

An Overview: Vapor Phase Corrosion Inhibitors

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ABSTRACT

When present as vapors, certain organic compounds offer inhibition against the corrosion of ferrous and nonferrous materials. The inhibitors include aliphatic, aromatic, cyclohexylamines, aminonitrobenzoates, heteroalkylated lower amines, etc. The mechanism of inhibition offered by these compounds was discussed and an unified mechanism was presented. Various methods of evaluating inhibition efficiency were discussed with a special reference to surface film characterization techniques. Methods of application of the vapor phase inhibitors and their industrial uses also were presented.

KEY WORDS: inhibitors, surface film, vapor phase

INTRODUCTION

During World War II, it became essential to protect military equipment and replacement parts against rusting during storage and climatic conditions. Many of these packaging procedures were expensive and time consuming. Then, vapor phase inhibition, obtainable with volatile compounds, opened a new avenue for attacking packaging problems. In earlier times, camphor was used to protect military materials and machines fabricated from ferrous metals.¹ With the advancement of science and technology, other new effective inhibitors for ferrous materials

were discovered, but their compatibility with nonferrous materials was a problem. These led to the ongoing development of vapor phase inhibitors (VPI) for ferrous and nonferrous parts.²⁻³

VPI are organic chemicals, which when present as vapor, inhibit the corrosion of ferrous and nonferrous metals. Their vapors form an extremely thin film over certain metal surfaces, especially those of iron and steel, thereby rendering them passive. This type of corrosion inhibitor is useful when oil, grease, or other adherent films are unsuitable. The inhibitor is transmitted as vapors, and the vapor phase is controlled by the structure of the crystal lattice and the character of atomic bond in the molecule. The protective vapors expand within the enclosed space until the equilibrium determined by their partial pressure of the vapor is reached. The higher the vapor pressure, the sooner the saturation of protected space. For practical purposes, it is preferable to use less volatile inhibitors that provide long-lasting and durable protection over periods of 2 years to 3 years and protection of breathable enclosures and enclosures where changes of local atmosphere occur.

EARLIER DEVELOPMENTS

Since the end of World War II, VPI have been tested extensively in the laboratory and field. Earlier reports on the use of dicyclohexyl ammonium nitrite were made in 1951.⁴ For rust inhibition, sodium, potassium, or ammonium nitrite (NH_4NO_3), urea ($\text{CO}[\text{NH}_2]_2$), and acetamide (CH_3CONH_2) were tried from 1947 to 1949.⁵⁻¹⁰ Stroud and Vernon suggested

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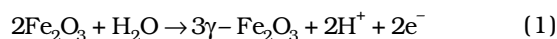
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sodium benzoate ($\text{NaC}_7\text{H}_5\text{O}_2$) as a contact rust inhibitor and esters of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) as VPI.¹¹ Later, they reported a series of amine carbonates as VPI.¹² The vapor rusting properties of nitrothiophenes neutralized with amines, guanidines, and metal carbonates were described by Moore and Wachter.¹³ Protective properties of volatile amines in preventing the tarnishing of silver in ammonia¹⁴ were identified.¹⁵ To pack steel materials and prevent rusting in steam systems, the use of amines, alkyloamines, and amine acid complexes were suggested, respectively, as early as 1952.¹⁶

MECHANISM OF VPI

In general, VPI reaches the metal surface and condenses to form a thin film of crystals. In the presence of even traces of moisture, crystals dissolve and immediately develop strong ionic activity. This layer separates the metal from the environment. Continuous condensation of vapors thicken this layer. Dicyclohexyl ammoniumnitrite is moderately soluble in water. It protects through the vapor by contributing its nitrite ion to condensed or adsorbed moisture on the metal surface. Amino benzoates inhibit corrosion of steel by not forming organometallic compounds. On an oxide surface (e.g., $\gamma\text{-Fe}_2\text{O}_3$), the inhibitor acts as an electron acceptor and the oxide as a donor. The oxidation takes place at the expense of oxygen in the water:



The formation of an oxide with higher valence on the surface portends the onset of anodic passivity. The organic cations formed by the hydrolysis of amine nitrobenzoates reduces the area of the active part of the surface and thereby facilitates oxidation of the surface by the oxygen of the water molecules.¹⁷

Amino ketones have two heteroatoms with free electron pairs — one pair on the nitrogen atom and two pairs on the oxygen atom of the $>\text{C}=\text{O}$ group. The nitrogen atom has a higher electron-donor capability than that of oxygen.¹⁸ The amino ketones abstract protons of the adsorbed water molecules, and they are desorbed from the metal. The surface becomes an electron acceptor, capable of adsorbing another molecule of inhibitor through the free electrons of the amine nitrogen or $>\text{C}=\text{O}$ group oxygen. The adsorption is accompanied by the formation of a bond that has a cyclic character:

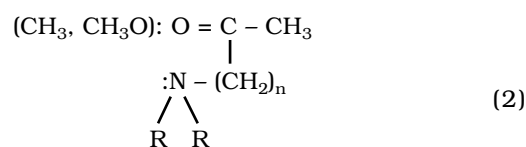




TABLE 1
Changes in the Electrode Potential of Steel in 30 mg/L NaCl + 70 mg/L Na_2SO_4 Electrolyte Under the Influence of Amines

Amine (0.1 M)	$\Delta\phi$ (mV) after 6 h ^(A)	
	20°C	40°C
$(\text{C}_2\text{H}_5)_2\text{NH}$	518	993
$(\text{HOOC}_2\text{H}_4)_2\text{NH}$	288	625
$\text{C}_2\text{H}_4(\text{NH}_2)_2$	308	958
	—	—
	313	550

^(A) $\Delta\phi = \phi_1 - \phi_2$; ϕ_1 = electrode potential of steel in the inhibited solution after 6 h; ϕ_2 = electrode potential of steel in uninhibited solution.

The formation of a donor-acceptor bond between the metal and inhibitor hinders the transfer of an ion-atom from the metal lattice into solution. α -amino ketones, which are planar molecules, are adsorbed and form a densely packed layer unlike β - and γ -amino ketones, which are nonplanar.

In some cases where the inhibitor could induce passivity, the stable passive surface is responsible for the protection. The protection offered by ammonium benzoate for steel is an example. The corrosion inhibition of steel by ammonium benzoate is possible only if two conditions are fulfilled:

- concentration of the inhibitor should be above the threshold level to keep the iron surface passive; and
- film thickness should be $< 10 \mu\text{L}$ to decrease the passivation current density and increase the rate of oxygen reduction.

Unified Mechanism

The inhibition offered by VPI is electrochemical in nature as corrosion is an electrochemical process. The ions or atoms present in the protective layer can change the potential and cause an increase in hydrogen overvoltage in some cases. The amines, especially on iron, form coordination bonds between the unshared electron pair of the nitrogen in the nonhydrated amine and metal. This causes a shift in potentials toward nobler values that is more pronounced at higher temperatures (Table 1). Amines adsorb on metals for which there are unoccupied electronic orbitals and through the defects present in the oxides on metals with fully occupied orbitals. In some cases of metals where the sublevels are complete, the adsorption could be caused by an electron exchange between the metal and the inhibitor molecule (e.g., adsorption of electron donor molecules on zinc surface). Further, the adsorption of electron donor molecules on such metals where there is no unoccupied electronic orbitals may take place on oxides that have defects and are capable of accepting electrons. In this case, the adsorption is determined solely by the surface changes.

Amines and other inhibitors first displaced adsorbed water molecules from the metal. Removal of water from the metal stifled the dissolution of metal. On an oxide-covered surface, the inhibitor underwent reduction favoring the formation of higher valent oxides or formed a van der Waal's type complex. The formation of a thick or multilayer prevented the diffusion of oxygen and the reduction of molecular oxygen was prevented. This behavior was observed in some classes of inhibitors such as nitrobenzoates.

In general, inhibitors displaced the water molecules, chemisorbed, and some formed surface chelation to construct a thick inhibitor film of amino ketones. The diffusion of oxygen through this layer was prevented, and corrosion rate was reduced.

VPI

Amines

Most of the volatile corrosion inhibitors that are used are amine derivatives that release free amine or its hydroxyl form upon hydrolysis and dissociation.¹⁹ In general, aliphatic amines offer vapor phase inhibition. As hydrogen atoms in the amine group are replaced by hydrocarbon radicals, there is a decrease in inhibition efficiency. A replacement of a CH₃ group hydrogen in an aliphatic amine by a second amine group or a hydroxyl group also is accompanied by a decrease in inhibition. Also, when the change is made from a straight chain to a branched chain in the case of aliphatic amines, the inhibition efficiency decreases. Further, when the branching is closer to the amine group, the inhibition becomes lower. The most effective of the aliphatic amines are primary straight chain amines with an even number of carbon atoms.

Some common hetero cyclic amines that are used as VPI are hexamethylene imine, piperidine, and morpholine. Hexamethylene imine has a seven-membered ring structure and others are six-membered rings. Morpholine has a second heteroatom oxygen in addition to nitrogen. This second heteroatom present in the amine decreases the inhibition of steel corrosion. Cyclohexyl amines and benzyl amine offer good inhibition for copper and steel. Benzyl amine is comparatively less effective than the former. Amines of the fatty acid series are more effective than cyclic amines, which, in turn, are more effective than aromatic amines.²⁰

An attempt was made to correlate inhibition efficiency with p^k_a , dipole moment, and the net Taft constant (σ^*). p^k_a is the negative logarithm of the concentration of the hydroxyl ions formed by hydrolytic cleavage by amines in aqueous solutions, and it characterizes the basicity of the amine. The dipole moment characterizes the displacement of negative and positive charges of the molecule (or ion) under the influence of an electric field. The larger the dipole

moment, the greater the capability of the species for electrostatic interaction with other substances. The σ^* is a measure of the polar influence of substituents in any reaction. It was found that an increase in dipole moment and the basicity of the amines enhanced inhibition in respect of steel and zinc. Often it is found that the basicity of amines play a more vital role than the net Taft constants in deciding their inhibition efficiency. An example can be cited with diethylamine and diethanolamine, where their net Taft constants are very similar. However, the former gives better protection because of its higher basicity constant value. The number of amines that completely suppress zinc corrosion is considerably smaller than for steel. The obvious reason could be attributed to the nature of the interaction between the metal and the amine. In the case of steel, which is a transition metal with incomplete sublevels, as opposed to zinc, which has completed sublevels, the adsorption could be solely a result of electron exchange.

In 30 mg/L sodium chloride (NaCl) and 70 mg/L sodium sulfate (Na₂SO₄) solutions, interesting results were reported. The increase in basicity or dipole moment of the amine resulted in the increased inhibitions of zinc corrosion.

Benzylamine, allylamine, and mono ethanolamine all have approximately the same basicity, but the inhibition efficiency differed for the corrosion of copper. For amines having very similar basicities, the inhibition increased as diisobutyl amine = diisopropylamine > diethyl amine = triethyl amine > isobutyl amine = piperidine > amyl amine > ethyl amine = butyl amine > hexyl amine > secondary (sec.) butylamine > tertiary (tert.) butyl amine = cyclohexyl amine. The inhibition efficiency and the dipole moment of amines was linear for the corrosion of copper. In the case of aliphatic amines, primary amines had the greatest tendency to form complexes. They proved to be more aggressive toward copper in contrast to sec. and tert. amines. Ethylene diamine ($D = 1.9$) was more aggressive than ethylamine ($D = 1.28$). This is because diamines form most stable complexes with copper ions. For the same reason, ethanolamine was more aggressive than ethylamine. Branching of the amine chain usually reduces its complexation with copper. Isobutylamine gave a marked reduction in corrosion compared to n-butyl amine. In the presence of sec. butylamine or tert. butylamine, the corrosion rates of copper were higher than in the presence of n-butyl amine, although the dipole moments of the first two of these amines were smaller than that of the n-butyl amine. Electrostatic characteristics of the copper ions and the sec. and tert. butylamines were the most favorable for the formation of strong complexes.

Heterocyclic amines with two heteroatoms were less aggressive toward copper than aliphatic series of amines with the same number of carbon atoms. Che-

lation, in the presence of nitrogen and oxygen atoms, was accomplished only if the formation of five-membered or six-membered rings was favored.

Morpholine ($D = 1.50$), because of the more rigid structure of its molecule, is practically incapable of entering into interaction with the metal. It was adsorbed on copper through an oxygen atom. In general, the smaller the dipole moment of an amine, the less it tended to form complexes, and hence, the less aggressive it was with respect to copper. Dicyclohexylamine, morpholine, and diisopropyl amine were recommended inhibitors for copper as they did not form chelates. To lower the vapor pressure of the amines, they generally were converted in their salts such as nitrates, benzoates, and other salts.

Cyclohexylamines

Bayer synthesized cyclohexylamine and dicyclohexyl amines in 1893.²¹ Cyclohexylamine is a strong base and forms salts with all acids. 2,2'-dichloroethyl ether reacts with cyclohexylamine to form N-cyclohexyl morpholine. Dicyclohexylamines form salts with all acids and soaps with fatty acids. Dicyclohexyl ammoniumnitrite (DICHAN) is slightly volatile at atmospheric temperature compared to alkali metal nitrite and are less or equally toxic. One gram of DICHAN saturates $\sim 20 \text{ ft}^3$ by 10^3 ft^3 (0.57 m^3 by 28.32 m^3) of air at 30°C .²² It is moderately soluble in water and very soluble in methanol. DICHAN usually is analyzed for its nitrite content by Colorimetric[†] method.²³ Slow loss of DICHAN also may occur by vaporization of the compound and will be influenced by temperature and wind velocity. Dicyclohexyl ammonium salts offer inhibition of rusting of steel at 150°F . The nature of the anion of the acid greatly influenced the percentage of the surface not rusted. More than 75% was observed in the case of benzoates, phosphonates, carbonates, sulfonates, and nitrites (Table 2).

Amine Nitrobenzoates

Amine nitrobenzoates suppressed corrosion when the metal surface was activated, and there was no air-formed film on the metal. This was found using the flame ionization detector method.²⁴⁻²⁵ Hexamethyleneimine-N-nitrobenzoate was adsorbed by nickel or iron. The strong adsorption increased with time and temperature. Radiochemical technique revealed that the adsorption of aminonitrobenzoates increased with time, and bonding was stronger than the corresponding amine benzoates. After 72 h, 85% of the copper surface, 52% of the iron surface, and 90% of the zinc surface were covered by m-nitrobenzoate. The adsorption was caused by chemical bonding accompanied by the formation of a protective film on the metal.

[†] Trade name.

TABLE 2
Inhibition of the Rusting of Steel at 150°F ^{34,(A)}

Compound	Surface Not Rusted (%)
Dicyclohexyl ammonium carbonate	75
Dicyclohexyl ammonium benzoate	75
Dicyclohexyl ammonium ethyl phosphonates	75
Dicyclohexyl ammonium ethyl sulfonate	75
Dicyclohexyl ammonium borate	50
Dicyclohexyl ammonium phosphate	25
Dicyclohexyl ammonium chromate	12
Dicyclohexyl ammonium nitrate	12
Dicyclohexyl ammonium nitrite	75
Dicyclohexyl ammonium sulfite	25

(A) Duration of the test: 168 h.

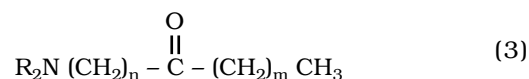
Impregnation of kraft paper: 2 g/ft² chemicals used.

Most of the amine nitrobenzoates were effective for steel and zinc. The protection given by the compounds was ranked in decreasing order. For steel and zinc, dinitrobenzoates > mononitrobenzoates > benzoates > amines. For copper, dinitrobenzoates > benzoates > mononitrobenzoates.

For a number of metals, it has been reported that the introduction of the nitro group into the benzene ring minimized corrosion. The pH of the medium can play an important role on the performance of compounds. For example, in acidic or weakly acidic electrolytes ($\text{pH} < 3$), hexamethyleneimine-3,5-dinitro benzoate becomes a corrosion promoter. Regarding the mechanism of protection by these amine benzoates, it was proposed that these compounds were capable of simultaneous displacement of water from the metal surface and conversion of the lower oxide of iron to the oxide with a higher valence.²⁶⁻²⁷

Hetero-Alkylated Lower Amines

Universal volatile inhibitors of the Institute of Physical Chemistry, USSR Academy of Sciences (IFKhAN) class are amine derivatives — amino ketones obtained by controlled heteroalkylation. These differ from amine nitrobenzoates in their vapor pressure and in the variety of metals that can be protected.²⁸⁻³⁰ The general formula is:



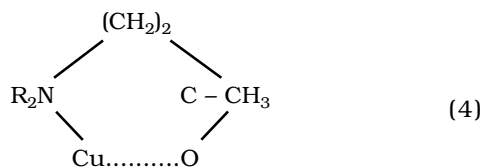
In the composition of these inhibitors, there is a carbonyl group. Depending upon the nature and composition of the amine taken for hetero alkylation, the position of the $-\text{C}=\text{O}$ group, and the choice of the original ketone, there would be variations in inhibition. Detailed studies were made on these inhibitors for various metals in 30 mg/L NaCl and 70 mg/L Na_2SO_4 solutions.³¹ The diethylamine ketones of

TABLE 3
Protective Properties of β -Diethyl Amino Ketones¹⁹

Amino Ketone	Number of Carbon Atoms	p ^K a	Protective Concentration (mM)		
			Iron	Copper	Zinc
1-diethylamino-3-butanone	4	8	31	5	6.2
1-diethylamino-2-methyl-3-butanone	5	7.93	20	20	60
1-diethylamino-2-methyl-3-pentanone	6	—	12.5	35	6.8
1-diethylamino-4, 4-dimethyl-3-pentanone	7	7.85	31	50	60
Diethylammonium ethyl cyclohexanone	8	—	20	2	50

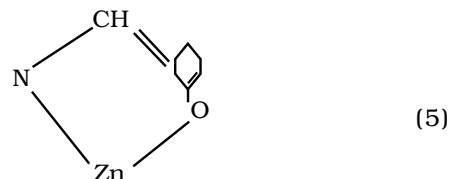
α -, β -, γ -derivatives exhibited different behaviors. The α derivative was most effective to control the corrosion of iron, while β -derivative was for ferrous and nonferrous metals. γ -derivative was the poor performer in the class. Thus, β -diethylamino ketones, which retarded both electrode reactions should have been the most effective and universal of these inhibitors. The nature of the amine group determined the protective property of β -amino ketones. The increase in the length of hydrocarbon radical had a favorable effect. This was related to the higher p^Ka of the amino ketone with the greater number of carbon atoms in the molecule and also the greater area shielded by one molecule of the larger amino ketone when it was adsorbed on a metal surface. 1-piperidino-2-methyl-3-butanone and 1-hexamethylene imino-2-methyl-3-butanone, though they have an equal level of basicity, higher inhibition was offered by the large molecule. 1-morpholine- 2-methyl-3 butanone and 1-piperidino-2-methyl-3-butanone have the same amine size, but the more effective compound was the one with the higher p^Ka of the original amine. Structure of the original amine played an important role. 1-diethylamino- 2-methyl-3-butanone was more effective than 1-piperidino-2-methyl-3- butanone.

The heteroalkylation of aliphatic secondary amines had the pronounced effect on the inhibition of zinc and copper corrosion. They inhibit corrosion of copper by forming chelate-type compounds with two coordinate bonds:



Such compounds were less soluble and more stable than the usual copper aminates that were formed as a result of a single coordination bond between a ligand and the metal R₂N....Cu; the breaking of these bonds by OH⁻ ions was more difficult.³² With an increase in the size of the amine and a decrease in solubility of the amino ketone in water, the effectiveness of the amino ketones increased. This resulted in

higher stability and lower solubility of the complex that was formed. The chain length and branching in the heteroalkyl radical of β -amino-ketones influenced the protective properties of the inhibitors differently (Table 3). To inhibit the corrosion in iron, β -diethyl amino ketone was less effective than other ketones. 1-diethyl amino-2-methyl-1,3 butanone (C₅) was more effective than 1-diethyl amino-3-butanone (C₄). As a result of shielding of the adsorption capable carbonyl group, 1-diethyl amino-4, 4-dimethyl-3-pentanone was less effective than 2-(diethyl aminomethyl) cyclohexanone. The high efficiency of inhibition observed for the corrosion of zinc by amino ketones was credited to its structure. The carbonyl radical and the amine radical participated in chemisorption, forming a metal-inhibitor bond as:



The participation of the carbonyl group in the formation of protective layers on copper enhanced the inhibition of corrosion. The interaction of the functional group with copper was favored by a small size of the heteroalkyl radical and an increase in size prevented interaction. If there was a decrease in the degree of shielding of adsorption capable groups, enhanced inhibition was noticed. The structure of the diethylamino-2-methyl-3-pentanone and 2-(diethyl aminomethyl) cyclohexanone were equally favorable for the reactivity of the functional groups. To prevent the corrosion of copper, the latter was more effective than the former. The high activity of the >C=O group of the diethyl aminoketone and a low solubility of the interaction products were responsible for this behavior. The general mechanism through which the amino ketones acted was related to their capability of the chemisorption on the metal surface and to the extent of the electrostatic adsorption by the molecules hindering the diffusion of oxygen to the metal surface, thereby retarding the cathodic process.

In most situations, VPI are evaluated or used in various combinations and formulations. Table 4 summarizes compounds or formulations of VPI used to inhibit the corrosion of ferrous and nonferrous materials.³³⁻⁸⁵

CHARACTERIZATION OF VPI

Vapor Pressure Measurements

At some temperatures and pressures, a solid or liquid is in equilibrium with its vapor. This equilibrium pressure is called the vapor pressure of the solid or liquid. One of the most convenient static methods is isoteniscope. This is used to determine the vapor pressure of liquids.⁸⁶ Ramsay and Young developed the gas-saturation method. An inert gas was passed through the liquid maintained in a thermostat. The volume of gas used was measured and its final vapor content or the loss in weight of the substance being studied was determined. If care is taken to ensure saturation of the following gas, the vapor pressure of the liquid may be calculated readily.

For solids, vapor measurements were carried out by the Regnault dynamic method.¹² A weighed amount of inhibitor was heated at constant temperature in a slow stream of oxygen-free nitrogen gas, and the loss in weight was measured. Barometric pressures were recorded to reduce the volume of nitrogen to 760 mm pressure. The temperature range was from 25°C to 60°C. The rate of volatilization of the compound at various temperatures was obtained:

$$\frac{\text{Total volume of the compound}}{\text{Volume of the vapor}} = \frac{\text{Total pressure}}{\text{Vapor pressure}} \quad (6)$$

Thus, a vapor pressure-temperature curve was obtained, which was used to predict the vapor pressure of the compound. The accuracy of the method was subject to the position of temperature control and barometric pressure measurements.

The vapor pressure also could be measured using microbalance by following loss in weight at controlled temperature after due calibration with compounds of known vapor pressure.⁸⁷

Criterion for the selection of a compound to be used as a VPI is that it should not have very low or very high vapor pressure as to give lasting protection.

Antibacterial Activities⁸⁸⁻⁸⁹

The antibacterial activities of the VPI were determined by disc diffusion method, which is a simple and more reliable method for routine bacteriological work.

For this method, discs were prepared by punching 0.25-mm discs from Whatmann[†] filter paper no. 1 that were sterilized before use. 10 μ L of each VPI was used in the disc and dried up. Using sterile bacterio-

logical loop, organisms were taken from the cultured medium and inoculated in peptone water. These were kept inside the incubator at 37°C for 4 h to 6 h. The bacterial suspension was poured onto the prepared Muller Hinton[†] agar plates and kept for a few minutes. Then, the excess bacterial suspension was discarded and the VPI-soaked discs were placed on the agar plate suitably spaced apart. The plates were incubated overnight at 37°C. The diameter of the zone of growth inhibition was measured in millimeters.

In this assay, the ceftazidime (a multidose antibiotic) was used as the control.

Antifungal Activities⁸⁸⁻⁸⁹

The process adopted for this test was the same as mentioned in the antibacterial activities section, but instead of peptone water, sabourauds broth was used for fungus growth. The cultured fungi were poured onto the prepared sabourauds agar plate and incubated at 37°C overnight. Zone of growth inhibition was noted.

METHODS OF INHIBITOR EVALUATION

Conical Flask Method¹²

Specimens (5 cm by 1 cm) were suspended by glass hooks fixed in a cork in the neck of a 250-mL conical flask. The flask contained 25 mL liquid made of water and 5% weight of the inhibitor under study. A battery of conical flasks were kept in an air thermostat at 35°C or at any desired temperature during the day and were removed at night, thereby inducing condensation on the specimens. The experiment was conducted for 6 months. The extent of corrosion and inhibition was evaluated using visual and gravimetric methods. Periodical flushing with fresh air is recommended. The method is often qualitative but also can be made quantitative with suitable precautions.

Boiling Tube Method

Specimens (5 cm by 2.5 cm) were suspended in the upper part of a boiling tube (25 cm by 3 cm inner diameter [ID]) from a glass hook passing through a piece of sheet rubber (3 cm³). A number of such tubes, usually 16, were held vertically in a copper tank by means of a wire grid at the lower end and a perforated wooden board across the top of the tank. Immediate contact with the bottom of the tank was prevented with a sheet of stout wire gauze on supports. The tank was lagged with asbestos, and heating was affected by an electric hot plate. Above the tank protruded 10 cm of each tube. The tank usually contained water at 40°C to a depth of 5 cm. Each boiling tube contained the appropriate amount of inhibitor dissolved or dispersed in 50 mL distilled water. Condensation occurred on all surfaces in the upper protruding part of the tube. Fourteen days duration of the test is recommended.

TABLE 4

The Compounds/Formulations of VPI for Ferrous and Nonferrous Materials

Material	Compounds/Formulations	Corrosive Conditions	Reference
Fe and its alloys	Dicyclohexylamine and its salts.	Humid atmosphere	4, 33, and 34
Steel	Tall oil mixed with industrial oils.	SO ₂ atmosphere	35
Fe, steel, and cast iron	A mixture of methanol, ethanol, acetone, or methylethyl ketone of recinoleic acid derivatives with ethylene oxide.	—	36
Steel	Naphthalene vapor.	HCl atmosphere	37
Cold-rolled iron	An inhibitor based on hexamethylene tetramine, Pb, Ca, and Al stearates and aromatic and aliphatic acids.	90% RH at 40°C	38
Ferrous alloys	A composition containing sodium nitrite, triethanolamine, and Naphthenic or aliphatic acids.	—	39
Fe and steel	Acylation product of lanolin or multibasic alcohols like glycerol, sorbitol, etc., dissolved in oil or kerosene.	Humid atmosphere	40
Steel	Alkylation mixture of 3- and 5-methyl pyrazoles.	H ₂ S environment	41
Steel	Ethylamine, butylamine, hexylamine, diethylamine, isobutylamine, tert. butylamine, cyclohexylamine, piperidine, diisopropylamine, and dicyclohexylamine.	30 mg/L NaCl + 70 mg/L Sodium sulfate electrolyte	19
Steel	Cyclohexylamine sorbate/ borate, morpholine laurate/ azelate/ sebacate/ thiophenolate, and morpholine mannich base derivatives	—	42
Steel	m-dinitrobenzene with β-naphthol.	SO ₂ and chloride atmospheres	43
Steel	Dicyclohexyl ammonium nitrite and dicyclohexylamine.	100% RH	44
Steel	Allyl thiourea.	100% RH	45
Ferrous and nonferrous metals and alloys	Aminotriazole (with R=H or C1-12 alkyl groups) polyurethanes.	—	46 and 47
Fe, Cu, Zn, Al, and their alloys	A solution containing ammonium benzoate 2.1-250, methyl-p-hydroxy benzoate 0.5-60, benzotriazole 1-120, dimethyl-amino ethanol 0.4-50, and polyacrylate 0.1-20g/L.	—	48
Metal or alloy articles	Cyclohexylamine benzoate 50-97, ethylaminebenzoate 1-20, dicyclohexylamine benzoate 1-20, and benzotriazole.	—	49
Food canning	An emulsion consists of octadecylamine 10, sodium oleate 15 propylene glycol 25, and water 50 parts.	—	50
Steel, Cu and its alloys	A mixture of benzotriazole (95-14-7) and alkyl imidazole (288-32-4).	Cyclic exposure at 20°C to 40°C and 100% RH	51
Cu	Hexamethylene tetramine.	—	52
Steel and bronze	A mixture of ammonium benzoate or sodium benzoate (10-85) and benzotriazole (2-86) (Weight parts).	—	53
VI group and VIII group metal articles	Ethyl benzoate 1.5, mono ethanolamine benzoate 95, oleic acid amide 2, and zinc stearate 1.5.	—	54
Steel	A mixture of silica gel 60, morpholine 20, nitrobenzene 10, and hexamethylenetetramine 10 (wt. parts).	1% NaCl Solution	55
Steel and copper	A slurry consisting of dicyclohexylammonium nitrite 25 and 1,2,3-benzotriazole 2 kg were dissolved in methanol 150 mL and mixed with Ca silicate powder.	50°C 100% RH	56
Cast iron, steel, brass, and Al	Benzotriazole or its salt benzoate 15-55, CaCO ₃ , and magnesium stearate 5-35, water soluble binder 1-10, and a complex hydrophobic agent 1-8%.	—	57
Fe, Cu, and Zn alloys	Dicyclohexylamine nitrite, cyclohexylamine carbonate, benzotriazole, 3-methyl-5-hydroxypyrazole, etc.	—	58
Fe, steel, Cu, and their alloys	A fine powder made of dicyclohexylamine H ₃ PO ₄ at pH 7.5-8.5 with a freshly prepared aq (NH ₄) ₂ M ₂ O ₄ with NaNO ₂ , benzotriazole.	—	59
Cu and its alloys	Triazole-based compounds like benzotriazole. A mixture consisting of 4-5 methyl benzotriazole in a ratio 4:6 to 7:6 and impregnated in paper.	SO ₂ or H ₂ S atmosphere	60
Brass	Cyclohexylamine chromate and phenyl-thiourea.	—	45, 61, and 62
Cu	Acetylenic alcohols in gelatine, dimethylaminomethyl triethoxysilane.	—	63 and 64
Cu	An aqueous solution of 5-50% complex phenol carboxylic acid or its esters and 0.1-20% water soluble heterocyclic compounds such as ethylene thiourea, mercaptobenzothiazole, 2-amino benzimidazole, 3-amino-1,2,4-triazole, 2-amino thiazole, 2-aminoimidazole, or 2-amino benzothiazole.	Aggressive environment	65
Cu	Morpholine, diisopropylamine, and dicyclohexylamine.	30 mg/L NaCl + 70 mg/L Na ₂ SO ₄ electrolyte	19
Zn and its alloys	Diisopropylamine and diisobutylamine.	30 mg/L NaCl 70 mg/L Na ₂ SO ₄ electrolyte	19
Cu, Al, Zn, and their alloys	Benzimidazole, 2-benzimidazolethiol, benzotriazole, and 2-mercapto	—	66

Cu, steel, Al, and Zn	Products obtained by reaction of benzotriazole, ethyl benzotriazole, and methyl benzotriazole with soluble urea compounds in a molar ratio of 1:0.5 to 1:2 at 10°C to 60°C.	—	67
Fe, Cu, Al, and Zn	Reaction product of benzotriazole with polyamine (e.g., ethylene diamine and carboxylic acid are dissolved in spindle oil).	—	68
Steel, Zn, Cu, and Cd	Mixtures of benzotriazole with benzoates of NH ₃ , guanidine, hexamethylenediamine, and monoethanolamine.	—	69
Fe, Al, steel, Cu, Ag, Zn, Ni, Cd, Mg, Pb, and their alloys	4-H, -1,2,4 triazole or its derivatives in combination with known inhibitors like dicyclohexylamine nitrite, urea, NaNO ₂ , etc.	SO ₂ and H ₂ S atmosphere	70
Cu, brass, Sn, and tin-plated steel	Reaction products of methyl benzotriazole with water soluble guanidine class compounds such as guanidine carbonate or nitrate or methyl, dimethyl, trimethyl, ethyl, or diethyl guanidine in a molar ration of 1:0.5-1:2.	—	71
Cast iron, steel, Cu, brass, Al, solder, and other metals	Reaction product of 1 mole of cinnamic acid with 1-1.05 mole of amine such as diethylamine, triethylamine, diethanolamine, cyclohexylamine, etc., with or without solvent.	—	72
Steel, cast iron, Cu, brass, galvanized iron, and Pb	A mixture of benzotriazole with substances of oxidative character (e.g., nitromethane, nitronaphthalene, dinitrophenol, and m-nitrobenzoic acid are dissolved in acetone).	—	73
Steel and Cu	A ternary mixture comprising benzotriazole and Na ₂ CO ₃ mixed with urotropine.	—	74
Ferrous metals, Cu, and Cu alloys, Al and Al alloys, Zn, Cd, Pb, Ni, and Cr, phosphate, and oxide coatings	A mixture containing by parts 3-30 of benzotriazole and higher aliphaticamine (octadecylamine).	—	75
Steel, Cu and brass	Dibutylphthalate, iso-amylcinnamate, triamylborate, or the nitrobenzoate and other esters.	85% to 98% RH	76
Al	Mixture of hexamethylene tetramine with NaNO ₂ .	90% RH at 40°C	77
Al, Cu, Zn, Sn, and other nonferrous metals	Substituted pyrazoles dissolved in CH ₃ OH, C ₂ H ₅ OH, or water.	—	78
Ag	Carboxylic acids are hexamethyleneimine salt of 0-nitrobenzoic acid or 3,5 - dinitrobenzoic acid.	—	79
Ag	m-nitrobenzoate of hexamethylene imine (14% alcoholic solution wash) and piperidine 3,5-dinitrobenzoate.	—	80
Ag	Benzotriazole and tolyltriazoles.	H ₂ S atmosphere	81
Ag	Neutral inhibitor (e.g., 61 g monoethanol amine in 61 g water, 172 g capric acid, and 69 g NaNO ₂ [in 69 g water] is gradually added and neutralized with benzoic acid and coated in packing paper).	—	82
Ag	Papers impregnated with Zn or Cd salts.	H ₂ S atmosphere	83
Ag	Packaging paper impregnated in a solution of chlorobenzotriazole in a polar solvent such as alcohol, ketone, cellosolve, or glycol.	H ₂ S atmosphere	84
Ag	Paper impregnated with Na or Mg salts of chlorophyll.	H ₂ S atmosphere	85

The previous two methods evaluated the compounds only after they were dissolved or dispersed in water and not in their native form. Hence, a modified cell design was suggested to overcome this difficulty.⁹⁰

Vapor Inhibiting Ability Test⁹¹⁻⁹³

The vapor inhibiting ability (VIA) test was carried out to assess the ability of VPI-coated papers and exhausted samples. The coated papers were exhausted by maintaining an air flow at 6 L/min for 48 h. The polished and degreased metal specimens then were wrapped with freshly coated paper and exhausted paper samples. Both specimens were kept hung in an air-tight glass bottle containing 100 mL distilled water maintained at 40°C ± 1°C. This test was continued for 120 h in the case of freshly coated paper and 96 h for the exhausted paper. Conditions of the specimens after the test were noted. The same test

also can be performed to evaluate VPI in liquid and powder forms.

A continuous condensation test of a similar nature was performed in an environment where it was possible to have continuous condensation of water vapor on the metal surface. Observations were made at the end of 96 h to evaluate VPI-coated papers.

Stevenson Chamber Test⁹¹

The Stevenson Chamber test was carried out to assess the long-term protection given by the VPI-coated paper. In this test, metal specimens wrapped with the most protective concentration of the VPI coated and uncoated papers were exposed in the Stevenson chamber, where free air flow was maintained. The exposure was continued for 90 days, and the condition of the specimens were examined through a metallurgical microscope under magnification.

Salt Spray Test⁹⁴

A salt spray test was made to assess the protective ability of the VPI-impregnated paper under marine environment using a salt spray chamber.

Metals specimens were wrapped with the most inhibiting concentration of VPI-impregnated and unimpregnated papers. They were hung in perforated plastic containers and kept inside the salt spray chamber in such a way that the wrapped specimens were exposed freely to the fog. The experiment was carried out for 8 h/day. This consisted of two cycles. Each cycle consisted of 1 h spraying and 3 h rest. Observations were made at the end of every 15 days for 45 days.

Vapor Phase Inhibitor Monitor⁹⁵

The vapor phase inhibitor monitor (VPIM) consisted of 20 foils of carbon steel (0.05 cm wide, 8 cm long). Steel plates were separated by a 170- μm thick layer of an insulating sheet. The surface area was 8 cm². Alternate steel plates were connected to establish a two-electrode configuration technique. In the VPIM, the central steel foil remained unconnected to the others and served as a reference electrode. To obtain a three-electrode configuration, a block of ten steel foils acted as the working electrode. The central steel foil remained unconnected to the others and served as a reference electrode and the other block of nine steel foils as the counter electrode. The working electrode surface area was 4 cm². This setup eliminated the use of a calomel reference electrode, which introduces chloride. The assembly was encapsulated in a polymer. One side of the assembly was polished with different grades of emery paper, degreased with acetone, and dried to expose the edges of the steel foils to the atmosphere. VPIM and VPI were placed in a 2-L volume desiccator at 100% relative humidity (RH).

Using two-electrode or three-electrode cell assemblies, electrochemical measurements were made. Tafel extrapolation, linear, and cyclic polarization measurements were used extensively to determine the corrosion rates in the presence and absence of inhibitors. Faradic impedance measurements used to find the film capacitance also are reported.

Often, these methods run the risk of overloading the instruments. An alternate method that uses the VPIM carries out the experiment in the presence of VPI-impregnated or unimpregnated kraft paper pressed against the electrode with a thin layer of electrolyte spread over them.⁸⁷

FILM THICKNESS AND INHIBITION MEASUREMENTS

Earlier reports are available on the use of radiochemical, infrared (IR), ultraviolet (UV), mass spectroscopy, and gas chromatography experiments

to determine the performance of inhibitors.⁹⁶ Following are the very recent applications of in-situ methods of the study of VPI.

Ellipsometry

Ellipsometry may be characterized as reflection polarimetry or polarimetric spectroscopy, and it involves the measured effect of reflection on the state of polarization of light.⁹⁷ Such measurements may be interpreted to yield optical constants of the reflecting material or when the reflecting material is a film-covered substrate, the thickness and optical constants of the film.

Earlier reports on the application of ellipsometry were made in 1987.⁹⁷ Interactions of dicyclohexylamine and dicyclohexyl ammonium nitrite on iron and platinum were made. The thickness of a film with a given refractive index and absorption coefficient can be characterized with the aid of polar diagrams showing the dependence of the phase shift (Δ) and the $\tan(\psi)$ on the thickness of the film. Seen from the curves, this method is suitable for determining the thickness of thin films ≈ 200 Å thick, even when the optical activity constants are unknown. To determine greater thicknesses, it is necessary to know the optical activity constant of the films, however, even when the later are not known, the method can be used for comparative determinations. To ascertain film thicknesses-200 Å, this method is no longer suitable. Adsorption of pyridine molecule on silver and the orientation of the molecules also were discussed.⁹⁸

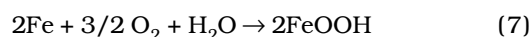
Quartz Crystal Microbalance

Earlier reports on the use of piezo quartz microweighing balance for calculating the vapor pressure of the inhibitors were made by Golyanitskiy.⁹⁹ The simpler and most reliable method was used for salt inhibitors that have strongly differing volatility of the cations and anions. Based on the method of diffusion rate of gases through a small orifice, an apparatus for measuring the vapor pressure of compounds also was suggested.¹⁰⁰ The rate of diffusion was determined by measuring shrinkage of a highly sensitive quartz spring with a cathetometer.

Detailed measurements were made on thin metal film-deposited crystals. The method uses the piezoelectric microbalance to the study of adsorption of volatile inhibitors on metals and the protective action of these inhibitors against atmospheric corrosion.¹⁰¹

Quartz crystal microbalance (QCM) technique also can detect sensitively a small weight change during minute corrosion of thin metal films from the measurement of change in resonance frequency of quartz crystal.¹⁰²⁻¹⁰³

If iron surface corrodes according to the following reaction:¹⁰⁴



then, the frequency change is given as:

$$\Delta f = -\left(C_f/A\right) \cdot \left([\Delta n]_{Fe}/M_{(OOH)}\right) \quad (8)$$

and the corrosion rate results as:

$$I_{corr} = 2F \cdot d([\Delta n]_{Fe})/dt = \left(-2FA/C_f M_{(OOH)}\right) \cdot \left(d(\Delta f)/dt\right) \quad (9)$$

where $(\Delta n)_{Fe}$ is the amount of corroded iron; $M_{(OOH)}$ is the molar mass of the $-OOH$ group responsible for the mass gain during corrosion; A is the area of the sample; F is the Faraday constant; 2 is the number of electrons transferred during electrochemical oxidation; $d(\Delta f)/dt$ is the rate of change of the resonance frequency; and C_f is the sensitivity constant ($2.26 \times 10^8 \text{ cm}^2/\text{Hz}\cdot\text{gm}$).

As a result of corrosion, a decrease in the frequency at the beginning would occur. The introduction of VPI would reverse the sign and cause an enhanced frequency decrease.

Kelvin's Probe

Kelvin's probe consists of a small disk vibrator mounted parallel to the sample surface, and a $10\text{-}\mu\text{m}$ to $100\text{-}\mu\text{m}$ gap was made. An audio frequency current was fed into the vibrator when both metals were connected; their Fermi levels were identical. The two surfaces formed a condenser, the capacity of which oscillated with the motion of the vibrator resulting in an alternating current in the circuit.

$$i_{ac} + dQ/dt = \Delta\psi (dc/dt) \quad (10)$$

where $\Delta\psi$ is the Volta potential difference between the points just outside the sample/electrolyte and the vibrator. When a battery of voltage (V) was added to the circuit, then the Fermi levels of the two metals differed by V , and $\Delta\psi$ was altered by:

$$i = (\Delta\psi - V) dc / dt \quad (11)$$

When $V = \Delta\psi$, the alternating current (AC) signal vanished. Signal amplification, analysis, and nulling allowed measurement of a Volta potential to an accuracy of 1 mV .

Application of Kelvin's probe to corrosion measurements was made.¹⁰⁵⁻¹⁰⁶ A linear relationship between Kelvin potential and corrosion potential usually was obtained. Studies made on water droplets revealed that the change in Kelvin's potential increased with humidity. In humid atmospheres, a thin electrolyte layer was formed. The Volta potential was determined mainly by the galvanopotential dif-

ference of the metal/water interface. These were related to corrosion potential as:

$$d\psi_{El}^{ref} = E_{corr} - \left[W_{ref} / F - \lambda_{El}^{gas} - E_{ref}\right] \quad (12)$$

where E_{corr} is the corrosion potential; λ_{El}^{gas} is dipole potential of the water/gas interface; and E_{ref} is the half cell potential of the standard reference electrode needed to relate the absolute potential scale to the electrochemical potential scale. This probe was used to monitor the local corrosion potential of the partly covered metal surface with adsorbed organic molecules.

METHODS OF APPLICATION OF VPI

When articles are to be protected for longer periods, the inhibitor is used either as an impregnant or coating on a paper. The vapors must have free access to all surfaces of the part to be protected. If access is denied, supplemental protection is needed. The face of the paper always should be placed toward the items to be protected. Indoor shelf storage for periods up to 1 year require only a good grade of wax paper or overwrap, but for intended storage of 3 years to 5 years required sealed metal containers or bags made of barrier material. Assemblies that possess critical working surfaces of nonferrous metals, as well as ferrous metals, require additional preservation. It is necessary to be careful of the type of inhibitor used because the various chemical compositions differ in their corrosive effect on nonferrous metals such as copper, nickel, silver, aluminum, and the bronzes. Halogenated solvents such as carbon tetrachloride (CCl_4), chloroform (CHCl_3), and trichloroethylene (CCl_2CHCl) should not be used for cleaning items prior to packaging with vapor phase inhibitors.

The inhibitor can be used in many types and variations of packaging procedures, the selection of which will depend on the article to be packed, corrosive conditions that the package is likely to encounter, duration of protection desired, and cost. One type of procedure involves merely wrapping the steel article in the inhibitor paper with a barrier coating on the outside to hinder escape of the inhibitor and ensure long-term protection. In such cases, a wax-coated inhibited paper or kraft asphalt laminated inhibited paper may be used. Simple fold closure of such packages is adequate. If a barrier film is not incorporated into the inhibited paper, a separate overwrap sheet of barrier paper or a box container is used. Suitable barrier overwraps would be wax paper, kraft asphalt-kraft paper, or metal foil laminates. When many individual items are to be packed in a single box, it might be advantageous to use separators of inhibitor paper instead of individual inhibitor paper wraps around each of the

items. Even greater simplification of packaging operations is possible if the box is fabricated of paper board with the inner surface coated with inhibitor.

One of the simplest procedures involves use of an envelope or bag prefabricated from an inhibitor with barrier paper. The article is placed in the envelope and the flap turned down and fastened by clips, staples, or adhesives. The simplest application is to dust the surface with the powder or suspend it in a loose or porous container close to the surface to be protected. VPI may be made as latex or bentonite suspensions. A sheath of latex or bentonite can be made by dipping the article in a hot solution and then drying. The surface is wiped with a wet cloth. Upon ageing, the latex coating may stick to the surface. To regulate the rate of escape of the VPI, various adsorbents were tried.¹⁰⁷ They differed in pore structure; some examples were activated carbon fabric, aminated carbon fabric, oxidized carbon fabric, activated carbon sodium zeolite, ultra stable dealuminized zeolites, sodium aluminium silicates, and silica gels. Where desiccant papers could not be used, VPI was sprayed. An alternative to VPI was to dip felt pads into the oil and attach to the machinery at strategic points prior to sealing in the polyethylene sheets. The vapors from the pads permeated the entire volume and helped protect the uncoated surface. An aqueous VPI paper has a number of advantages and it forms a fog or mist that permeates throughout the interior condensing on the content.

INDUSTRIAL USES OF VPI

Unlike oils or coatings, VPI inhibitors allow the electrical and mechanical parts to operate at 100% efficiency. Switch boxes, electrical and electronic equipments, instrument cases, and junction conduits are a few examples. VPI allow protection of hard-to-service areas and areas where the physical contacts of stored parts can create galvanic couples. Tool chests, auto and aircraft parts, storage, molds-storage, and others are a few instances.

VPI are used during shutdown as well as during operating conditions. After shutdown, VPI are introduced. The rapid initial protection achievable with VPI assures rapid corrosion control, which is prolonged for the whole period of the shutdown.

CONCLUSIONS

- ❖ Since World War II, research has been pursued toward the development of VPI, owing to their increased demands. The attempt to correlate corrosion inhibition and the structure of organic compounds was a rewarding exercise.
- ❖ However, in view of the toxic and carcinogenic nature of many VPI, a judicious selection of inhibitors with good corrosion inhibition and the fewest health

hazards is to be made. To protect complicated machinery during shipment, storage, and use, VPI still offer an excellent solution without impairing the functional properties of the machinery used.

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