FUNDAMENTAL PRINCIPLES OF CORROSION PROTECTION WITH VAPOR PHASE INHIBITORS

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SUMMARY

The inhibition of atmospheric corrosion of both ferrous and nonferrous metals demands the application of chemical compounds which posses high passivating properties, strong tendencies toward surface adsorption, and the ability to form a comparatively strong and stable bond with metal surface. The delicate and yet complex nature of atmospheric corrosion processes occurring under thin films of electrolyte preordains the transport mechanism of corrosion inhibitor which- in order to become effective, must diffuse through the electrolyte film and cover the substantial portion of the surface. The precise parameters of the corrosion inhibiting mechanism are still unknown. It is believed that certain physical and chemical properties of the benevolent molecules are critically important, e.g., vapor pressure saturation levels, molecular structural characteristics, availability of reactive groups for surface physical or chemical binding, the polarity, the contamination, the resultant conductivity of the electrolyte, etc. There is a considerable controversy over the importance of, and the relationship between the saturated vapor pressure and its influence on the effectiveness of the specific VCI compound. Various investigations have either (1) emphasized the significance of minimum acceptable values of vapor pressure to achieve vaporization or (2) stressed the importance of electrochemical factors in altering the kinetics of partial corrosion processes.   The many critical requirements made on an inhibitor of atmospheric corrosion have severely limited the number of compounds acceptable to solve the practical corrosion problems existing in the industry.

INTRODUCTION

It is sincerely believed that it is indeed the time to bring the spirit of innovation in to the field of atmospheric corrosion inhibitors.

What happened in 1973, 1974 and as recently as a few months ago, was an early sign of complex problems that will employ much skilled human resource to bring an acceptable and economical solution. Since the subject of potential energy and material resource shortages is well known to you, I will stay with it only long enough to bring a point across, my belief that those energy and material shortages do represent a serious challenge, and perhaps, an unusual opportunity for future innovative ideas and concepts.

Due to their unique protective mechanism, I trust inhibitors of atmospheric corrosion do fall in the category of innovative concepts, concepts which may help preserve natural resources, so important to our modern society.

However, an equally serious potential shortage is much less tangible. In essence it is a shortage of one of the most essential ingredients of technical innovation:

The Results of Basic Scientific Research

Support of basic research in the area of chemical corrosion inhibitors by the National Science Foundation, by professional societies, by research institutes, and by trade association has been minimal. Support of basic research in the area of volatile corrosion inhibitors, to the best of my knowledge has been negligible in the past twenty five years. With increasing barriers to innovation there is a need to initiate and to continue the innovation process by stimulating the basic research.

Volatile Corrosion Inhibitors represent the most economical and yet extremely powerful tool in combating the atmospheric corrosion damage to metals and alloys. It is estimated that in the U.S. alone direct cost of atmospheric corrosion to the industry, government and consumers amounts to about $20 billion annually. Indirect damages are almost impossible to express in terms of dollar value since they consist of such important resources as energy needed to manufacture replacements for corroded objects, humans killed or disabled as a result of failures of corroded structures, artifacts lost as a result of corrosive attack, etc.

The concept of volatile corrosion inhibition utilizes conditioning of the environment with trace amounts of inhibitive material to achieve the protective effect. Classical methods involve either changing the composition of an alloy or covering the metal with a protective coating. In some instances, like, scientific instruments, electrical and electronic equipment, etc. it is even impossible to adopt classical methods of prevention and that is the area where the usefulness of VCI's is probably most obvious.

However, due to scarce information and general disinterest of the public for new and improved methods of protection, very little has been done in the past thirty years to develop new VCIs. Two compounds that have been developed in the late forties, dicyclohexylamine nitrite and diisopropylamine nitrite, have been accepted as standards, and virtually no effort has been made to upgrade or develop new compounds with improved performances.

The National Association of Corrosion Engineers has only recently recognized the importance of these compounds by sponsoring an International Symposium and a task group devoted exclusively to the VCIs. The purpose was to initiate new researches, to collect and develop the information on VCI technology and to make the information available to the industry and other interested parties.

THE NOMENCLATURE

According to Fischer, (1) corrosion inhibitors can be divided in two categories (Table 1).

1. Interface Inhibitors
   Interface inhibitors decrease the velocity of
   physical, electro-chemical and/or chemical processes
   of electrode reactions taking place immediately at the
   metal/electrolyte interface.

2. Electrolyte - Layer Inhibitors
   Electrolyte - Layer inhibitors may decrease the velocity
   of physical and chemical processes of the electrode reactions
   taking place in the electrolyte layer which adheres to the inter-
   face. This layer may be a diffusion part of the double layer,
   the Nernst diffusion layer or Prandtl's flow boundary layer.
   Electrolyte-layer inhibition is caused by substances dispersed
   or dissolved in the mentioned electrolythe-layer.

Further, Fischer classifies inhibitors into Primary Inhibitors or Secondary Inhibitors depending upon the origin of protective species:

- Primary Inhibitors are substances that are a priori present in the
   bulk of the electrolyte layer without chemical change of their
   composition.

- Secondary Inhibition is caused by the substances which are not
   a priori present in the bulk of the electrolyte. They must be
   generated at the interface or in the electrolyte layer by a chemical
   or electrochemical process.

In order to contribute to the problem of classification and proper identification of VCI compounds the following definition is proposed:

Volatile Corrosion Inhibitors are secondary electrolyte layer inhibitors that possess appreciable saturated vapor pressure under atmospheric conditions, thus allowing vapor phase transport of the inhibitive substance.

By definition, only compounds that are volatile under atmospheric conditions and can act as electrolyte layer inhibitors by electro-chemically changing the kinetics of electrode reactions should be classified as VCI's. Neutralizing amines, for instance, do have an appreciable vapor pressure, and are effective inhibitors for ferrous metals, but their mechanism is based on adjusting the pH value of the electrolyte thus creating conditions inhospitable for formation of rust; hence, they should not be necessarily classified as volatile corrosion inhibitors.

By definition a VCI compound in addition to being volatile is required to promote the electrochemical effects such as change of the ψo, - potential in the diffuse part of the double layer which controls the migration of components of the electrode reactions.

THE MECHANISM

It was pointed out by Balezin, (2) that every inhibitor of corrosion, including volatile ones, should:

  a. be capable of establishing a stable bond with the metal surface in
      a given environment of a certain range of acidity and pressure.

  b. create a layer impenetrable to the corroding ions.

The Mechanism of inhibition is shown in Fig. 1.

The functional group R_1 linked to the nucleous Ro of the inhibitor molecule is responsible for adsorption in a given environment. The functional group R_2 also linked to the nucleus Ro is responsible for the thickness and the impenetrable nature of the film formed. In designing the inhibiting compound for particular environment, it is first necessary to vary the functional group R_1 until a substance capable of being firmly adsorbed on the metal surface is obtained. Having thus determined R_1 we vary the functional group R_2 until satisfactory resistance to penetration of aggressive ions is achieved. The use of the above principles of selection enables one to develop corrosion inhibitors effective over a variety of metals and environments.

In designing a volatile corrosion inhibiting compound, however, we have to assure ourselves that the compound will have an appreciable vapor pressure, as well as the capability of forming a stable bond with the metal surface. It is well known that the vapor pressure of a chemical compound largely depends upon the structure of the crystal lattice and the character of the atomic bond in the molecule. Therefore, if an inorganic

compound contains a desired protective group (anion), an organic radical can be substituted for the inorganic cation, so that an organic salt is obtained which will possess the two desired properties:

- a protective group

- a volatility

However, it is not always possible to obtain successfully both of these properties in one compound. The protective anion may be too heavy to vaporize into the air. This, in all possibility is the reason why so few volatile inhibitors have been synthesized with chromate as the anion. Sometimes the vapor pressure of the synthesized compound becomes so high that the steps must be taken to reduce it.

High vapor pressure compounds reach the protective vapor concentration rapidly, but in the case of enclosures that are not airtight, the consumption of inhibitor is quick and resulting protective periods are short. On the other hand, low vapor pressure inhibitor is not used up so quickly and can assure more durable protection, but more time is required to achieve a protective vapor concentration. Furthermore, there is a possibility of corrosion during initial period of saturation, and if the space is not hermetically sealed, a protective inhibitor concentration may never be obtained (Fig. 2).

Therefore, the chemical compound used as a volatile inhibitor must not have too high or too low vapor pressure, but some optimum vapor pressure (Fig. 3).

To determine the saturated vapor pressure of volatile inhibitors and their temperature dependence, two experimental methods have been employed: Rosenfeld Martin Knutsen effusion method (3) and (4) dynamic flow method. Analysis of data found in the literature points at certain inconsistency in vapor pressure values published by different authors. It is believed that the reproducibility of data depends upon experimental parameters that are inherent properties of the test method employed. It was showed (5) that measured vaporization rates in vacuo and in the atmosphere are not equal and that differences for the same compound could be relatively large. This partially explains difficulties encountered in correlating vapor pressure data obtained with different experimental techniques. According to Rosenfeld few effects are possible:

1.   the change in the total pressure modifies Gibbs' free energy for the components of the condensed phase.

2.   an extraneous gas slows down the vaporization of the condensed phase components (kinetic effect).

3.   part of the vapor, for instance the water vapor, dissolves in the condensed phase and modifies Gibb's free energy of the latter.

All of the above mentioned factors can show different effects, even in sign, on the vaporization rate. However, a researcher should be aware of the fact that vapor pressure values depend on the total pressure and, as should be expected, on the composition of the surrounding atmosphere. The vapor pressure dependence of volatile inhibitors upon temperature is given in Fig. 2.

Considering that the vapor pressure of VCIs satisfactorily conforms to straight lines (in the - LgP vs 1/T coordinate system), the latent heat of sublimation can be calculated by Clapeyron - Claussius equation (6).

$$LgP \ = \ A/T \ + \ B$$

The comparison between the vapor pressure of a compound and its molecular heat of sublimation shows a marked decrease in vapor pressure values with increase in a heat sublimation. This is a reason to believe that decrease in vapor pressure may be accounted for by steric intermolecular interactions between functional groups and by increase in molecular weight of the compound (Table II).

It is significant that all of the most effective volatile corrosion inhibitors are the products of reaction of weak volatile base with a weak volatile acid. Such substances, although ionized in aqueous solution undergo a substantial hydrolysis, the extent of which is almost independent of concentration. In the case of the amine nitrites and amine carboxylates the net result of those reactions may be formulated as:

$$R_2NH_2^{\ +} + NO_2^{\ -} \qquad R_2NH \quad +HNO_2$$

$$R_2NH_2^{\ +} +R^1 \ COO^- \ R_2NH + R^1COOH$$
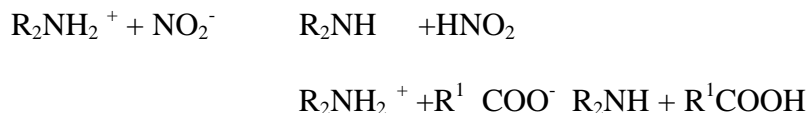
In further support of the mechanism of vapor-phase transport postulated it can be noted that amine salts such as dicyclohexylammonium nitrate or diisobutylammonium sulfate, which are not extensively dissociated by water, do not give significant vapor phase inhibition. The same is true for slightly hydrolized alkali metal salts such as sodium nitrite or sodium benzoate, although the latter are excellent rust inhibitors when their solutions are in direct contact with metal surface.

A series of interesting experiments have been run by Zisman and Baker (7) at the Naval Research Laboratories to determine the relationship between pH of solution and the rate of emission of hydrolytic or thermal dissociation products. It was shown that appreciable volatilization of both components of an amine carboxylate or an amine nitrite will probably be only in the approximate pH range of 5.5 to 8.5. On the acid side of the neutral point the useful inhibiting range is limited by the fact that when the volatile acid constituent is present in the vapor in excess it will dissolve in the condensate on the metal surface to give it an even lower pH, which in the case of nitrous acid or short chain organic acids, may actually accelerate rusting.

The results of indicator experiments with various solutions of dicyclohexylamine nitrite and of diisopropylamine benzoate are summarized in Table II which shows that the pH produced by such inhibitors in the condensate forming on exposed steel surfaces depends strongly on the saturated inhibitor solution from which the protective vapors originate (Table III).

The pH of the inhibitor preparation, therefore, affects not only the initial volatilities of the inhibitor, but also the effectiveness of its operation after it reaches the metal surface. At a pH above 8.5 an acid is present almost exclusively as nonvolatile anion and any inhibition noted from an amine carboxylate in this range is attributable to the volatile amine, which has definite, although inadequate, corrosion-inhibiting properties in its own rights.

The secondary alkylamine nitrites react in the presence of small traces of inorganic acid to give nitrosoamine, which is not an efficient corrosion inhibitor. This limits their use to acid free systems or indicates the use of an alkaline buffer. On the other hand, in the presence of excess alkali the free amine and an alkali nitrite are formed. Thus, for satisfactory operation an effective buffer must be used to maintain the pH at a level definitely on the alkaline side.

NATURE OF ADSORBED FILMS

Even more important for the efficiency of volatile corrosion inhibitors than the pH effects just discussed, is the nature of adsorbed film formed at the steel-water interface. Metal surfaces exposed to vapors from the VCI's in closed containers give evidence of having been covered by a hydrophobic adsorbed layer. The contact angle of distilled water on such surfaces, increased with the time of exposure as shown in Fig. 4 (8).

The change in the contact angle by the interaction between the inhibitor and the metal surface has been measured after removing excess inhibitor with the solvent. It has been established that after 7 days exposure the contact angle increased from 170 - 200% of original value. Further increase is only moderate and levels off at about 275% for steel, 137% for copper and magnesium and 120% for zinc after 3 months exposure.

The greatly increased protection against rusting that results when both acid and amine are present is noteworthy and deserves further study. The data available does not make clear whether the gain is a result of synergism between adsorbed acid and amine to give a more firmly held momolayer that could be formed by either one alone. It is important that the mixed film when adsorbed at the water-air interface is highly condensed. It is also conceivable that the mixed film serves as a buffer to hold the pH at the interface in the optimum range for corrosion resistance. Another possibility is that amine and acid contribute to the corrosion inhibition by different but additive mechanisms.

Experimental studies on the adsorption of volatile inhibitors from the gas phase confirm the assumption that VCI's react with the metal surface thus providing corrosion

protection. When a steel electrode is exposed to vapors of a volatile inhibitor, the steady-state electrode potential shifts considerable into the region of positive values (Fig. 5).

The higher the vapor pressure, the stronger is the shift of the electrode potential in positive direction. Inhibitor adsorption is not a momentary process and requires much time for completion. This indicates that the adsorption is chemical and not physical in nature, resulting in a chemisorbed layer on the metal surface. However, these chemisorbed layers cannot be considered as protective phase films since the bond between the inhibitor and the metal surface is not strong enough to prevent the adsorbed inhibitor from leaving the metal surface when the metal is removed from the inhibitor saturated atmosphere. It is obvious that if stable chemical compounds were formed to produce a phase film on the metal surface, the adsorbed inhibitor could not leave the metal surface as freely as it does.

Therefore, it can be concluded that to insure continuous reliable protection a steady supply of inhibitor should be maintained from the gas phase to the metal surface. The nature of adsorbed films has been studied with the use of autoradiography (9). The results were indicative of the fact that separation takes place in the atmosphere, and the inhibitor's molecule is separated when adsorbed on the metal surface. The mixed nature of adsorbed film has been thus experimentally confirmed, showing the existence of inhibitor's molecule in dissociated (separate) form, an anodic and cathodic inhibitor respectively, which explains the synergism that has been postulated in studies of Zisman and Baker over thirty years ago.

The attempts to adopt flame ionization detector with sensitivity of 10^{-7} - 10^{-9} g/m^2 to study the process of adsorption of volatile corrosion inhibitors have proven reasonably successful in having sufficient sensitivity to detect adsorption of compounds with vapor pressure of 10^{-7} mm Hg and lower (10). It was found that the amount of adsorbed inhibitor increases with temperature which is indicative of above mentioned activated character of adsorption. Knowing the pressure of saturated inhibitor vapor, and the flow rate of the carrier gas, it is possible to calculate the amount of inhibitor molecules adsorbed on the metal. It proved much lower than the amount necessary to form monomolecular layer. A negligible surface coverage on highly polished metal surfaces is attributed to equilbrated adsorption - desorption process. The parameters of the process change, however, with the change in surface roughness; it was found that corrosion growth on the surface, for instance, will promote adsorption sites for volatile inhibitor by probably increasing the active surface area. It is likely that inhibitors saturate the free valencies of surface metal ions, changing the chemical properties of the surface. These changes, however, take place on activated sites only, and not on inactive ones, where the inhibitor desorbs at the same rate as it is being adsorbed.

OVERVIEW OF PERFORMANCE TESTS

Attempts to develop a reliable laboratory experiment that would provide usable information on behavior of volatile corrosion inhibitors have been only partially successful. It is extremely difficult to reproduce atmospheric conditions encountered during field application and to design the test that would give meaningful results in a relatively short period of time. Acceleration of test conditions with artificially increased concentrations of sulfur dioxide, hydrogen sulfide or sodium chloride are representative of specific atmospheres, industrial, oil-field and marine for instance, but information obtained in those tests should not be directly correlated to actual field performance.

One of the first experimental set-ups used to study VCIs was developed by Vernon and Stroud (1).

Solution on the bottom of the test chamber contains dissolved corrosive gases, i.e., sulfur dioxide, at desired concentrations, which causes the acceleration of corrosion experiment.

By using the above described test method amine carbonates have been shown to afford corrosion protection to steel, and a variety of non-ferrous metals in moist atmospheres polluted with sulfur dioxide. The same inhibitors, however, initiated corrosion of copper and copper base alloys which is probably due to corrosive action of carbonic acid formed by combining carbon dioxide and water in condensed moisture layer on the metal surface. Carbon dioxide and volatile amine are products of dissociation of amine carbonate inhibitor.

As shown in (11). amine carbonates are effective inhibitors of steel corrosion in atmospheres containing rather high concentrations of sulfur dioxide.

Considerable effort has been applied by Wachter and Stillman (12) to development of a rapid laboratory test that would give a more reliable indication of the efficacy of volatile corrosion inhibitors for protective packing than is offered by humidity cabinet tests. The dynamic test accordingly developed is made by passing clean air at $105^{o}F$ at a rate of 120 cc per minute for the test period of 44 hours through the apparatus illustrated schematically in (12). It is interesting that several amines, which passed some static tests perfectly failed in the dynamic test.

By using this method it was possible to study the kinetics of vaporization of volatile corrosion inhibitors. The rate at which vaporization of dicyclohexylamine nitrite occurs at room temperature is shown in Fig. (10) from experiments in which sheets of Dichan impregnated paper were suspended in an air stream flowing at constant velocity of 100 ft. per minute over both sides of each sheet.

It was demonstrated that a sheet containing 1 gram of Dichan per square foot would be deleted in about three weeks under those test conditions (12). Accelerated test method has been developed by Levin to study the effectiveness of VCIs in simulated tropical climates (8).

The results of those tests are indicative of the influence of chain length of the aliphatic acid used in preparation of the inhibitor on the effectiveness of protection. Fig. (11).

The efficiency of volatile corrosion inhibitor with increase in the chain length of aliphatic acid can probably be explained by a stronger hydrophobisation effect which is due to increased contact angle, as discussed above.

The need for a suitable electrochemical method for studying volatile corrosion inhibitors has been pronounced ever since VCIs were discovered. The attempts to correlate the electrochemical measurements in a volume of electrolyte with actual atmospheric conditions happening under thin films of electrolyte, have been unsuccessful due to drastic changes in electrochemical behavior of metals under those two conditions. Rosenfeld and his co-workers have succeeded to develop an apparatus suitable for electrochemical measurements of atmospheric corrosion of metals under thin films of electrolyte (13). That apparatus was later adopted for the study of volatile corrosion inhibitors when the inhibitors saturated those films with condensation of their vapors.

The potential shift to the region of positive values led Rosenfeld to believe that the volatile inhibitors slow down the rate of the anode reaction.

Indeed, kinetic studies of the anode process in the atmosphere of amines and their salts have shown that anode reaction sharply diminishes, the effect being mostly pronounced in the presence of free amines. The effect of amine salts also is to slow down the reaction of ionization of metals, but however, the effect is considerably less pronounced.

It has been demonstrated that, hydroxyl ions and anions of acids formed as a result of dissociation and hydrolysis of amines and their salts determine the mode of inhibition of the corrosion process. Protection given by those compounds is due to the presence in their structure of complex organic cations which contain pentavalent nitrogen in the ring. According to literature sources, nitrogen of the amine group is capable of entering into a coordinate bond with metals thus enhancing the adsorption process. Adsorption of cations increases the overpotential of metal ionization and slows down the corrosion. In the case of amine salts the protective role is also attributed to the acid portion of the molecule. It is known that nitrites and benzoates are capable of inhibiting the anode reaction. Certain compounds, namely salts of amines and substituted benzoic acids, and esters of chromic acid are capable of slowing down the kinetics of cathode reaction in addition to being effective anodic corrosion inhibitors.

Traditional VCI's mainly compounds containing nitrite group, possess one essential shortcoming; they protect ferrous metals and attack non-ferrous metals, like zinc and its alloys. Electric and electrolic equipment, instruments, engines, etc., are only rarely built of exclusively ferrous metals and this severely limits application of nitrite VCIs. The

recent development in the field of VCIs represents the synthesis of compounds which can act at the same time as anodic and cathodic inhibitors and have satisfactory volatilization rates. These inhibitors are (usually) called mixed inhibitors and their main advantage over traditional VCI's is the fact that they do not adversely affect certain non-ferrous metals, but, in fact, they do protect most of the common engineering metals and alloys (Fig. 7).

The inhibition of cathodic process is achieved by incorporation of one or more oxidizing anions in an organic molecule of a VCI compound. In contrast to inorganic anions which reduce with a great difficulty on an iron cathode in neutral electrolyte, the same anions introduced into the benzene ring, for instance, will show enhanced reduction process of the neutral group. Further acceleration of the cathodic process rate can be accomplished by the introduction of an electrophilic substitute which can reduce the nitrogen electron density and thereby accelerate the reduction process. Carboxyl and second nitrite groups are considered to be very effective electrophilic substituents, and with them a compound can be obtained that rapidly reduces on an iron cathode. However, inhibitors designed in this manner show weakness in environments containing high concentrations of aggressive ions, i.e., chlordie ions, where the current density required for acceleration of cathodic reaction is commensurate with passivation current.

We have investigated the influence of volatile corrosion inhibitor on hydrogen embrittlement of high strength steel (15). It was postulated that those inhibitors could promote hydrogen embrittlement resistance in neutral or near neutral environment. For that study a test method was developed by using fatigue precracked compact tension specimens. A layer of electrolyte of controlled thickness of 160 M was created on the crack; the electrolyte was distilled water containing 1.0% concentration of volatile corrosion inhibitor.

It was felt that these test conditions correlate fairly well with conditions found during exposures to humid atmospheres, that enhance hydrogen embrittlement of high strength steels. The concentration on inhibitor in the electrolyte layer is representative of concentrations obtained by sublimation and condensation of inhibitor vapors in electrolyte films on metal surfaces.

Plotting crack velocity versus stress intensity (Table IV) shows definite improvement in retarding crack growth from hydrogen chemisorption when inhibited distilled water was used, as compared to uninhibited water (Table III).

Of three inhibited environments, amine carbonate inhibitor showed the least improvement but still was significantly better than the control (uninhibited) environment. Organic nitrite salt inhibitor was by far the most effective, not only having the highest threshold stress intensity but also a crack growth rate that increased very slowly until applied stress intensity approached the catastrophic stress intensity at which point it increased very rapidly to failure.

This presentation is intended to be an overview and a summary of information on atmospheric corrosion inhibitors.

In conclusion, we would like to express our belief that for people involved in the work with chemical corrosion inhibitors, VCIs should represent a serious challenge since they encounter all aspects of inhibition and adsorption phenomena plus an unique vapor phase transport mechanism. We feel that the key to future success of VCI technology lies:

1.   In initiating basic research studies, and;

2.   In developing information on their effect on the environment.

Potential users like steel and automotive manufacturers, oil refining and transportation that suffer enormous damages due to atmospheric corrosion are not in a position to use VCIs on a larger scale unless clearance from governmental agencies concerned with toxicity and pollution becomes available.

If this talk in any way will solicit interest of you corrosion people present in this room, I will feel as though I made a major contribution. Benefits that potentially could be derived from new and improved methods of corrosion control, will, in a long run help preserve important raw materials and energy resources.

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Table II - Saturated vapor pressures of common VCIs

Substance	Temperature oC	Vapor Pressure	Melting Point °C
Morpholine	20	8.0	
Benzylamine	29	1.0	
Cyclohexylamine Carbonate	25.3	.397	
Diisopropylamine Nitrite	21	4.84×10^{-3}	139
Morpholine Nitrite	21	3×10^{-3}	
Dicyclohexylamine Nitrite	21	1.3×10^{-4}	179
Cyclohexylamine Benzoate	21	8×10^{-5}	
Dicyclohexylamine Caprylate	21	5.5×10^{-4}	
Guanadine Chromate	21	1×10^{-5}	
Nexamethyleneimine Benzoate	41	8×10^{-4}	64
Nexamethyleneimine Nitrobenzoate	41	1×10^{-6}	136
Dicyclohemylamine Benzoate	41	1.2×10^{-6}	201

$$\text{Log } T = {}^{-}A/T - B$$

Table III -   pH of water in equilibrium with vapor above aqueous
solutions of volatile corrosion inhibitors as compared
with pH of later phase

Inhibitor	Concentration Wt%	Solution pH	Condensate pH
Diisopropylamine benzoate	5.0	7.0	7.0
Diisopropylamine benzoate + excess bezoic acid	6.0	5.0	4.0
Diisopropylamine benzoate + excess diisopropylamine	6.0	3.0	10.00
Dicyclohexylamine nitrite	7.00	10.0	10.0
Dicyclohexylamine nitrite + excess $NaNO_2$ + HCI	5.0 6.0	7.2 4.5	7.0 + 3.0÷4.0
Dicyclohexylamine nitrite + excess dicyclohexylamine	6.0 7.0	8.0 8.0+	9.0 9.0

TABLE IV   -   Effectiveness of Different Organic Corrosion Inhibitors
                in Preventing Hydrogen Embrittlement of 300M Steel.
                          Distilled Water

Average velocity (in/sec)	Average Applied Stress Intensity (pat-in).
7.38×10^{-6}	22500
7.02×10^{-6}	29000
9.50×10^{-6}	34700
1.64×10^{-5}	44600
1.90×10^{-5}	57300
2.61×10	73800
Threshold stress intensity	6404

Inhibitor Code C-1

4.17×10^{-7}	29000
1.96×10^{-6}	35900
9.15×10^{-6}	42500
9.56×10^{-6}	52400
1.79×10^{-5}	64900
Threshold stress intensity	29700

Inhibitor Code C-8

0.0	32650
0.0	38500
6.37×10^{-6}	45950
9.81×10^{-6}	56300
Threshold stress intensity	37600

(continued)

Table IV - (continued)

<u>Distilled Water</u>

<u>Inhibitor Code A-4</u>

<u>Average Velocity (in/sec)</u>	<u>Average Applied Stress Intensity (psi-in).</u>
0.0	32600
0.0	70800
8.56×10^{-7}	49300
0.0	55750
7.85×10^{-6}	55800
3.04×10^{-6}	62600
8.33×10^{-5}	66700
1.74×10^{-5}	69000
Threshold stress intensity	40800

Fig. 1 - The mechanism of corrosion inhibition
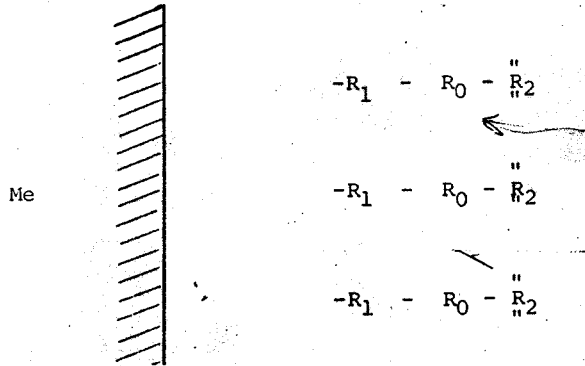
Fig. 2 - Dependence of saturated vapor pressure
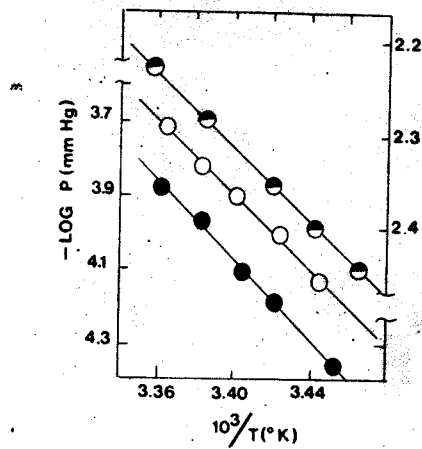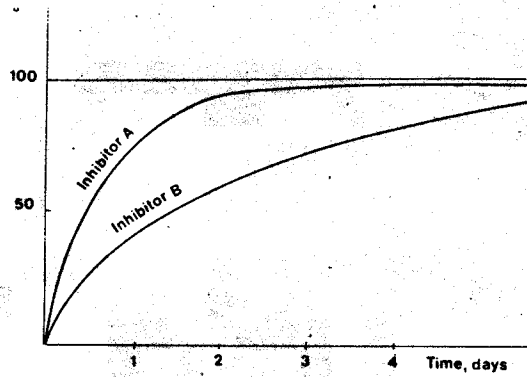of volatile corrosion inhibitors upon
temperature.

Fig. 2. The -log P (mm of Hg) of the vapor pressure
as a function of $10^3/T$ ($^\circ$K.)
● Dicyclohexylammonium nitrate
o Cyclohexylammonium benzoate
● Diisopropylammonium nitrite

Fig. 3 - Time - to - equilibrium for two typical VCI com-
pounds.

Inhibitor A - saturated v.p. 0.1 mm Hg at R.T.
Inhibitor B - saturated v.p. 0.4 x 10^{-5} mm Hg at R.T.

Fig. 4 - The time dependence of contact angle of cyclo-
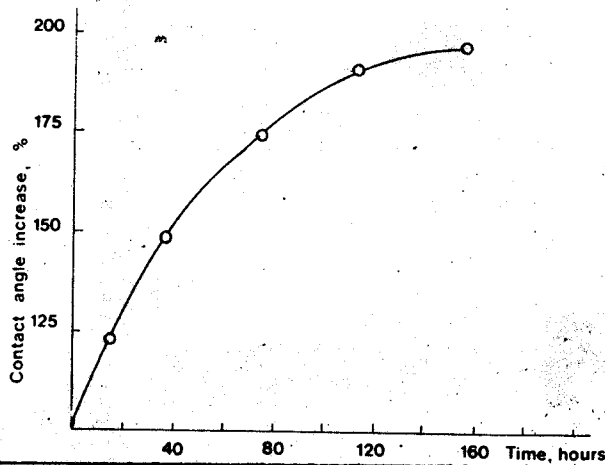hexylamine chromate deposited on mild steel.

Fig. 5 - The effect of duration of exposure of a
        steel electrode to VCI vapors on the
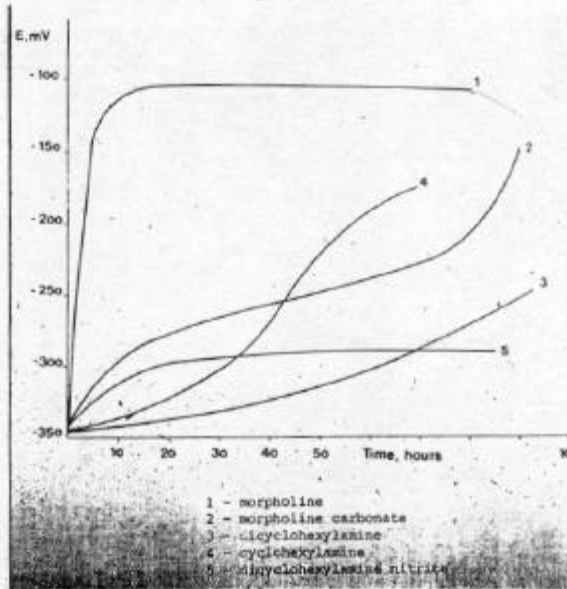   value of initial potential.

E,mV

1 - morpholine
2 - morpholine carbonate
3 - dicyclohexylamine
4 - cyclohexylamine
5 - dicyclohexylamine nitrite

Fig. 6 - The influence of acid chain length on
        the corrosion inhibiting efficiency of
        salts of dicyclohexylamine with aliphatic
        acids.

1 - control (uninhibited sample)
2 - inhibited; acid chain length 6 carbon atoms
3 - inhibited; acid chain length 9 carbon atoms
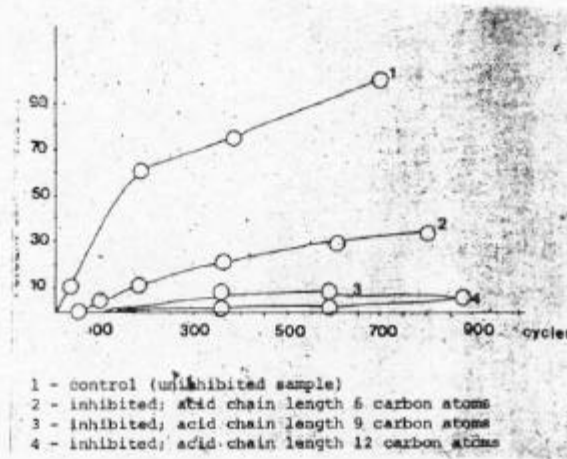4 - inhibited; acid chain length 12 carbon atoms

Figure 7

Typical Corrosion Rates for Non-ferrous Metals
Exposed to Atmosphere Containing VCI