C (glycerin/water mass ratio about 1:2)
4. Sand Paper
5. Forced-air heating chamber

Sample	Before	After 24th Hour
Control		
1		
2		
3		



Corrosion Protection Tests

Corrosion rates are most commonly reported as penetration rates. The usual way of reporting protection efficiency is in terms of percent protection. Although this reporting method is useful for comparing inhibitor performance, it obscures the actual number of interests the inhibited corrosion rate.

Film persistency tests are more complex than constant concentration experiments. The test metal is exposed to an inhibited test solution for a fixed period of time, then the corrosion rate is determined in a similar solution containing no inhibitor. Test variables include inhibitor concentration in the initial filming solution and the number of rinse solution repetitions. A typical experiment might film for one hour with 1000 ppm inhibitor, rinse one time for an hour, and finally measure the corrosion rate in a third solution. Film, rinse, and corrode solution are the same composition except for inhibitor in the filming step.

Conclusion

All newly developed Vappro VBCI products are considered effective and have good vapor inhibition properties if they passed the German Vapor Inhibition Ability Test [23] [24].

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Nelson Cheng PhD (Honoris Causa) is the founder and chairman of Magna Group, consisting of Magna International; Magna F.E. Chemical Pte., Ltd.; Magna Chemical Canada, Ltd.; Magna Australia Pvt., Ltd.; and Lupromax International Pte., Ltd.

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His key responsibilities at Magna International as follows: assisting the CEO in research and development of new products, finding out customers' needs and develop customized new products, helping in synthesizing new compounds by making appropriate modifications of known methods, recommending and implementing methods to increase the quality of products and service, management of hazardous raw materials.

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