THE EFFECT OF CERTAIN NITROGEN-CONTAINING ORGANIC COMPOUNDS ON THE CORROSION OF STEEL IN PHOSPHORIC ACID

by

George W. Nickel, Jr.

A Thesis Submitted for Partial Fulfillment

of the Requirements for the Degree of

MASTER OF SCIENCE

in

CHEMISTRY

APPROVED:

_____

In Charge of Investigation

_____

Head of Department

_____

Director of Graduate Studies

_____

Dean of College

Virginia Polytechnic Institute

Blacksburg, Virginia

1949

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. E. F. Furtsch, Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia, and to Dr. N. F. Murphy, Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia, thesis advisors, for the helpful suggestions and criticisms given to the author during the course of this investigation. The author also wishes to express his gratitude to the Reeves Manufacturing Company, Dover, Ohio, for furnishing information on the composition of the steel used in this investigation, and to Dr. R. E. Hussey, Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia, and Robert A. Kasey, graduate student in chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia, for making an organic qualitative analysis of Rodine 50.

TABLE OF CONTENTS

TABLES

FIGURES

I. INTRODUCTION

The process of pickling iron and steel, in phosphoric acid, in preparation for surface coatings and in phosphatizing requires the use of an inhibitor. The process actually amounts to the dipping of steel sheets into an acid solution to remove the oxide film and deposit a film of phosphate or make bare the metal surface. In order to remove only the oxide film, it is necessary to have an inhibitor present which will, when the metal surface is exposed, produce a thin invisible film which will protect the metal from attack by the acid medium, and prepare the metal surface for treatment.

The information on such inhibitors for phosphoric acid is very inadequate, although for hydrochloric and sulfuric acid the information is voluminous.

Research work at the University of Minnesota on preventing corrosion of steel in sulfuric acid served as a basis for a new theory on the mechanism of inhibitors. It was found that organic compounds containing nitrogen act as inhibitors for steel. The compounds used were of high molecular weight, usually anilines and other amino compounds. Research work at Virginia Polytechnic Institute on the corrosion of copper in phosphoric acid has brought forth a new theory on inhibition. Edward R. Whaley proposed that chelate ring bonding may be responsible for inhibition.(73)

It is the purpose of this investigation to determine the

effects of several nitrogen-containing organic compounds on the corrosion of steel in phosphoric acid solution.

II. LITERATURE REVIEW

A. Definition of Corrosion

Corrosion may be defined, according to Uhlig[63] and Evans[19] as the destruction of a metal by chemical or electrochemical action, or as Burns[9] states in the most general terms, as the chemical reaction of a metal with the non-metallic constituents of its environment. Speller[58] defines it as "the chemical action of certain external agencies on metals which cause their deterioration or destruction, followed by a reversion to a more stable combination".

B. Theories of Corrosion

During the past fifty years various theories have been introduced to explain the mechanism of corrosion. Some of these theories involve only a few factors while others are comprehensive explanations of the whole problem of corrosion.

The Peroxide Theory. The mechanism of this theory as given by Dunstan and Hill[16] and also by Dunstan, Jowett, and Goulding[15] depends on the following reactions:

$$Fe + O_2 + H_2O = FeO + H_2O_2$$

$$2FeO + H_2O_2 = Fe_2O_3 + H_2O$$

and $$Fe + H_2O_2 = FeO + H_2O$$

$$2FeO + H_2O_2 = Fe_2O_3 + H_2O$$

Against this theory is the fact that the peroxide has never been isolated in the reaction with iron, although with other metals[15,30] peroxide has been isolated during corrosion. It has

been found that many soluble substances which decompose and therefore interfere with the existance of the peroxide, also prevent the rusting of iron. Speller[59] states that, according to this theory, corrosion should cease if a reducing agent (against peroxide) is present; however, his own experiments have proven this to be false.

The Theory of Direct Chemical Attack. This theory was advanced by Bengough and Stuart[5]. It may be represented by the equation:

$$Fe + H_2O + \tfrac{1}{2}O_2 = Fe(OH)_2$$

Bancroft[4] concluded that "the most striking characteristic of an electrolytic solution is that it occurs in two places, at the anode and cathode. This peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes, we have a chemical reaction in the ordinary sense of the word and not an electrochemical reaction".

The Electrochemical Theory. This theory was first advanced by Whitney[77] in 1903, and has been accepted as the best offered to explain the complexities of corrosion.

The idea of this concept is that a metal when placed in a solution tends to ionize through the evolution of an equivalent of hydrogen ions. Walker[69], in developing Nernst's theory of solution pressures, states that the solution pressure of metals, i.e. the tendency of a metal to go into solution, is variable, metals falling into two general classes:

(1) Those whose solution pressures are greater than hydrogen, for example, iron and zinc.

(2) Those whose solution pressures are less than hydrogen, for example, gold and copper.

This means, then, that if the solution pressure of a metal is greater than hydrogen, the metal should corrode more readily than one whose pressure is smaller. Watts and Whipple[71] came to the same conclusion after studying the potential differences of the metals. They considered metals with potentials greater than hydrogen as being readily corrodible and those with potentials less than hydrogen as more likely to be stable.

The designation[6] of corrosion as an electrolytic process makes necessary the presence of an anode area and a cathode area in order to have a current flow. Thus, the process consists of the loss of electrons at the anode and a corresponding gain of electrons at the cathode. In other words, it is a true oxidation-reduction reaction.

Speller[72] states that "the magnitude of electrochemical potential, which varies with environment and the metal, determines the tendency for the reaction to proceed; but the rate of corrosion is determined mainly by the resistance to continued progress of the reaction set up by certain of the corrosion by-products".

Mann[44,45,47] thinks of corrosion as the formation of a Helmholtz double layer on the metal i.e. two layers of oppositely charged electricty. When a metal is placed in solution it ionizes into positive ions, thus leaving the metal surface negative. This sets up the Helmholtz double layer.

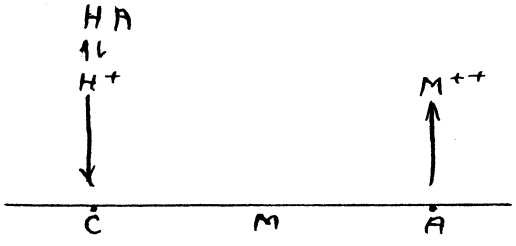
By the electrochemical theory, hydrogen is displaced when a metal goes into solution. Thus, for a bivalent metal, M, as most metals are,

$$M \longrightarrow M^{++} + 2(e)$$

$$2H^{+} + 2(e) \longrightarrow 2H$$

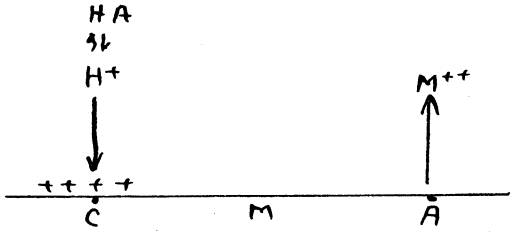
If the reaction is to continue, the hydrogen thus displaced must be liberated as a gas, or it must react with dissolved oxygen from the atmosphere or from some oxidizing agent to form water. The loss of this hydrogen thus makes the metal surface available again for further deposition of hydrogen from the corroding medium, thereby continuing the process. Bogart[7] illustrated the mechanism by the following diagrams.

STEP I



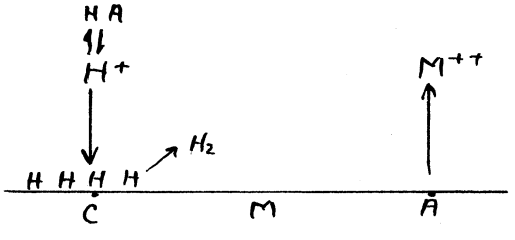
Metal dissolves at (A) anode. Positive charge ions (M^{++}) displace positive charge hydrogen ions (H^{+}) which move to cathode (C) and plate out on metal surface.

STEP II



Solution of metal and plating-out continues until cathode surface is entirely covered or polarized by hydrogen atoms.

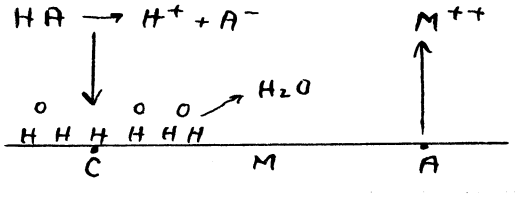
STEP III



Hydrogen atoms combine in pairs to form hydrogen molecules. Hydrogen gas then liberated from surface, making cathode surface reavailable.

Or

STEP IV



Dissolved oxygen diffuses to metal surface, reacts with hydrogen to form water and makes cathode surface reavailable.

The rate of corrosion proceeds then only as fast as the slowest chain in the process, which in the above case is probably the rate of diffusion of dissolved oxygen, STEP IV.

It should be noted that it is also possible for the cathode to depolarize by diffusion or solution of atomic hydrogen from the metal surface. This cannot be proven, but it may be drawn as a conclusion[31] from the fact that there is always a certain residual current even in the absence of a depolarizer, although hydrogen is not being visibly evolved as a gas.

The Acid Theory[15]. According to this theory, which is accredited to Calvert[11], corrosion occurs only in the presence of water, oxygen, and an acid medium. The corrosion of iron may be represented by the following equation:

$$4(Fe + H_2O + CO_2) = 4FeCO_3 + 4H_2$$

$$4FeCO_3 + 6H_2O + O_2 = 2Fe_2(OH)_6 + 4CO_2$$

Here, carbon dioxide and water form the acid medium. The failure of some metals to corrode in the presence of alkali is explained by the neutralization of the carbonic acid by the alkali. While it is true that this theory holds for some cases, it does not explain corrosion in neutral or alkaline solutions.

C. Factors Influencing Corrosion

There are many factors influencing the process of corrosion which may either accelerate or retard the process. It is perhaps these factors that make the corrosion problem so difficult to deal with for they are seldom constant. They may vary due to season or location or for numerous other reasons . Therefore, to understand the problem, we should consider the effects of some of these factors:

1. Oxygen. Oxygen is perhaps the most important, and one of the controlling factors in corrosion, for in many cases without the presence of oxygen there would be no corrosion. It usually exists as dissolved oxygen and may come from several sources, such as, the atmosphere, oxidizing agents, etc. The primary function of oxygen in corrosion is that of a depolarizer. That is, it removes the hydrogen which is plated out on the metal's surface by chemical reaction. Walker[69] is perhaps the first to note this effect.

McKay[32] finds that the presence of dissolved oxygen increases the rate of all corrosion. He states[33] "the possibility of atmospheric oxygen entering into a corrosive reaction with the most telling effect should never be neglected in considering corrosion".

According to Evans[18], oxygen can react in two ways in the corrosion process:

(1) depolarize the hydrogen formed

(2) react with corrosive product to give a more soluble compound.

Those advocates[47] of the direct chemical theory characterize the reaction as a direct combination of a metal with another element, usually oxygen. Experiments[76] show that in the presence of oxygen, the rate of corrosion of iron is accelerated. The effect of dissolved oxygen on the corrosion of a metal in an oxidizing acid is over shadowed by the oxidizing effect of the acid. It has been reported[34,76] that the corrosion of iron is approximately proportional to the dissolved oxygen content of the solution. McKay and Worthington[36] state that the rates of corrosion are higher with oxygen gas than with air as a gas.

Iron[29,56,57] is resistant to non-aerated concentrated chemically pure phosphoric acid. Aerating twenty-five per cent acid increases the corrosion rate. In chemically pure acid no pitting is observed, while in crude acid heavy loose deposit is formed.

2. Temperature. Increase in temperature has been found to increase the rate of corrosion[35]. A rise in temperature increases the ionization and mobility of all reacting bodies, increases the diffusion rate and lowers the viscosity.

Heat[37,56,57] causes abnormal acceleration of corrosion of metals in phosphoric acid solution.

Machu[44] finds that, for an agitated medium, the temperature coefficient is abnormally high, but the addition of an inhibitor reduces the temperature coefficient to normal.

3. Velocity. The velocity of agitation of a solution tends to increase the rate of corrosion. McKay[32] states that this factor tends to remove any films formed or retard film formation. Similarly, Whitman, Russell and co-workers[74,75,76] say that the effect of velocity is to

(1) thin the relatively quiet film of solution surrounding the metal, thus attaining the diffusion of oxygen to the cathode area,

(2) remove protective films, and

(3) make it easier for corrosion products to diffuse away from the metal.

As McKay and Worthington[35] put it, agitation of solution acts only indirectly through other factors in the corrosion process but it

can cause variable results if velocities are not constant.

According to Friend, Hammond, and Trobridge[22], the rate of solution of a metal is a linear function of the velocity of rotation. Thompson and McKay[62] find that the motion of coupons increase the rate of corrosion but also give reproducible results over non-moving coupons.

4. Films. Films are helpful in anti-corrosion work due to the fact that they, as a rule, decrease the ionization of the metal, since the metal ions cannot penetrate the film. Films are formed by the oxidation of the metal, by the formation of other insoluble compounds on the metal, or by the addition of inhibitors.

Films, however, may act as accelerators in corrosion by being penetrable, thus causing a concentration of attack at some one point, resulting in the pitting of the metal surface.

Blum and Rowdon[6] state that anode polorization may be caused by a change in the surface composition of the metal through the formation of visible or invisible films on the surface; or by changes in the composition of the film of solution adjacent to the anode.

Brown, Roethels, and Forrest[8] find that the initial corrosion rate of all metals which they tested decreases after a relatively short time, indicating the formation of partially or completely protective films in all cases. Burns and Haring[10] find the same results. They express them, however, in terms of electro-potentials, i.e., the potential of the metal becomes more electro-positive (noble) with time.

It has been reported[14] that the film growth of oxides of metals takes place as a parabolic function over a limited thickness range

and then changes to a logarithmic function. The theory is that the positive ions move outward across the film while negative ions move inward; the change from parabolic to log-type function is said to be due to polarization.

5. Galvanic Action. A metal[28], when in close contact with another metal (dissimilar), will result in the corrosion of the more anodic metal, usually at a more rapid rate than normal. This is true for both metals and alloys.

D. Passivity

The following definitions of passivity are attributed to Uhlig[64].

1. "A metal active in the EMF Series, or an alloy composed of such metals, is considered passive when its electrochemical behavior becomes that of an appreciably less active or noble metal, i.e., transition metals of the Periodic Table."
2. "A metal or alloy is passive if it substantially resists corrosion in an environment where thermodynamically there is a large free energy decrease associated with its passage from the metallic state to appropriate corrosion products, i.e., transition metals, special cases of lead, zinc, aluminum, metals in inhibited pickling baths and tarnished copper."

To passivate a metal is to make it less active by either physical or chemical treatment. This may be accomplished by exposure to either oxygen or an oxidizing solution, or by anodic polarization. Thus, in general, oxidizing conditions favor passi-

vity while reducing conditions destroy it or cause increased activity.

According to Mears[52], who has developed a unified mechanism of passivity based on the behavior of local elements in metal surfaces, passivity may be achieved either by

(1) reduction of the open circuit potential differences between the local anodes and cathodes,

(2) increased anodic polarization,

(3) increased cathodic polarization,

(4) a combination of these factors.

Mears claims that this mechanism of passivity can be applied to the mechanism of inhibition also.

E. Inhibitors

Mears and Eldridge[51] define an inhibitor as a chemical with the property of reducing the total amount of corrosion of a metal. Speller and Chappel[60,61] define it as a substance added for the primary purpose of decreasing the rate of attack of an acid solution upon a metal. Since most inhibitors operate in acid media, there is some justification for the latter definition.

Ever since Speller[61] reported the use of hydrochloric acid containing an organic inhibitor for cleaning out badly scaled water pipes there has been an increasing interest in the study of or-

ganic inhibitors of corrosion. As early as 1872 Marangoni and Stephanelli[48] stated that essential oils were effective in reducing the speed of action of acids on iron.

Aldehydes[23] and organic compounds containing nitrogen, arsenic, phosphorus, sulfur, selenium and other complex synthetic or natural organic substances and by-products[13,45] have been proposed as inhibitors or have been investigated.

A number of explanations have been offered as to the mechanism of protection of iron against the corroding action of acids by organic inhibitors. It is generally agreed that these inhibitors prevent the discharge of hydrogen on the cathodic areas of iron, thus eliminating corrosion. In this respect they behave like catalysts as suggested by Speller[61]. Speller, Rhodes and Kuhn[55] and others[3,12,20,70] suggest that the inhibitors form a blanketing layer or film which prevents the discharge of hydrogen.

According to Rhodes and Kuhn[55] and others[61], high molecular weight is an essential for a good inhibitor. There is considerable evidence that metal is unprotected against corrosion by a more or less continuous and permanent layer of inhibitor molecules; this layer reduces the rate of discharge of hydrogen and likewise changes the electrode potential and the apparent hydrogen overvoltage, adds electrical resistance to the passage of current, and reduces the rate of solution of iron as any inert impervious film would do.

According to Uhlig[66], if the inhibitor functions by increas-

ing the polarization at the anode it is then regarded as an anodic inhibitor; on the other hand, if the inhibitor functions by increasing the polarization at the cathode, it is regarded as a cathodic inhibitor.

Evans[18] says that inhibitors may be classified as (1) ANODIC INHIBITORS, which tend to suppress the anodic reaction, i.e., hydroxide, phosphate or silicate which form sparingly soluble compounds with the metal, and (2) CATHODIC INHIBITORS, those which tend to suppress the cathodic reaction, i.e., zinc or magnesium salts which often precipitate a hydroxide on a normally cathodic surface. If the anode does not polarize and the cathode does, then in solution of low resistivity the current flow will be controlled entirely by the cathodic electrode. This is termed cathodic control. On the other hand, if the anode polarizes and the cathode does not, the status is reversed and the system is said to be under anodic control. These can lead to four different combinations of extreme cases of inhibition. They are:

(1) Anodic Control, Anodic Inhibitor. Here the inhibitor will increase the chance of formation of an insoluble body (film) in physical contact with the metal - leading to stifling of the attack. Consequently the damage done by corrosion is decreased rather than augmented as the concentration of inhibitor is increased. The addition of an anodic inhibitor to a metal whose corrosion in anodically controlled may not always be very effective, but

it is a "safe" treatment in the sense that there is no concentration which will make matters worse than if no inhibitor had been added.

(2) Anodic Control, Cathodic Inhibitor. In case (2) an addition of inhibitor will not at first decrease the total corrosion, but sooner or later a stage must be reached at which the cathodic reaction becomes so much impeded that the control is no longer solely anodic, and the total corrosion will fall off. In this case also, the addition of an inhibitor should be a "safe" proposition, since there is no fear of making matters worse.

(3) Cathodic Control, Anodic Inhibitor. Here the addition of an inhibitor will clearly reduce the corroded area, but since the corrosion is controlled by the cathodic reaction, the total corrosion will not at first be reduced; on the contrary, since a larger area is now available for the cathodic reaction, small amounts of an anodic inhibitor will actually increase the total corrosion, as has been found by Mears[50] to be the case. Since now small additions of inhibitors greatly decrease the area corroded and slightly increase the amount of corrosion, (pitting), the intensity of corrosion will be increased. It follows that the addition of an anodic inhibitor to a cathodically controlled reaction is a "dangerous" practice, liable to intensify corrosion if the quantity needed has been underestimated. If larger amounts of inhibitor are

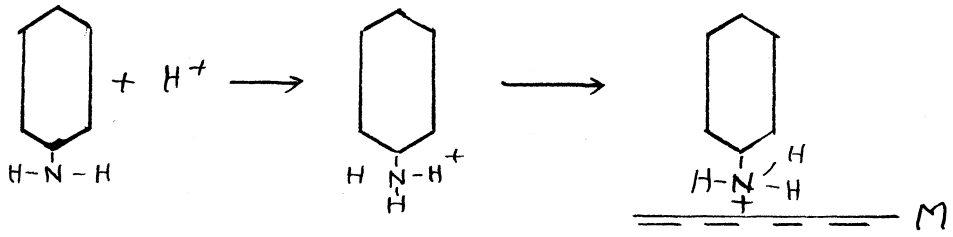
added, the anodic areas are sufficiently reduced to form bottle-necks, and the corrosion becomes controlled, by the anodic reaction.

(4) Cathodic Control, Cathodic Inhibitor. Here the addition of inhibitor will steadily lower the total attack, but the area available for anodic corrosion, will be somewhat increased by interference with the cathodic reaction. Thus, the intensity of attack will steadily fall off. This type of inhibition is essentially "safe" and although it is not so effectual as to prevent visible attack, it is often sufficiently complete for practical purpose.

Most writers attribute the effective action of inhibitors to the adsorption of the inhibitor on the metal surface. Mann[44,45,46,47] reports that when the inhibitor is placed in the medium, it forms an ionizable salt with the corroding solution. There will then be available positive inhibitor ions which can replace the metal ions, these metal ions being in a Helmholtz double layer with the metal. The inhibitor ions will not be discharged, but will be attracted by electrical forces to the cathodic areas of the metal and will be held there as a covering layer by adsorption. Therefore, if the inhibitor layer is not attacked by the corrosive medium it can be classed as a protective layer, thus reducing the corrosive rate. According to Mann, any nitrogen-containing organic compound, if at all soluble, should form an ionizable salt with the acid

medium and the positive charge will concentrate on the group containing nitrogen. The inhibitor would then be attracted to the metal through the nitrogen containing ion.

The reaction of an inhibitor might be represented as follows, according to Mann:



where:

M = metal surface

- = negative charge

+ = positive charge

Warner[70] has intimated that the blanketing layer is formed by the adsorption of colloids. These would have to be positively charged and the inhibitors, being colloids, would have considerable covering power. Warner also stated that large, positively charged, oily ions are necessary. As far as the nitrogen-containing organic inhibitors are concerned, it is true that those soluble in acids form salts that ionize to produce positive ions which must be large as far as cross-sectional area is concerned, but they do not necessarily have to be oily in nature. Even ammonia[45]

has some inhibiting value. In no case is there evidence that these inhibitors are true colloids.

Chappell, Roetheli, and McCarthy[12], as well as Forrest, Roberts, and Roetheli[20] think of the inhibitor action as an adsorption phenomena, but they further postulate that when a metal corrodes or ionizes the cathodic areas occur principally in the narrow spaces of grain boundaries, as in steel, or between metal and slag, as in wrought iron. Thus, as hydrogen ions travel to the cathodic areas they take inhibitor ions with them. Inhibitor ions cannot escape as gases and are accordingly adsorbed to the metal surface, thereby building up a protective layer.

Mears and Eldridge[51], looking at inhibitors from an electrochemical view point, find that in order for an inhibitor to be effective, it must accomplish at least one of the following:

(1) Increase resistance of electrolytic path between local anodes and local cathodes.

(2) Increase polarization at local anodes.

(3) Increase polarization at local cathodes.

(4) Decrease the open circuit potential difference between the local anode and cathode.

Brown, in summing up the work of Evans[18], takes a similar view of inhibitor action.

Machu[38,39,40,41,42] found a direct relation between film resistance and inhibitive efficiency. However, he made no attempt to explain whether this substance is offered by a cathodic or anodic film or both on the same surface, but it has been proven[47]

that there is no regular relation between increase in electrical resistance and inhibitive efficiency.

Hackerman[34] gives a generalized theory for the mechanism of organic corrosion inhibitors which states that the adherence of the inhibitor on the metal surface may be either physical or chemical in nature. The adsorption of the inhibitor on the surface of the metal takes place through polar groups and covers the surface more or less completely when in sufficient concentration. It is the opinion of this investigator that to require adsorption to take place primarily at the cathodic areas is too specific to meet the general requirements of the adsorption theory. He agrees that the positive ions of the inhibitor will have a greater tendency to go to cathodic areas, but contends that some ions will be attracted also to the anodic areas. Hackerman believes that the type of coverage, is important in determining the effectiveness of inhibition. In the case of physically adsorbed substances, the inhibiting effects are due primarily to the decreased ability of the corrosive molecules to reach the metal surface. This may appear as increase in either the film resistance or the hydrogen over-voltage, or may be considered simply in terms of a diffusion controlled reaction rate. The chemisorbed molecule, on the other hand, not only duplicates the effect of impeding the corrosive material, but also decreases the tendency of the metal atom, to which it is attached, to leave the metal surface. Another advantage in this case is that the chemisorbed molecule is not as easily removed or redissolved. Hackerman's reasons for pos-

tulating two types of bonding forces is based on the fact that one of the characteristics of physical adsorption processes is that it takes place instantaneously provided the adsorbate has free access to the solid surface, but a time lag has been noted by several authors[27,55]. Also, it has been noted by some, that an increase in temperature has a tendency to increase the effect of the inhibitor in some cases, while it is known that physiosorbed bonds tend to decrease in effectiveness with temperature. Hackerman's reasoning is also based on the difference in the ease of removal of the adsorbed inhibitor.

In general[68], for steel, the same inhibitors are said to be effective, although not to the same degree, for sulfuric, for hydrochloric, or for phosphoric acid.

The continuance of solution of iron scale in an inhibited pickling bath is explained by Munger[54] as being due to the fact that the high voltage of the electrolytic cell is great enough to break through the protective layer of inhibitor. It may also be explained on the basis that the adsorption of the inhibitor by a negatively charged scale is not sufficiently strong to build up to the interfacial resistance necessary to prevent this electrochemical reaction.

McKay and Worthington[36] state that although phosphoric acid is less active than either sulfuric or hydrochloric acids, its rate of corrosion ranks with them for most metals.

Lawrence and Walton[30], as well as Mann[26,44,45,46,47] give

data that indicate the order of increasing effectiveness of an inhibitor for a particular nitrogen concentration as being tertiary> secondary > primary. For primary amines, the order is: n-amyl > n-butyl > ethyl > ammonia.

The fact that it is necessary to have only a monomolecular layer of ions for protection explains the fact that such a small amount of inhibitor may be effective. The size[26,44,45,46,47] of the ion and especially the configuration determine the number of ions per unit area necessary to attain effective coating. Smaller amounts of high molecular weight inhibitors will produce the most effective results, but this depends on the packing of their ions on the surface of the metal, which in turn depends on the configuration of the ion.

Speller and Chappell[60,61] and others[22] find that at high temperatures, the nitrogen-based inhibitors tend to break-down. They also conclude that inhibitors have a strong electrochemical effect in raising the hydrogen over-voltage.

The stereo-chemical arrangement of these organic chains determines how closely the ions can be packed parallel to the surface, which in turn determines the penetrability of the film by hydrogen ions. An increase in the number of aliphatic chains and greater length of these chains increase the velocity of the amines and their greater ionization enhances the adherence of the positive ions to the cathodic area. Any factor that tends to cause the inhibitor ions to bend or to be inclined will aid the inhibiting power of the compound.

Friend and Vallance[21] and others[17,22] find that emulsoids and colloids act as good inhibitors and attribute this fact to their adsorptive power.

Mann[45,46] has checked several effective aliphates and aromatic amines for steel in sulfuric acid. These are shown in Table I, page 24. He also states[47] that organic inhibitors have never been found to act as stimulators.

TABLE I

EFFECT OF SOME NITROGEN CONTAINING

COMPOUNDS ON THE CORROSION RATE OF STEEL

Conditions for test: Steel coupons, IN-sulfuric Acid, 25° C., 46 hour exposure (apparently unaerated or agitated). Measured rate of corrosion by loss of weight in grams per hour per square centimeter.

Name of Compound	Concentration % N_2	Efficiency %
Propylaniline	0.10	90
	0.25	92
Dibutylaniline	0.10	96
	0.25	98
2,3-xylidine	0.10	91
	0.25	92
Dimethylamine	0.10	85
	0.25	91
Triethylamine	0.10	78
	0.25	97
Tri-n-propylamine	0.10	92
	0.25	97
Tri-n-butylamine	0.10	98
	0.25	98
Tri-n-amylamine	0.05	98
	0.10	98
	0.25	98

Per cent efficiency determined as follows:

$$\% \text{ eff.} = \frac{R_B - R_I}{R_B} \times 100$$

where R_B = rate blank R_I = rate inhibitor

Mann, D. A., Lauer, B. E., and Hultin, C. T. Organic Inhibitors of Corrosion - Aliphatic Amines. Ind. Eng. Chem. 28, 159, (1936).
Mann, C. A., Lauer, B. E., and Hultin, C. T. Organic Inhibitors of Corrosion - Aromatic Amines. Ind. Eng. Chem. 28, 1049, (1936).

Hosting and Heine[29] made tests on corrosion of metals by using chemically pure and crude phosphoric acid. Accelerated corrosion tests on fifty-two metals and alloys were carried out under various conditions, using 10, 25, 50, and 85 per cent chemically pure acids and dilute and concentrated crude acids. The effects of temperature, aeration, and purity of solution were investigated. It was found that temperature rise increases the rate of corrosion. One non-ferrous alloy showed a maximum rate between 75 and 85° C. In concentrated acid, the corrosion rates of stainless steels suddenly increased near the boiling point. They found that the purity of the phosphoric acid affects the resistance of the metals, and that the reaction that takes place when phosphatizing, i.e., the process of making iron rustproof by dipping it into a dilute solution of phosphoric acid containing many different phosphates, ceases in a short time owing to the phosphate film deposited on the iron.

The effect of some inhibitors on the corrosion of iron in phosphoric acid is summarized in Table II, page 26.

EFFECT OF INHIBITORS ON THE CORROSION OF ARMCO IRON IN PHOSPHORIC ACID

Conditions for test: Armco iron, 50 % phosphoric acid, 80° C., one hour exposure (apparently unaerated or agitated), 100 c.c. volume of solution.

Inhibitor	Concentration %	Surface	Loss in weight (grams)
None	—	Pitting, film	0.13
Pentavalent arsenic	0.49	Bright	0.00
Hydrochloric acid	0.75	Film	0.04
Pine Oil	1 c.c.	Film	0.05
Mucilage	1 c.c.	Film	0.06 (frothing)
Pyridine	0.75	Film	0.10

Kosting, P. R. and Heins, Jr., C., Corrosion of Metals by Phosphoric acid. Ind. Eng. Chem. 23, 140, (1931).

F. Chelation

Chelation is the ability of an organic compound to form chelate ring bonding[73]. An organic or chelating compound may be considered as a "complex" type of substance in which an ion is bonded simultaneously to two or more positions in a molecule, forming one or more chelate rings. The only difference, therefore, between a chelate compound and a complex compound lies in the formation of such ring structures[49]. Chelate compounds are usually much more stable than complex compounds, and a metal or hydrogen ion is bound into a chelate ring much more firmly than would be the case with ordinary complexes. Figures I and II, page 29, represent schematically this fundimental distinction between metal chelates and metal complexes.

A metal ion is bound covalently to groups represented by A. In Figure I the groups are independent, while in Figure II, the groups are internally bonded so as to form chelate rings with the metals.

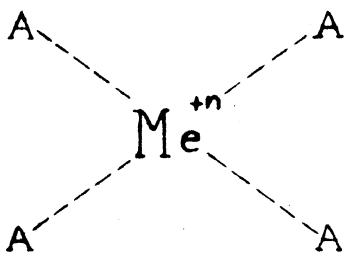
Typical inner complexes of mono carboxylic amino acids are shown in Figures III, IV, and V.

It can be shown[2] that two of the polycarboxylic alpha amino acids, namely ethylene diamine tetra acetic acid and triglycine also form chelates with metals. The chief advantages of these sequestering agents over the simple amino acids lie in their greater tendency for complex formation. This is probably due to the larger number of negative carboxyl groups in the

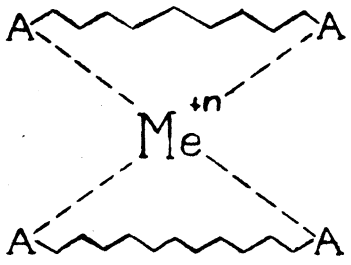
molecule which results in the formation of much stronger bonds with metallic ions. Figures VI and VII represent the typical structure of the metal complexes with the calcium complexes of triglycine and of ethylene diamine tetra acetic acid as examples.

Thus ethylene diamine tetra acetic acid and similar substances readily form stable chelates with calcium, magnesium, barium, and strontium as well as with ions of the heavy metals, and by so doing, effectively remove these metals from solution. Such materials have come to be known as "sequestering agents" because of this ability to remove or "sequester" metal ions. Another important feature of these reagents is the fact that the chelate compounds formed in solution remain in the dissolved state, and do not cause turbidity or result in the formation of precipitates.

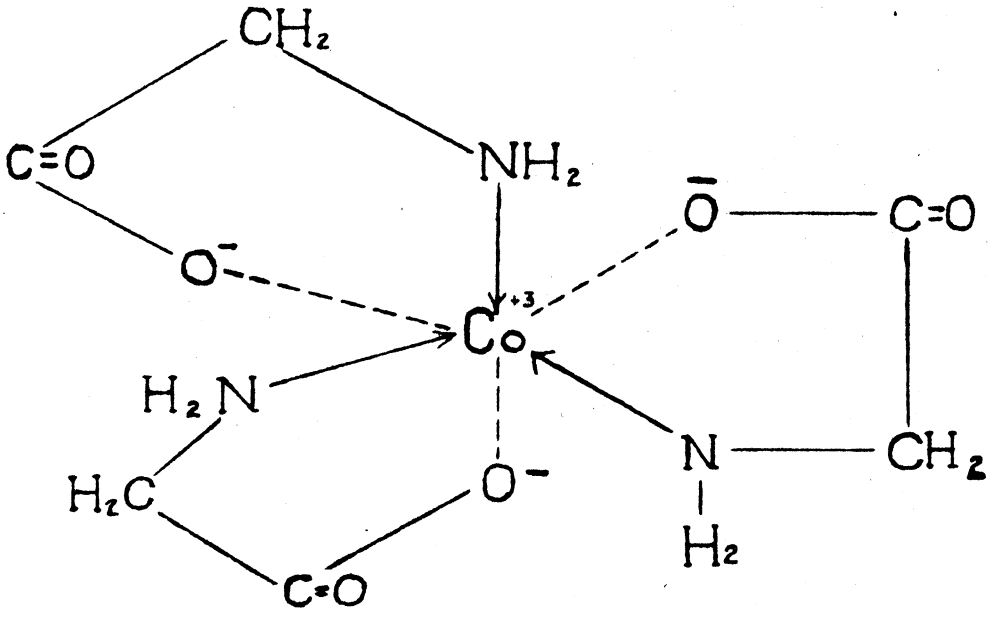
According to Whaley[73], 2-nitro-1-butanol is a very efficient inhibitor(94 per cent) on the corrosion of copper in a five per cent phosphoric acid solution, at 25°C.; and he explains this inhibition ability as being due to the formation of a chelate ring bonding of the compound with the metal surface.



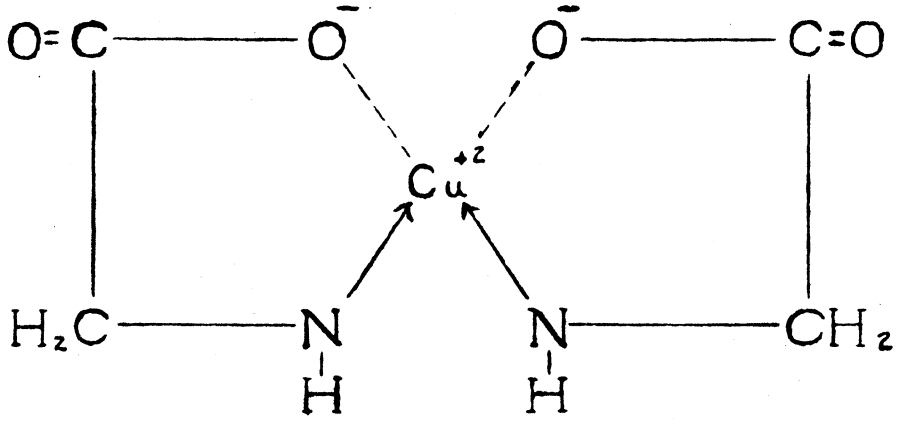
I METAL COMPLEX



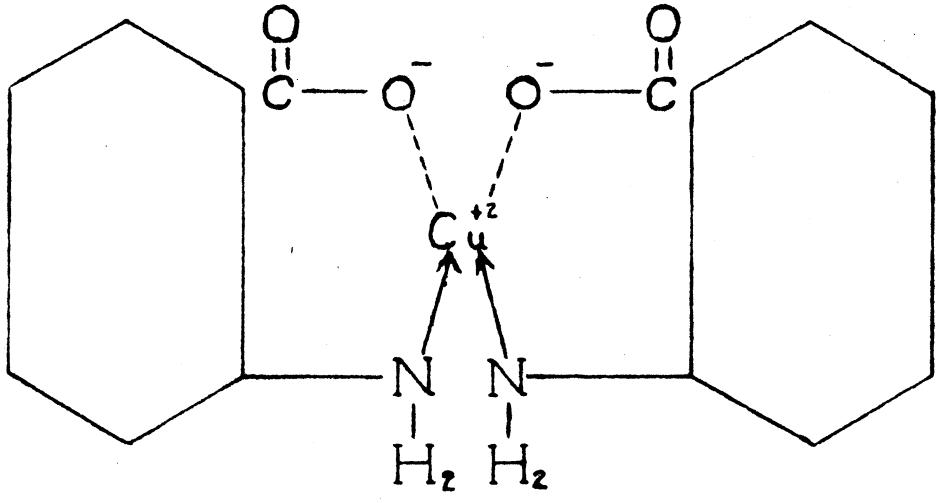
II METAL CHELATE



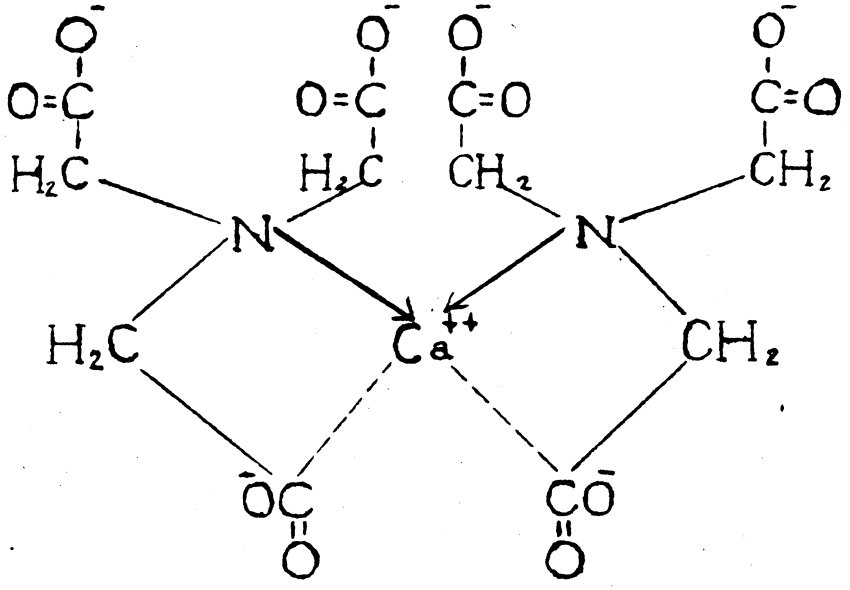
III COBALT AMINOACETIC ACID



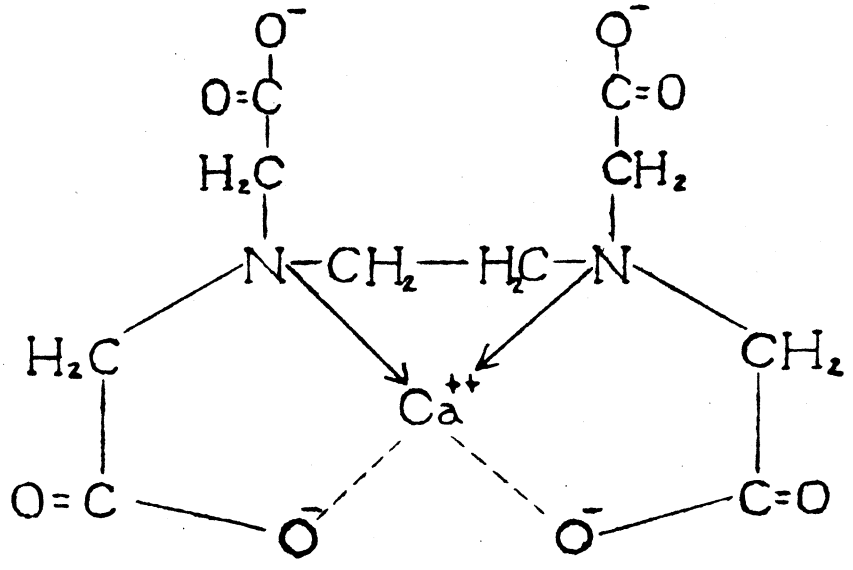
IV COPPER AMINOACETIC ACID



V COPPER ANTHRACENIC ACID



VI CALCIUM TRIGLYCINE



VII CALCIUM ETHYLENEDIAMINE TETRA ACETIC ACID

III. EXPERIMENTAL

Purpose of Study

It was the purpose of this investigation to determine the effects of several nitrogen-containing organic compounds on the corrosion of steel in phosphoric acid solution.

Plan of Investigation

The rate of corrosion was determined by measuring the weight loss due to submerged corrosion. In general, the plan of attack was that outlined in the Standard of the American Society for Testing Materials[1]. Steel coupons, which were cut from a cold rolled steel sheet, were cleaned, dried, weighed, and submerged in a five per cent, agitated, aerated, fresh solution of phosphoric acid, to which an inhibitor may or may not have been added. The apparatus used in this investigation is shown in Figure 1, page 33. The temperature was kept constant at 25°C., and the coupons were kept submerged for a period of 24 hours after which they were removed, cleaned, dried, and weighed. Having previously measured the area of each coupon, the corrosion rate was determined in milligrams per square decimeter per day.

The inhibitors were generally tested in concentrations of 0.10 and 0.01 per cent nitrogen, if the compound contained nitrogen. If it did not contain nitrogen it was tested in various concentrations by weight. The organic compounds tested were:

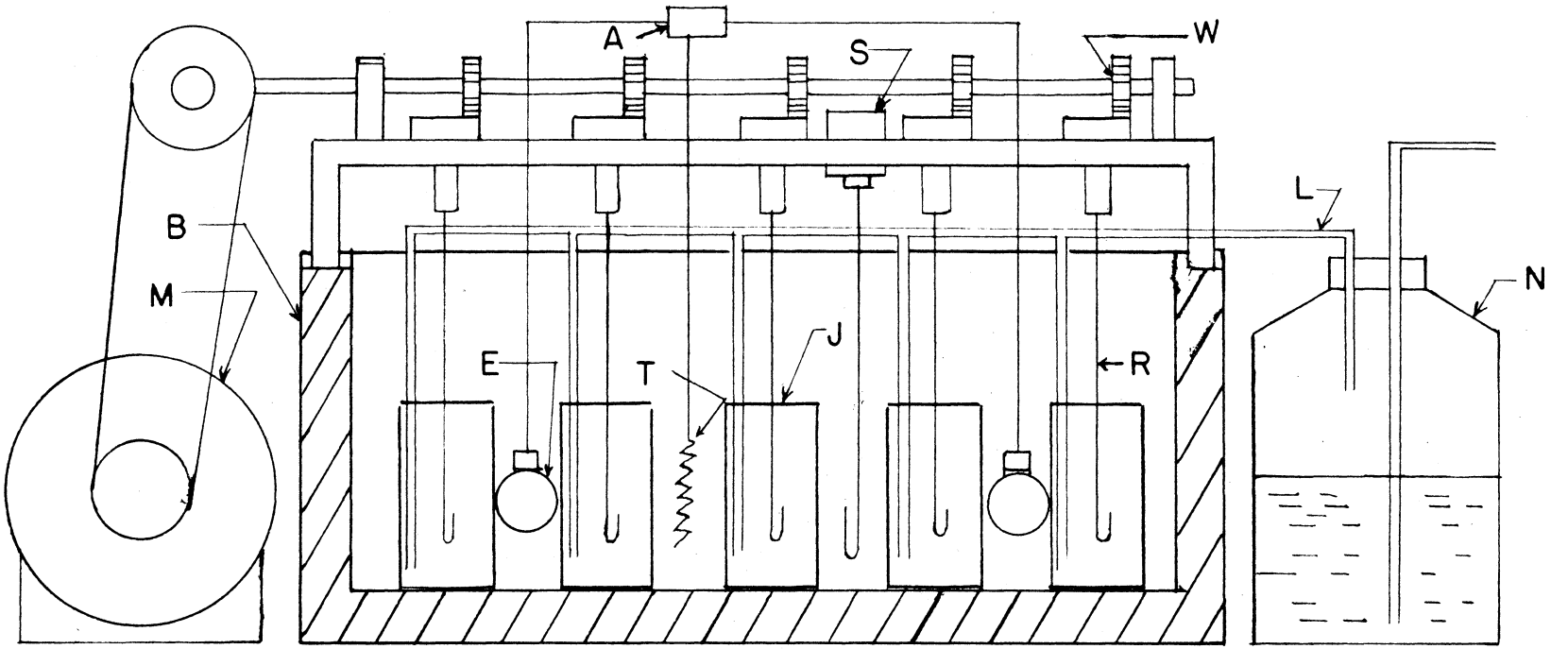


FIGURE I

M — 0.25 HP ELECTRIC MOTOR
J — WIDE MOUTH QUART JARS
W — GEAR TRAIN
S — BATH STIRRING MOTOR
R — GLASS STIRRING ROD
E — ELECTRIC LIGHT BULB
B — INSULATED BOX
T — THERMO — REGULATOR
L — GLASS AIR LINE
A — RELAY UNIT
N — MOISTURIZER

SUBMERGED CORROSION TESTING APPARATUS

2-nitro-1-butanol
Acetyl acetone
Beta-alanine
Cyanoacetic acid
Di-n-amyl-amine
Diphenyl amine
Ethylene diamine
Glycine
Nitrophenol
O-phenylenediamine
P-nitrobenzoic acid
Pyridine
Rodine 50
Triethanol amine
Trimethylol nitromethane
Triethylenetetramine
Tri-n-amyl-amine
Tri-n-butyl-amine

The inorganic compounds tested were:

Sodium arsenate
Sodium chromate
Sodium nitrate
Hydrochloric acid
Ferric sulfate

Materials

Alcohol: 95% grain alcohol. Used as degreasing agent. Obtained from U. S. Industrial Chemicals, Curtis Bay Plant, Baltimore, Md.

Steel: Used as test specimens. Manufactured by Reeves Manufacturing Company, Dover, Ohio, as "Snaplok" stove pipe. For composition see under Data and Results.

Pumice: Fine mesh. Used as cleaner. Obtained from J. T. Baker Chemical Company, Phillipsburg, N. J.

Phosphoric Acid: 85%, ACS Standard. Obtained from J. T. Baker Chemical Company, Phillipsburg, N. J.

Ether: Purified, for manufacturing use only. Used as drying agent. Obtained from J. T. Baker Chemical Company, Phillipsburg, N. J.

Hydrochloric Acid: Used as a cleaning agent and inhibitor. Obtained from J. T. Baker Chemical Company, Phillipsburg, N. J.

Inhibitors: Used as addition agent.

Rodine 50: Obtained from American Paint Company, Ambler, Pa.

Di-n-amyl amine, tri-n-amyl-amine, tri-n-butyl-amine: obtained from Sharples Chemicals Inc., New York, N. Y.

2-nitro-1-butanol: Obtained from Commercial Solvents Company, New York, N. Y.

Remaining organic compounds were obtained from Fisher Scientific Company, New York, N. Y.

The four inorganic compounds tested were obtained from the General Chemical Company, New York, N. Y.

Apparatus

Analytical Balance: Christan Becker Inc., New York. Obtained from Fisher Scientific Co., Pittsburgh, Pa.

Bottles: Three, 5 gallon. Used for containing phosphoric acid, distilled water, and moisturizing air.

Constant Temperature Bath Assembly, see Figure I, page 33. Composed of:

1. Box: Tin, $3\frac{1}{2}$' x 1' x 1', insulated and enclosed.
2. Gear Train: Used for multiple stirring at 63 rpm.
3. Heater: Two, light bulbs, 100 watt each.
4. Motor: Powr-Kraft capacitor electric motor, thermotron protected, $\frac{1}{4}$HP, 60 cycle, 5.0 amps, 115 volts, 1725 rpm, Serial H-47, 40° C. rise, Mfg. No. 74DP4551-$\frac{1}{4}$A, obtained from Montgomery Ward, Baltimore, Md. Used for running gear train.
5. Motor: Electric, 60 cycle, 110 volts. Obtained from Fisher Scientific Company, Pittsburgh, Pa. Used for stirring constant temperature bath.
6. Thermometer: Mercury, marked in tenths of degrees Centigrade. Source unknown.
7. Pulley and Belt: Used for connecting motor and gear train.
8. Relay Unit: Bulletin 700 A. C. Contactor 1 pole Normally open 110 volts, 25 amps, 60 cycle, No. C25374. Obtained from Allen-Bradley Company, Milwaukee, Wis. Used in conjunction with bimetallic thermostat.

9. Thermostat: Cenco-Dekhotinsky Bimetallic Thermo-regulator.

Gas Meter: No. 3123. Obtained from American Meter Company, New York, N. Y.

Jars: Five Mason type, wide-mouth, 1-quart. Used as containers for corrosive media.

Assorted Glassware and Laboratory Equipment: Miscellaneous laboratory glassware and equipment.

Method of Procedure

The method of procedure followed was, in general, that outlined in the Standard of the American Society for Testing Materials[1].

1. Preparation of Coupons. The coupons were all cut from the same cold rolled steel sheet. They were cut to approximately 0.1250 sq. dm. by means of tin-smith shears. Figure 2, page 39, gives the average dimensions and shape of the coupons. One 5/16 inch hole was then drilled into each coupon, this being accomplished by bolting a number of coupons between two steel blocks, one block already having a 5/16 inch hole. This was necessary in order to prevent the formation of a burr on the coupons while drilling. After the holes were drilled, identifying numbers were lightly stamped onto the pieces. The steel sheet was covered with a blue covering, which was removed by first dipping each coupon into a hot solution of 10 Normal sodium hydroxide solution, containing about 20% "Tide"; this was found to be necessary in order to completely degrease the metal surface. Then while the coupon was still wet with caustic solution, it was put into a hot solution of 12 Normal hydrochloric acid containing 2% Rodine-50, by volume. The coupon was left there for approximately 8 seconds, depending upon the strength of the solution. Immediately upon removal, the coupon was rinsed under tap water, and rubbed with pumice to remove any covering that remained. Then the sample was re-rinsed under tap water, partially dried with a towel, rinsed in 95% alcohol, and finally rinsed in ether and allowed to dry in the air. Only then was the metal surface clean and shiny. The sample was

NOTE — THICKNESS 0.013"

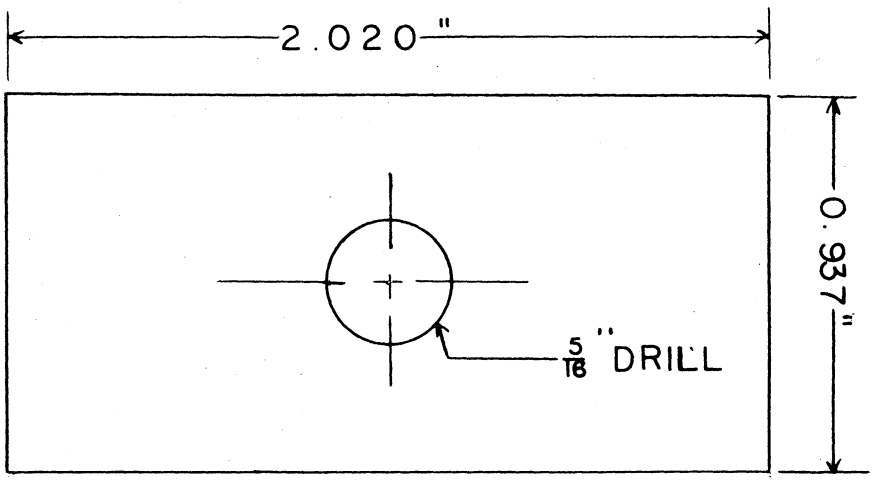


FIGURE 2

CORROSION TEST COUPON

SCALE 2" = 1"

then weighed on an analytical balance.

2. Cleaning Samples after Testing. After the coupons were removed from the corrosive media, they were rinsed under tap water, and the black film that was deposited during testing was removed by rubbing with pumice; then re-rinsed under tap water to remove the excess pumice, partially dried with a towel, rinsed in 95% alcohol, rinsed in purified ether, and let dry in the air. Then the coupons were placed in a dessicator to dry completely and await weighing. The accuracy of this method was within experimental error.

3. Composition of Steel. The specifications on the steel used as samples was obtained from the Reeves Manufacturing Company[78], and is given under the section on Data and Results.

4. Determination of Area of Coupon. The exact area of the individual test coupons was determined with a metric rule, after the measurements of the thickness was made using a micrometer. The area of the metal removed by drilling the suspension hole was calculated using the diameter of the drill.

5. Aeration of Corrosion Media. The corrosion media was aerated by introducing a flow of moisturized air into the container. The air was premoisturized in order to prevent evaporation of the corrosion media. This was accomplished by bubbling the air first

into a large jar containing water and then allowing it to pass over into the bottles containing phosphoric acid through capillary tubes. The air was introduced into the bottles, a few bubbles per minute, estimated by means of a gas meter to be about 0.1 cubic feet per hour per bottle, and not allowing it to come into direct contact with the samples. The air valve was kept open without change throughout the entire run. However, the flow of air did vary because the compresser kept the pressure between 20 and 80 pounds per square inch, and due to use, the average pressure was lower during the day.

6. Preparation of Corrosive Media. The corrosive media used was a 5% phosphoric acid solution. The preparation of the solution was a batch process and consisting of adding distilled water to 669 ml of 85% phosphoric acid and diluting to a volume of 18.9 liters.

7. Determination of Amount of Inhibitor Required. In order to determine the correct amount of inhibitor required for the desired percentage of nitrogen, the following equations were used. The calculations were made on the "as received" basis since the liquids were free flowing.

(1) Vol. of acid used x specific gravity of acid = weight of acid used

(2) Weight of acid used x desired per cent nitrogen/100 = weight nitrogen required for that per cent nitrogen

(3) $\frac{\text{Weight nitrogen required} \times 100}{\text{Per cent nitrogen in compound}}$ = weight

inhibitor compound required for desired per cent nitrogen.

If the compound was a liquid,

$\frac{\text{Weight inhibitor compound required}}{\text{Specific gravity of inhibitor compound}}$ =

volume of inhibitor compound required for desired per cent nitrogen.

8. General Procedure. After the coupons were cleaned and weighed they were immersed in bottles containing 750 ml of fresh 5% phosphoric acid. The usual run was four inhibited bottles and one bottle containing only acid, i.e., a blank. The length of the run was twenty four hours. This period was of sufficient duration to obtain a satisfactory corrosion rate[1].

The immersed coupons were suspended in the solution by means of glass hooks, one coupon per bottle. The samples were held in the approximate center of the bottles, each being approximately two inches beneath the surface of the liquid. The glass hooks, attached to a constant speed gear train, revolved at 63 rpm.

The air was introduced as described previously. The temperature was held at 25±0.5° C. by means of a bimetallic thermostat placed in one end of the water bath. The heat was obtained from

two 100 watt light bulbs, one placed at each end of the bath. The water in the constant temperature bath was circulated by means of a stirring motor.

When the twenty four hour period had elapsed, the samples were removed from the corrosive media, and rinsed under tap water to remove acid, and then cleaned as described before.

The weight loss signified the amount of corrosion taking place and expressed as a rate, i.e., as milligrams per square decimeter per day (mdd), and was determined from the following equation:

$$\text{Corrosion Rate} = \frac{\text{weight loss in mg per day}}{\text{area in sq dm}} = \text{Mdd}$$

In order to determine the per cent effectiveness of the inhibitor, the following equation was empolyed:

$$\text{Per cent inhibition} = \frac{R_B - R_I}{R_B} \times 100$$

where:

R_B = rate corrosion in blank

R_I = rate corrosion with inhibitor.

Sample Calculations

1. To make a 5% phosphoric acid solution from 85% syrupy phosphoric acid:

Specific gravity, 85% acid: 1.705

$\therefore 1.705 \times 0.85 = 1.449$ g. H_3PO_4/ml

Specific gravity, 5% acid: 1.027

$\therefore 1.027 \times 0.05 = 0.0514$ g. H_3PO_4/ml

To make 5 gallons (18.9 liters) 5% acid solution:

$0.0514 \times 18{,}900 = 970.5$ g. H_3PO_4 required for 18.9 liters of 5% acid solution.

$\frac{970.5 \text{ g.}}{1.449 \text{ g./ml}} =$ 669.7 ml of 85% acid per 18,900 ml of solution.

2. To determine amount of inhibitor compound required in terms of nitrogen content; example, ethylene diamine, $NH_2CH_2CH_2NH_2$ (as received):

Amount of 5% H_3PO_4 used per container: 750 ml

Specific gravity, 5% acid: 1.027

$\therefore 750 \times 1.027 = 770$ g., weight of 750 ml 5% acid

$770 \times 0.001 = 0.77$ g. nitrogen required for 0.10% N

Molecular weight of compound: 60.10

Per cent nitrogen in compound: $\frac{28 \times 100}{60.10} = 46.6\%$ N

$\therefore$ To determine amount of nitrogen necessary to obtain 0.10%N:

$\frac{0.77}{46.6} \times 100 = 1.65$ g. compound necessary to obtain 0.10% N.

3. To determine amount of corrosion and inhibitor efficiency of a 0.10% nitrogen addition of ethylene diamine; example, run number 27.

Coupon No. 67 (Blank), i.e., no inhibitor added.

(a) Weight loss due to exposure:

wt before exposure (g.) - wt after exposure (g.) = wt loss (g.)

i.e., 2.7047 - 2.4981 = 0.2066 g. = 206.6 mg loss

(b) Corrosion rate, expressed as mg/sq dm/day:

Area Coupon No. 67 = 0.2280 sq dm

$$\frac{\text{wt loss (mg)}}{\text{area (sq dm)}} = \text{Mdd}$$

i.e., $\frac{206.6}{0.2280} = 906$ Mdd

Coupon No. 64 (inhibited)

(a) Weight loss due to exposure:

wt before exposure (g.) - wt after exposure (g.) = wt loss (g.)

i.e., 2.7858 - 2.5790 = 0.2068 g. = 206.8 mg loss

(b) Corrosion rate, expressed as mg/sq dm/day:

Area Coupon No. 64 = 0.2400 sq dm

$$\frac{\text{wt loss (mg)}}{\text{area (sq dm)}} = \text{Mdd}$$

i.e., $\frac{206.8}{0.2400} = 862$ Mdd

(c) Deviation from average corrosion rate of inhibited coupons (average Mdd for inhibited coupons for Run No. 27 = 874):

Mdd for individual inhibited coupon - average Mdd for inhibited coupons = deviation from average

i.e., 862 - 874 = -12

(d) Per cent deviation from average corrosion rate of inhibited coupons:

$$\frac{\text{dev. from ave. cor. rate of inhibited coupons}}{\text{ave. cor. rate of inhibited coupons}} \times 100 = \% \text{ dev.}$$

i.e., $\frac{12}{874} \times 100 = 1.4\%$ deviation

(e) Per cent inhibition efficiency:

Cor. rate (Mdd) of blank - ave. cor. rate (Mdd) for inhibited coupons x 100/ corrosion rate (Mdd) for blank = per cent efficiency

i.e., $\frac{906 - 874}{906} \times 100 = 1.4\%$ efficiency

Data and Results

Composition of Steel. The steel used in this investigation was cut from a section of Snaplok stovepipe produced by the Reeves Manufacturing Company, Dover, Ohio. This company purchased the steel under the following specifications: (78)

Carbon:	0.08%
Manganese:	0.30 - 0.45%
Phosphorus:	0.06 - 0.09%
Sulfur:	0.05% Maximum

Tables III, IV, and V. Tables III, IV, and V show data and results for the amino compounds, nitro compounds, and Rodine 50 and inorganic compounds, respectively, in the inhibition of steel corrosion by phosphoric acid. The tables show the run number, the particular inhibitor tested, the concentration of nitrogen used, the weight loss, and the corrosion rate. The column showing deviation from average rate is based on the average inhibited corrosion rate. The per cent deviation is determined by dividing the deviation from the average inhibited corrosion rate by the average inhibited corrosion rate and multiplying by one hundred. The accepted control limit for this investigation was plus or minus 10 per cent deviation from the average. The per cent efficiency was determined by re-averaging only those coupons with inhibitors that were under control and comparing this new average, recorded as average inhibition corrosion rate, with the blank for that particular run. Those coupons that were

out of control were disregarded and are shown in the tables as being lined out. A lack of complete data in the tables indicate that the sample disintegrated in the corrosive media, and no quantitative result could be obtained.

Table VI. Table VI gives the data and results for acetyl acetone in varying concentrations. This was the only organic compound tested that did not contain nitrogen. Due to the fact that only a small quantity of this compound was available, only one run was made.

Table VII. Table VII gives a summary of the results for the organic compounds investigated, including acetyl acetone. The numbers with a minus sign indicate a negative efficiency or acceleration by the inhibitor.

Table VIII. Table VIII gives a summary of the results for the inorganic compounds and Rodine 50. The numbers with a minus sign indicate acceleration by the inhibitor.

Table IX. Table IX gives the tabulation of the measurements of all the coupons used in this investigation. The area of the edge was neglected. Since this area was fairly constant throughout, it introduces a constant error in all of the determinations. However, this factor will have no appreciable bearing on the results, which are only relative.

Table III

Corrosion Inhibitor Efficiency- Data and Results for Amano Compounds

Aerated and Agitated 5% Phosphoric Acid- Steel Coupon- Time 24 Hours- 25°C.

Run No.	Inhibitor	Conc grams/750 ml	N %	Acid Sol No.	Metal Sample No.	Wt Before grams	Wt After grams	Wt Loss milligrams	Corrosion Rate Mdd	Dev Ave Rate	Dev Rate %	Ave Inh Corrosion Mdd	Eff %
27	Ethylene Diamine	1.65	0.10	6	63	2.7324	2.5118	220.6	938	+64	7.3		
		1.65	0.10	6	64	2.7858	2.5790	206.8	862	-12	1.44		
		1.65	0.10	6	65	2.7837	2.5720	211.7	885	+11	1.3		
		1.65	0.10	6	66	2.7721	2.5780	194.1	813	-61	7.0	874	+3.5
		0.0	0.0	6	67	2.7947	2.4981	296.6	906				
28	Ethylene Diamine	0.165	0.01	6	68	2.7191	2.5100	209.1	902	+67	8.0		
		0.165	0.01	6	70	2.6974	2.5079	189.5	806	-29	3.5		
		0.165	0.01	6	71	2.6198	2.4228	197.0	875	+40	4.8		
		0.165	0.01	6	72	2.7619	2.5839	178.0	758	-77	9.2	835	+0.8
		0.0	0.0	6	73	2.7418	2.5438	198.0	842				
51	Triethylenetetramine	9.820	0.49	11	114	2.4582	2.2356	222.6	928	-12	0.1		
		9.820	0.49	11	116	2.5230	2.3044	218.6	939	-1	0.0		
		9.820	0.49	11	117	2.5128	2.3107	202.1	879	-61	6.5		
		9.820	0.49	11	118	2.4128	2.3702	242.6	1013	+73	7.8	940	-3.3
		0.0	0.0	11	116	2.5885	2.3692	219.3	910				
52	Triethylenetetramine	4.910	0.24	11	110	2.5122	2.2707	241.5	1088	+153	16.3		
		4.910	0.24	11	111	2.5893	2.3673	221.5	932	-6	0.6		
		4.910	0.24	11	113	2.6327	2.4123	220.4	939	+1	0.0		
		4.910	0.24	11	118	2.2264	2.0049	221.5	944	+6	0.6	938	-1.2
		0.0	0.0	11	112	2.3932	2.1876	205.6	927				
53	Triethylenetetramine	2.01	0.10	12	110	2.2707	2.0824	188.3	848	+6	0.7		
		2.01	0.10	12	111	2.3678	2.1750	222.8	937	+95	11.2		
		2.01	0.10	12	112	2.1876	2.0060	181.6	820	-22	2.6		
		2.01	0.10	12	113	2.4123	2.2325	179.8	765	-77	9.1	842	-4.5
		0.0	0.0	12	120	2.0049	1.8153	189.6	806				
33	Triethylenetetramine	2.01	0.10	7	74	1.6169	1.3653	151.6	637	-51	7.4		
		2.01	0.10	7	75	2.5848	2.4040	180.8	756	+68	9.9		
		2.01	0.10	7	77	1.5212	1.3764	144.8	614	-74	10.7		
		2.01	0.10	7	78	1.6203	1.4400	180.3	746	+58	8.4	688	+10.3
		0.0	0.0	7	76	1.4893	1.3124	176.9	767				
34	Triethylenetetramine	0.201	0.01	8	80	2.6531	2.4896	163.5	691	-33	4.6		
		0.201	0.01	8	81	2.7736	2.6013	172.3	730	+6	0.8		
		0.201	0.01	8	82	2.7164	2.5455	170.9	714	-10	1.4		
		0.201	0.01	8	84	2.6514	2.4687	172.8	762	+38	5.2	724	- 6.8
		0.0	0.0	8	83	2.7423	2.5617	160.6	678				
35	Triethanolamine	8.22	0.10	8	85	2.7324	2.5175	214.9	920	-12	1.3		
		8.22	0.10	8	87	2.6662	2.4333	232.9	1010	+78	8.4		
		8.22	0.10	8	88	2.6335	2.4254	208.1	917	-15	1.6		
		8.22	0.10	8	65	2.6038	2.1937	210.1	980	-52	5.6	932	-25.6
		0.0	0.0	8	86	2.6626	2.4926	170.0	742				
36	Triethanolamine	0.822	0.01	8	68	2.3346	2.0539	280.7	1210	+50	4.3		
		0.822	0.01	8	70	2.3287	2.0611	267.6	1140	-20	1.7		
		0.822	0.01	8	71	2.2456	2.0798	265.8	1160	+20	1.7		
		0.822	0.01	8	72	2.4322	2.1737	258.5	1110	-50	4.3	1160	-27.0
		0.0	0.0	8	73	2.3427	2.1475	215.2	913				
7	Triethanolamine	0.822	0.1	3	17	2.9325	2.6900	242.5	967	+37	4.0		
		0.822	0.10	3	18	2.9278	2.6843	243.5	977	+47	5.0		
		0.822	0.10	3	20	2.9281	2.7157	212.4	847	-83	8.9	930	-18.3
		0.0	0.0	3	15	2.9816	2.7850	196.6	786				
37	Beta-Alanine	4.90	0.10	8	74	1.3653	1.1820	183.3	770	-22	2.8		
		4.90	0.10	8	75	2.4040	2.2058	198.2	835	+43	5.4		
		4.90	0.10	8	77	1.3764	1.1985	177.9	754	-38	4.8		
		4.90	0.10	8	78	1.4400	1.2447	195.3	808	+16	2.0	792	+11.7
		0.0	0.0	8	76	1.3124	1.1057	206.7	897				
38	Beta-Alanine	0.490	0.01	8	81	2.6013	2.4216	179.7	760	-29	3.7		
		0.490	0.01	8	82	2.5455	2.3655	180.0	761	-28	3.6		
		0.490	0.01	8	83	2.5817	2.3869	194.8	824	+35	4.4		
		0.490	0.01	8	84	2.4687	2.2847	184.0	812	+23	2.9	789	-2.1
		0.0	0.0	8	80	2.4896	2.3064	183.2	773				
11	Tri-n-butyl-amine	4.02	0.10	3	1	2.4751	2.2421	233.0	930	+36	4.0		
		4.02	0.10	3	2	2.2008	2.0006	200.2	883	-11	1.2		
		4.02	0.10	3	3	2.3916	2.1768	214.8	895	+1	0.0		
		4.02	0.10	3	10	2.3800	2.1710	209.0	870	-24	2.7	894	-20.1
		0.0	0.0	3	0	2.4459	2.2651	180.8	744				
12	Tri-n-butyl-amine	0.402	0.01	3	12	1.9655	1.7496	215.9	852	-15	1.7		
		0.402	0.01	3	15	2.5992	2.3881	211.1	845	-22	2.5		
		0.402	0.01	3	19	2.8024	2.5714	231.0	903	+36	4.1	867	+13.3
		0.402	0.01	3	25	2.8983	2.6030	295.3	1235	368	42.5		
		0.0	0.0	3	11	1.8030	1.5628	233.2	1000				
16	Aminoacetic Acid	4.125	0.10	4	36	2.8404	2.6189	221.5	914	-18	1.9		
		4.125	0.10	4	37	2.7747	2.5494	225.3	950	+18	1.9	932	-7.5
		0.4125	0.01	4	38	2.6940	2.4835	210.5	903	+22	3.3		
		0.4125	0.01	4	40	2.7613	2.5608	200.5	846	-28	3.5	874	-0.8
		0.0	0.0	4	41	2.7561	2.5515	204.6	867				
19	Di-n-amyl-amine	8.64	0.10	4	52	2.7139	2.4537	260.2	1120	-1	0.0		
		8.64	0.10	4	53	2.7503	2.5144	235.9	958	-122	11.3		
		8.64	0.10	4	55	2.6813	2.4157	265.4	1104	+24	3.3		
		8.64	0.10	4	56	2.6461	2.3949	251.2	1080	-41	3.6	1121	-26.0
		0.0	0.0	4	54	2.7964	2.5842	212.2	890				
20	Di-n-amyl-amine	0.864	0.01	5	36	2.6189	2.2685	350.4	1450	+99	7.3		
		0.864	0.01	5	37	2.5494	2.2517	297.7	1258	-93	6.9		
		0.864	0.01	5	38	2.4835	2.1637	319.8	1372	+21	1.6		
		0.864	0.01	5	41	2.5515	2.2392	312.3	1323	-28	2.1	1351	-29.9
		0.0	0.0	5	40	2.4608	2.2145	246.3	1040				
21	Tri-n-amyl-amine	12.47	0.10	5	44	2.5687	2.2772	291.5	1220	+53	4.5		
		12.47	0.10	5	47	2.4771	2.2068	270.3	1100	-67	5.8		
		12.47	0.10	5	50	2.5980	2;3086	289.4	1197	+30	2.6		
		12.47	0.10	5	51	2.5542	2.2833	270.9	1150	-17	1.5	1167	-38.0
		0.0	0.0	5	48	2.5158	2.3190	196.8	846				
22	Tri-n-amyl-amine	1.247	0.01	5	52	2.4537	2.1761	276.8	1150	+91	7.5		
		1.247	0.01	5	53	2.5144	2.2465	267.9	1088	-21	1.9		
		1.247	0.01	5	55	2.4157	2.1728	242.9	1050	-59	5.3		
		1.247	0.01	5	56	2.3949	2.0886	306.3	1310	151	13.0	1109	-22.0
		0.0	0.0	5	54	2.5842	2.3673	216.9	909				
15	O-Phenylenediamine	2.98	0.10	4	31	2.7747	2.6809	93.8	390	+73	23.2		
		2.98	0.10	4	32	2.7617	2.7034	58.0	244	-73	23.2	317	
		0.298	0.01	4	33	2.7273	2.5290	198.3	853	+7	0.8		
		0.298	0.01	4	34	2.7616	2.5639	220.7	940	-6	0.7	846	+27.5
		0.0	0.0	4	35	2.8025	2.5211	281.4	1168				
25	O-Phenylenediamine	2.98	0.10	6	47	2.2668	2.0595	156.3	638	-38	5.6		
		2.98	0.10	6	48	2.3190	2.1655	153.5	660	-16	2.4		
		2.98	0.10	6	51	2.2833	2.1086	174.7	730	+54	8.0	676	+19.0
		0.0	0.0	6	44	2.2772	2.0751	202.1	845	835			
		0.0	0.0	6	52	2.1769	1.9843	192.6	826				
26	O-Phenylenediamine	2.98	0.10	6	57	2.7526	2.5570	195.6	815	+58	7.7		
		2.98	0.10	6	60	2.6740	2.5034	165.6	700	-57	7.5	757	-4.8
		0.298	0.01	6	58	2.7322	2.5467	186.4	773	-51	6.2		
		0.298	0.01	6	62	2.7143	2.5057	208.6	875	+51	6.2	824	-14.1
		0.0	0.0	6	61	2.7209	2.5537	170.2	722				
54	Diphenylamine	0.225	0.002	12	114	2.2356	2.0483	187.3	780	-38	4.6		
		0.225	.002	12	115	2.3044	2.1061	198.3	857	+38	4.6		
		0.225	.002	12	116	2.3692	2.1762	193.0	800	-18	2.2		
		0.225	.002	12	117	2.2107	2.1190	191.7	834	+17	2.1	318	-5.0
		0.0	0.0	12	118	2.2702	2.1836	186.6	779				
55	Diphenylamine	0.100	-	12	87	2.0427	1.8559	186.8	811	+ 6	0.7		
		0.100	-	12	121	2.2861	2.0815	204.6	890	+85	10.5		
		0.100	-	12	122	2.5709	2.3902	180.7	750	-55	6.8		
		0.100	-	12	123	2.2506	2.0753	175.3	771	-34	4.2	805	+3.0
		0.0	-	12	124	2.2377	2.0486	189.1	830				

Table IV

Corrosion Inhibitor Efficiency- Data and Results FOR Nitro-Derivatives

Aerated and Agitated 5% Phosphoric Acid- Steel Coupon- Time 24 Hours- 25°C.

Run No.	Inhibitor	Conc grams/750 ml	N %	Acid Sol No.	Metal Sample No.	Wt Before grams	Wt After grams	Wt Loss milligrams	Corr RATE Mdd	Dev Aver Rate	Dev Rate %	Ave Inh Corr Rate Mdd	Eff %
23	P-nitrobenzoic Acid	9.20	0.10	5	19	2.5714	1.6562	915.2	3575	—	—	3575	-293
		9.20	0.01	5	15	2.3381	1.7215	666.6	2665	-55	2.0		
		0.920	0.01	5	25	2.6030	1.9640	639.0	2680	-40	1.5		
		0.920	0.01	5	12	1.7496	1.0360	713.6	2815	+94	3.5	2720	-199
		0.0	0.0	5	11	1.5698	1.3577	212.1	910				
17	O-nitrophenol	7.670	0.10	4	45	2.7619	0.00	2761.	—	—	—	∞	-∞
		0.767	0.01	4	42	2.6952	1.7073	987.9	4310	+67	1.6		
		0.767	0.01	4	43	2.7210	1.6947	1026.	4370	+127	3.0		
		0.767	0.01	4	46	2.7920	1.8234	968.6	4050	-193	4.5	4243	-354
		0.0	0.0	4	44	2.7920	2.5687	223.3	934				
9	2-nitro-1-butanol	6.55	0.10	3	16	2.5758	—	—	—	—	—		
		6.55	0.10	3	17	2.6900	—	—	—	—	—		
		6.55	0.10	3	18	2.6843	—	—	—	—	—		
		6.55	0.10	3	20	2.7157	—	—	—	—	—	∞	-∞
		0.0	0.0	3	10	2.7801	2.5924	187.7	781				
10	2-nitro-1-butanol	0.655	0.01	3	21	2.7457	2.1651	580.6	2320	-20	0.9		
		0.655	0.01	3	22	2.8167	2.2317	585.0	2340	0	0.0		
		0.655	0.01	3	23	2.8546	2.2611	593.5	2395	+55	0.2		
		0.655	0.01	3	24	2.9201	2.3451	575.0	2300	-40	0.2	2340	-205
		0.0	0.00	3	19	2.9989	2.8028	196.1	768				
29	Trimethylol Nitromethane	8.300	0.10	7	74	2.7533	1.5169	1236.	5190	+130	2.6		
		8.300	0.10	7	76	2.7075	1.4893	1218	5270	+210	4.2		
		8.300	0.10	7	77	2.7310	1.5212	1210	5120	+ 60	1.2		
		8.300	0.10	7	78	2.7463	1.6203	1126	4660	-400	7.9	5060	-615
		0.0	0.0	7	75	2.7531	2.5848	168.3	708				
30	Trimethylol Nitromethane	0.830	0.01	7	57	2.5570	1.9758	581.2	2420	+62	2.6		
		0.830	0.01	7	58	2.5467	1.9717	575.0	2395	+37	1.6		
		0.830	0.01	7	61	2.5507	2.0397	511.0	2162	-196	8.3		
		0.830	0.01	7	62	2.5057	1.9197	586.0	2455	+97	4.1	2358	-144
		0.0	0.0	7	60	2.5084	2.2797	228.7	965				
31	Cyanoacetic Acid	4.68	0.10	7	63	2.5118	2.3140	197.8	840	-23	2.7		
		4.68	0.10	7	64	2.5790	2.3665	212.5	886	+23	2.7	863	-24.2
		4.68	0.10	7	66	2.5780	2.4167	161.3	676	+25	3.8		
		4.68	0.10	7	67	2.4901	2.3551	143.0	627	-24	3.7	651	+6.9
		0.0	0.0	7	65	2.5720	2.4038	168.2	699				
32	Cyanoacetic Acid	0.468	0.01	7	68	2.6100	2.3346	175.4	757	+18	2.4		
		0.468	0.01	7	70	2.5079	2.3287	179.2	762	+23	3.1		
		0.468	0.01	7	71	2.4228	2.2456	177.2	787	+48	6.5		
		0.468	0.01	7	72	2.5839	2.4322	151.7	649	-90	12.8	739	+3.8
		0.0	0.0	7	73	2.5438	2.3627	181.1	768				
39	Pyridine	4.35	0.10	9	86	2.4926	2.3492	143.4	627	-71	21.4		
		4.35	0.10	9	87	2.4333	2.2393	194.0	845	+47	5.9		
		4.35	0.10	9	88	2.4254	2.2436	181.8	800	+2	0.2		
		4.35	0.10	9	65	2.1937	2.0152	178.5	748	-50	6.3	798	+4.1
		0.0	0.0	9	85	2.5175	2.3230	194.5	832				
40	Pyridine	5.892	0.135	9	100	2.6773	2.4929	184.4	791	-33	4.0		
		5.892	0.135	9	102	2.7891	2.5850	204.1	851	+27	3.3		
		5.895	0.135	9	103	2.7352	2.5467	188.5	799	-25	3.0		
		5.895	0.135	9	104	2.7523	2.5485	203.8	857	+33	4.0	824	-3.9
		0.0	0.0	9	101	2.6789	2.4917	187.2	793				
41	Pyridine	7.856	0.180	9	80	2.3064	2.1083	198.1	836	+5	0.6		
		7.856	0.18	9	81	2.4216	2.2169	205.2	870	+39	4.7		
		7.856	0.18	9	83	2.3869	2.2009	186.0	786	-45	5.4		
		7.856	0.18	9	84	2.2847	2.1561	128.6	567	-264	31.8	831	0.0
		0.0	0.0	9	82	2.3635	2.1648	198.7	830				

Table V

Corrosion Inhibitor Efficiency- Data and Results for Rodine and Inorganic Compounds

Aerated and Agitated 5% Phosphoric Acid- Steel Coupon- Time 24 Hours- 25°C.

Run No.	Inhibitor	Conc grams/750 ml	by WT %	Acid Sol No.	Metal Sampl No.	Wt Before grams	Wt After grams	Wt Loss milligrams	Corr Rate Mdd	Dev Ave Corr Rate	Dev Rate %	Ave Inb Corr Rate Mdd	Eff %
14	Rodine 50	15.90	2.06	3	1	2.2421	2.0504	191.7	765	+46	6.4		
		~~15.90~~	~~2.06~~	~~3~~	~~2~~	~~2.0006~~	~~1.8166~~	~~189.0~~	~~833~~	~~114~~	~~15.8~~		
		15.90	2.06	3	3	2.1768	2.0073	169.5	707	-12	1.7		
		15.90	2.06	3	10	2.1710	2.0067	164.3	685	-34	4.7	719	+3.8
		0.0	0.0	3	0	2.2651	2.0835	181.6	747				
4	Rodine 50	3.980	0.52	2	1	2.6871	2.4751	212.0	846	-43	4.8		
		3.980	0.52	2	2	2.4136	2.2008	212.8	938	+49	5.4		
		3.980	0.52	2	3	2.6044	2.3916	212.8	887	-2	0.2		
		3.980	0.52	2	10	2.5924	2.3800	212.4	886	-3	0.3	889	-20.0
		0.0	0.0	2	0	2.6257	2.4459	17918	741				
6	Rodine 50	0.7930	0.10	2	8	2.6342	2.4119	222.3	942	-6	0.6		
		0.7930	0.10	2	9	2.6394	2.4151	224.3	959	+11	1.2		
		0.7930	0.10	2	11	2.4666	2.2541	212.5	913	-35	3.7		
		0.7930	0.10	2	12	2.6314	2.3824	249.0	978	+30	3.2	948	-5.0
		0.0	0.0	2	7	2.7432	2.5237	219.5	903				
45	Sodium Chromate	7.70	1.0	10	110	2.6486	2.6474	1.2	5.4	-1	15.6		
		7.70	1.0	10	111	2.7625	2.7623	0.2	8.4	+2	31.2		
		7.70	1.0	10	112	2.5936	2.5924	1.2	5.4	-1	15.6		
		7.70	1.0	10	113	2.7377	2.7362	1.5	6.4	0	0.0	6.4	+99.3
		0.0	0.0	10	75	2.0073	1.8025	204.8	859				
46	Sodium Chromate	3.85	0.5	10	80	2.1083	--	--	--	--	--		
		3.85	0.5	10	81	2.2164	--	--	--	--	--		
		3.85	0.5	10	83	2.2009	--	--	--	--	--		
		3.85	0.5	10	84	2.1561	--	--	--	--	--	∞	-∞
		0.0	0.0	10	82	2.1648	2.0240	140.8	590				
47	Sodium Chromate	~~0.770~~	~~0.10~~	~~11~~	~~110~~	~~2.6474~~	~~2.5122~~	~~135.2~~	~~609~~	~~214~~	-		
		0.770	0.10	11	111	2.6725	2.5893	83.2	350	-45	11.4		
		0.770	0.10	11	113	2.7362	2.6327	103.5	441	+46	11.6	395	+56.1
		0.770	0.10	11	102	2.3940	1.8386	555.4	2320	--	--		
		0.0	0.0	11	112	2.5924	2.3932	199.2	900				
48	Hydrochloric Acid	4.38	0.57	11	114	2.6748	2.4582	216.6	903	+75	9.1		
		4.38	0.57	11	115	2.7212	2.5230	198.2	856	+28	3.4		
		4.38	0.57	11	117	2.6997	2.5128	186.9	813	-15	1.8		
		~~4.38~~	~~0.57~~	~~11~~	~~118~~	~~2.7897~~	~~2.6128~~	~~176.9~~	~~739~~	~~-89~~	~~10.7~~	828	+5.9
		0.0	0.0	11	116	2.8005	2.5885	212.0	880				
50	Ferric Sulfate	2.000	0.26	11	120	2.6554	2.2264	429.0	1830	-45	2.4		
		2.000	0.26	11	121	2.7214	2.2861	435.3	1892	+17	0.9		
		2.000	0.26	11	123	2.6726	2.2506	422.0	1855	-20	1.1		
		2.000	0.26	11	124	2.6763	2.2377	438.6	1922	+47	2.5	1875	-111
		0.0	0.0	11	122	2.7849	2.5709	214.0	889				
56	Sodium Nitrate	7.70	1.00	12	110	2.0824	1.6555	426.9	1925	+8	0.0		
		7.70	1.00	12	111	2.1450	1.7097	435.3	1830	-86	4.5		
		7.70	1.00	12	112	2.0060	1.5901	415.9	1880	-36	1.9		
		7.70	1.00	12	113	2.2335	1.7565	476.0	2030	114+	6.0	1916	-111
		0.0	0.0	12	120	1.8153	1.6021	213.2	908				
42	Sodium Arsenate	7.70	1.00	9	85	2.3230	2.1592	163.8	700	+8	1.2		
		7.70	1.00	9	86	2.3492	2.1917	157.5	689	-3	0.4		
		7.70	1.00	9	88	2.2436	2.0751	168.5	742	+50	7.2		
		7.70	1.00	9	65	2.0152	1.8633	151.9	635	-57	8.2	692	+19.1
		0.0	0.0	9	87	2.2393	2.0427	196.6	855				
43	Sodium Arsenate	3.850	0.50	10	105	2.6702	2.5073	162.9	711	-60	7.8		
		3.850	0.50	10	106	2.6841	2.5098	174.3	742	-29	3.8		
		3.850	0.50	10	107	2.6505	2.4636	186.9	809	+38	4.9		
		3.850	0.50	10	108	2.6461	2.4591	187.0	823	+52	6.7	771	+7.2
		0.0	0.0	10	75	2.2058	2.0073	198.5	831				
44	Sodium Arsenate	0.770	0.10	10	100	2.4929	2.2937	199.2	854	+56	7.0		
		0.770	0.10	10	101	2.4917	2.3120	179.7	761	-37	4.6		
		0.770	0.10	10	103	2.5467	2.3521	194.6	860	+62	7.8		
		0.770	0.10	10	104	2.5485	2.3781	170.4	718	-80	10.0	798	0.0
		0.0	0.0	10	102	2.5850	2.3940	191.0	797				

Table VI

Corrosion Inhibitor Efficiency - Data and Results for Acetyl Acetone

Aerated and Agitated 5% Phosphoric Acid - Steel Coupon - Time 24 Hours - 25°C.

Run No.	Inhibitor	Conc grams / 750 ml	by wt %	Acid Sol No.	Metal Sample No.	Wt Before grams	Wt After grams	Wt Loss milligrams	Corr Rate Mdd	Eff %
18	Acetyl Acetone	6.832	0.886	4	47	2.7343	2.4711	257.2	1050	12.6
		2.928	0.380	4	48	2.7346	2.5158	218.8	942	1.1
		1.952	0.253	4	50	2.8225	2.5980	224.5	929	0.3
		0.0	0.0	4	51	2.7814	2.5582	223.2	932	

Table VII

Average Corrosion Inhibitor Efficiency for Organic Compounds Investigated

Aerated and Agitated 5% Phosphoric Acid - Steel Coupon - Time 24 Hours - Temp 25°C.

Inhibitor	Concentration % Nitrogen	Efficiency
Ethylene Diamine	0.10 0.01	3.5 0.8
Triethylenetetramine	0.489 0.245 0.10 0.01	- 3.3 - 1.2 2.9 - 6.8
Triethanolamine	0.10 0.01	- 21.9 - 27.0
Beta-Alanine	0.10 0.01	11.7 - 2.1
Tri-n-butyl-amine	0.10 0.01	- 20.1 13.3
Aminoacetic Acid	0.10 0.01	- 7.5 - 0.8
Di-n-amyl-amine	0.10 0.01	- 26.0 - 29.9
Tri-n-amyl-amine	0.10 0.01	- 38.0 - 22.0
O-Phenylenediamine	0.10 0.01	7.1 6.6
Diphenyl amine	0.002 0.0008	- 5.0 3.0
P-Nitrobenzoic Acid	0.10 0.01	- 293.0 - 199.0
O-Nitrophenol	0.10 0.01	- ∞ - 354.0
2-Nitro-1-butanol	0.10 0.01	- ∞ - 205.0
Trimethylol Nitromethane	0.10 0.01	- 615.0 - 144.0
Cyanoacetic Acid	0.10 0.01	- 8.6 3.8
Pyridine	0.135 0.10 0.18	- 3.9 4.1 0.0
Acetyl Acetone	0.886* 0.380* 0.253*	- 12.6 - 1.1 0.3

* Indicates concentration by weight

Table VIII

Average Corrosion Inhibitor Efficiency for Rodine 50 and Inorganic Compounds Investigated

Aerated and Agitated 5% Phosphoric Acid - Steel Coupon - Time 24 Hours - Temp 25°C.

Inhibitor	Concentration % by weight	Efficiency
Rodine 50	2.06 0.52 0.10	3.8 - 20.0 - 5.0
Sodium Chromate	1.00 0.50 0.10	99.3 $-\infty$ * 56.1
Hydrochloric Acid	0.57	5.9
Ferric Sulfate	0.26	- 111.0
Sodium Nitrate	1.00	- 111.0
Sodium Arsenate	1.00 0.50 0.10	19.1 7.2 0.0

* Indicates reduction of chromate

TABLE IX.

COUPON MEASUREMENTS AND AREA*

No.	Length dm	Width dm	Area dm^2
0	0.526	0.240	0.2426
1	0.521	0.250	0.2506
2	0.514	0.230	0.2266
3	0.516	0.242	0.2401
4	0.518	0.242	0.2411
5	0.522	0.248	0.2496
6	0.521	0.244	0.2446
7	0.514	0.246	0.2431
8	0.500	0.246	0.2361
9	0.516	0.236	0.2341
10	0.516	0.242	0.2400
11	0.511	0.238	0.2330
12	0.531	0.248	0.2536
13	0.514	0.244	0.2409
14	0.528	0.246	0.2500
15	0.520	0.250	0.2501
16	0.515	0.250	0.2476
17	0.525	0.248	0.2511
18	0.518	0.250	0.2491
19	0.527	0.252	0.2559
20	0.520	0.251	0.2511
21	0.523	0.248	0.2501
22	0.523	0.248	0.2501
23	0.519	0.248	0.2476
24	0.520	0.250	0.2501
25	0.513	0.242	0.2386
31	0.516	0.240	0.2381
32	0.515	0.240	0.2371
33	0.509	0.238	0.2324
34	0.513	0.242	0.2381
35	0.512	0.245	0.2414
36	0.518	0.243	0.2421
37	0.513	0.260	0.2364
38	0.514	0.236	0.2331
40	0.515	0.240	0.2371
41	0.512	0.240	0.2361
42	0.510	0.235	0.2296
43	0.514	0.238	0.2346
44	0.517	0.240	0.2386
45	0.518	0.238	0.2376
46	0.518	0.240	0.2391

Continued on page 56.

TABLE IX. (Cont.)

COUPON MEASUREMENTS AND AREA*

No.	Length dm	Width dm	Area dm^2
47	0.510	0.240	0.2451
48	0.513	0.236	0.2324
50	0.518	0.243	0.2419
51	0.512	0.243	0.2391
52	0.506	0.240	0.2326
53	0.518	0.247	0.2461
54	0.517	0.240	0.2384
55	0.508	0.237	0.2311
56	0.514	0.236	0.2326
57	0.516	0.242	0.2400
58	0.518	0.241	0.2400
60	0.520	0.238	0.2370
61	0.519	0.237	0.2360
62	0.518	0.240	0.2385
63	0.518	0.237	0.2355
64	0.526	0.238	0.2400
65	0.521	0.239	0.2390
66	0.518	0.240	0.2385
67	0.523	0.228	0.2280
68	0.521	0.232	0.2318
70	0.512	0.239	0.2350
71	0.502	0.234	0.2250
72	0.518	0.235	0.2337
73	0.520	0.236	0.2355
74	0.525	0.236	0.2380
75	0.522	0.238	0.2385
76	0.519	0.232	0.2305
77	0.520	0.237	0.2360
78	0.514	0.240	0.2417
80	0.516	0.239	0.2365
81	0.514	0.239	0.2360
82	0.520	0.240	0.2395
83	0.518	0.238	0.2365
84	0.503	0.235	0.2265
85	0.513	0.238	0.2340
86	0.502	0.238	0.2290
87	0.504	0.238	0.2300
88	0.500	0.237	0.2270
100	0.518	0.235	0.2235
101	0.519	0.237	0.2360
102	0.520	0.240	0.2395
103	0.521	0.236	0.2360
104	0.520	0.238	0.2375
105	0.520	0.230	0.2290

Continued on page 57

TABLE IX (Cont.)

COUPON MEASUREMENTS AND AREA*

No.	Length dm	Width dm	Area dm^2
106	0.510	0.240	0.2350
107	0.510	0.236	0.2310
108	0.502	0.236	0.2270
110	0.500	0.232	0.2220
111	0.518	0.240	0.2380
112	0.503	0.230	0.2215
113	0.511	0.240	0.2350
114	0.519	0.241	0.2400
115	0.520	0.232	0.2315
116	0.527	0.238	0.2410
117	0.520	0.231	0.2300
118	0.520	0.240	0.2395
120	0.508	0.235	0.2345
121	0.512	0.234	0.2300
122	0.522	0.240	0.2405
123	0.507	0.234	0.2275
124	0.513	0.232	0.2280

* Thickness = 0.013 inches = 0.0033dm
Diameter hole = 0.79 dm

IV. DISCUSSION

Corrosion Rate Units. The standard unit for expressing weight loss data in corrosion work is milligrams per square decimeter per day, or mdd. However, some writers prefer to express these data in various other ways, one of which is average penetration in inches per year, or "ipy". To express the rate as ipy is sometimes helpful in that it aids in the forming of a mental picture of the actual deterioration of the metal, i.e., the wearing away of the metal surface.

To determine average penetration in inches per year, it is necessary to know the loss in weight, the area exposed, the weight of the metal per unit volume, and the duration of the experiment. The formula is:

$$P(\text{or ipy}) = \frac{WK}{SAT}$$

where:

P (or ipy)= average penetration in inches per year

W = weight metal removed (grams)

K = constant (0.003937)

S = specific gravity of metal

A = area exposed (sq dm)

T = duration of test (years)

Provided the corrosion is uniform on the metal surface, a conversion may be made from mdd to ipy or vice versa, using the following equation:

$$\text{ipy} \times 696 \times \text{density} = \text{mdd}$$

If pitting has occured, a conversion can not be made. The pits are usually expressed as maximum penetration in inches per year (depth of penetration). The term "pitting factor", is often used to determine the approximate time of deterioration of the metal by perforation, i.e.,

$$\frac{\text{Max. penetration}}{\text{ave. penetration}} = \text{pitting factor}$$

Effect of Aeration and Agitation of the Corrosion Rate. E. P. Whaley[73], has previously pointed out that aeration and agitation have a pronounced effect upon the corrosion rate. He showed that there is a 30 to 60 per cent increase in the corrosion rate of an aerated solution of five per cent phosphoric acid over an unaerated solution of the same strength using copper as a metal. He also showed that there is an increase in the corrosion rate when the rotation of samples is increased. During this investigation the flow of air to the corrosive media and the rotation of the coupons was kept constant, thereby eliminating any inconsistancy.

Effect of the Method of Cleaning on the Results of the Investigation. The same cleaning procedure was followed for all samples, thus weight losses due to cleaning were constant throughout and did not appreciably affect the relative results.

Duration of Run. The length of the individual runs was 24 hours. During this time between 700 and 100 mg/sq dm/day, corrosion rate, was observed in blank runs. This is more than the minimum weight loss prescribed by the Standard of the American Society for Testing Materials(1).

Variation in Data for Inhibited Runs. The Standard of the American Society for Testing Materials(1) on immersed corrosion testing states that the per cent deviation from the average for a four coupon run should be plus or minus 7 per cent. However, in this investigation a plus or minus 10 per cent deviation has been accepted since an inhibitor, in order to be a good inhibitor, must be at least 50 to 70 per cent efficient. A 10 per cent error will have little or no effect upon the final decision as to the practical value of an inhibitor. Another reason for accepting a plus or minus 10 per cent deviation limit is that the corroding system was not under strict control, since it was open to the atmosphere. An evaporation error was thus introduced. The volume change may be as much as 5 per cent in 24 hours. It should be pointed out, that where there is little or no weight loss, the slightest variation in the weight will introduce considerable error. This can be illustrated in the case of sodium chromate in Run 45, Table VI. Here the deviation in three samples out of four was greater than 10 per cent; however the greatest weight loss was only 1.5 milligrams and the least 0.2 milligrams.

Reason for Testing Inorganic Compounds. During this investigation no organic compounds were found that had any appreciable affect in inhibiting the corrosion process. The literature mentions sodium arsenate, sodium chromate, and other compounds that do act as inhibitors. Also, in the phosphatizing treatment of steel, certain inorganic inhibitors are used. It was then decided to test some of these compounds and try to find an inhibitor that had a greater efficiency.

Rodine 50. Rodine-50 is a commercial inhibitor that is used with hydrochloric acid in pickling of steel. During this investigation it was used with hydrochloric acid to clean the samples, as mentioned before. A qualitative organic analysis was made of Rodine 50 and it was found to contain the tertiary amine group, formaldehyde, hydrochloric acid and water. In table V, Run 4, in a concentration of 0.517 per cent by weight, Rodine 50 showed a negative efficiency of 20 per cent, thereby not being an inhibitor at all under the conditions tested. From this action it can be concluded that a compound which is a good inhibitor in one acid or solution may not necessarily have the same action in another medium.

Classification of Organic Compounds Tested. Some of the organic compounds tested may be classified as poor inhibitors or inert. Most of organic compounds tested may be classified as accelerators. These are: 2-nitro-1-butanol, trimethylol nitromethane, nitro phenol, di-n-amyl-amine, tri-n-amyl-amine, tri-n-butyl-amine, and triethanolamine.

Classification of Inorganic Compounds Tested. Sodium chromate may be classified as a very good inhibitor in concentrations of one per cent while sodium arsenate may be classified as a poor inhibitor. Ferric sulfate and sodium nitrate were found to be accelerators.

Comparison of Amines. From a study of the literature, several amines are shown as good inhibitors (over 90 per cent) of sulfuric acid, (Table I). But (Table III) all the amines do not show an efficiency of greater than the experimental error and some are definitely negative. Uhlig[68] states that compounds which show inhibitive properties for one acid, should have similar inhibitive effect on other acids. However the results of this investigation do not lead to such a conclusion.

Discrepany of Sodium Arsenate. According to Table II, it can be noted that Kosting and Heins found no weight loss using sodium arsenate in a concentration of 0.49 per cent by weight, in a 50 per cent phosphoric acid solution at a temperature of 80°C. In Table V, Run 42, sodium arsenate shows an efficiency of 19.1 per cent, at a concentration of 1 per cent, under the conditions tested. This discrepancy may be caused by one of the following reasons: (1) The samples tested showed very large pits that indicate sodium arsenate intensifies corrosion in small areas, thereby not completely blanketing the metal surface. (2) The activity of a 5 per cent phosphoric acid solution is greater than the activity of a 50 per cent solution. (3) The temperatures employed were different. (4) The velocity and aeration may have been different.

Action of Sodium Chromate. It can be seen from Table V, Run 45, that sodium chromate inhibits corrosion almost completely in a concentration of 1 per cent, using new samples. In Run 46, sodium chromate was tested in concentrations of 0.5 per cent on used samples, and the samples disintegrated. This may be explained in the following manner. When the samples were introduced into the corrosive media containing sodium chromate, the solution turned a greenish color after a few hours, indicating reduction of the chromate ions to chromic ions. Evans[18] points out that chromates precipitate ferrous salts in the absence of alkali, giving a precipitate containing ferric ion, chromic ion, hydroxide ion, and the chromate ion. In this run the samples were not clean and shiny, but contained a greyish black film which might be called ferrous phosphate. The chromate was reduced by this ferrous phosphate and in this way the chromate never reached the actual metal surface where it could inhibit the action of the phosphoric acid. As more ferrous phosphate was produced by the action of the acid on the steel, it too was oxidized to ferric phosphate, and so the sample disintegrated in this manner.

Acceleration of Corrosion. In Table IV, Run 9, 2-nitro-1-butanol in concentrations of 0.10 per cent nitrogen, was such a stimulator that the samples had disintegrated before the 24 hour period had elapsed; therefore no quantitative results could be determined. In the same Table, Run 17, nitrophenol shows

similar action in the same concentration. In a lower concentration of 0.01 per cent nitrogen, both compounds, however, did give a corrosion rate that could be determined. In the case of 2-nitrobutanol, Run 10, the efficiency obtained was minus 205 per cent, and in the case of nitrophenol, Run 17, the efficiency was minus 354 per cent. However, the samples of both runs were badly pitted and could not be used again. This action is very curious since Mann[47] states that "organic inhibitors have never been found to act as stimulators", yet here is one organic compound (an inhibitor in copper and phosphoric acid) that does act as a stimulator in the corrosion of steel by phosphoric acid. The corrosion rate was approximately three to four times greater with the inhibitor than without.

Evans[18] divides inhibitors into two classes, safe and dangerous. An inhibitor can only be dangerous when it is an anodic inhibitor and is added to a cathodically controlled reaction in small amounts. An example that can be given is the inhibition of corrosion of steel in water by sodium chromate. If an insufficient amount of sodium chromate is added to such a system, corrosion will be intensified, and therefore be greater than without the inhibitor. The inhibitor will reduce the area being corroded still more rapidly, thereby increasing the pitting factor. Evans points out[79] that a single compound may belong to a safe and dangerous class under different conditions. This

seems to be the case with 2-nitro-1-butanol. With copper and 5 per cent phosphoric acid the compound is a very good inhibitor (94 per cent), while with steel and 5 per cent phosphoric acid, it is an accelerator.

A possible explanation for this difference is that 2-nitro-1-butanol is only slightly soluble in 5 per cent phosphoric acid. Weights of this compound that would give a nitrogen concentration over 0.10 per cent will not go into solution. In this investigation, the corrosion of steel is under cathodic control. The compound, 2-nitro-1-butanol, can be considered to be an anodic inhibitor and in small amounts can only serve to increase the total corrosion. Larger amounts of 2-nitro-1-butanol might conceivably inhibit, but it is impossible to put larger amounts in solution, under the conditions of these experiments.

Whaley[73] has shown that aeration increases corrosion of copper in 5 per cent phosphoric acid at 25°C. This may seem to indicate that copper is under cathodic control. However, it may be postulated that the oxygen goes to the anode forming copper oxide, which is then dissolved by the phosphoric acid. Since the rate of corrosion is dependent upon the rate of the anodic reaction of copper with dissolved oxygen, the corrosion can be said to be under anodic control. Therefore, when 2-nitro-1-butanol, an anodic inhibitor, is introduced into 5 per cent phosphoric acid, the corrosion of copper can be stifled by

adsorption of the inhibitor on the anodic area. This may be the reason why, under these conditions, 2-nitro-1-butanol is an inhibitor for copper and an accelerator for steel.

Limitations

This investigation was carried out under the following limitations:

1. The temperature employed was 25° plus or minus 0.5°C.
2. The time alloted for each run was 24 hours.
3. The concentration of the phosphoric acid used was 5 per cent, and the solution was prepared from 85 per cent, chemically pure, ortho phosphoric acid, in a batch process.
4. Steel containing approximately 0.08 per cent carbon was the only material tested.
5. Samples that were used were cut from a single sheet of steel using tin-smith shears, and the areas were not constant throughout.

Recommendations

This investigation has suggested that the following work be done:

1. Further electrode potentiometric measurements should be studied with steel and copper in inhibited and uninhibited phosphoric acid solution.
2. Inhibitors in various concentrations, especially the amines should be studied in varying acid concentrations.
3. Corrosion of steels of different carbon content should be studied.
4. Compounds that are inhibitors for one acid and metal should be studied in other acids and metals to determine whether they are effective.
5. Similar investigations using higher temperatures should be studied.
6. Further investigation should be made on the nature of copper in aerated acids to determine the mechanism of the corrosion of metals more noble than hydrogen.
7. Sodium chromate and other inhibitors used in this investigation should be studied using a slower velocity of rotation.

V. CONCLUSIONS

From the results obtained in this investigation, the following conclusions can be drawn:

1. A substance inhibits corrosion only under certain conditions, and under other conditions it may not be an inhibitor, but may be inert or an accelerator.
2. No compounds tested in concentrations of 0.01 and 0.10 per cent nitrogen, were found to inhibit the corrosion of steel in 5 per cent phosphoric acid at 25°C. and under the conditions of aeration and agitation used.
3. Sodium chromate is an inhibitor in concentrations of 1 per cent for the corrosion of steel by a 5 per cent, aerated, agitated, phosphoric acid solution at 25°C.
4. The mechanism of the corrosion of copper proposed by Whaley is not substantiated. Chelation probably is not the mechanism by which 2-nitro-1-butanol inhibits the corrosion of copper in a 5 per cent phosphoric acid solution.
5. Inhibitors that are used and are efficient for one acid under certain conditions cannot always be said to work for other acids under other conditions.

VI. BIBLIOGRAPHY

1. ASTM Standard, 1946, Part I-B Non-Ferrous Metals, "Tentative Method of Total Immersion Corrosion Test of Non-Ferrous Metals". p. 793-802. American Society for Testing Materials, Philadelphia, Pa.

2. Anon., The Modern Chelating Agent. Tech. Bull. 1, Bersworth Chem. Co., Framington, Mass., 1949.

3. Ardagh, E. G. R., Roome, R. M. B., and Owens, H. W., Mechanism of Corrosion of Iron in Sodium Chloride Solution. Ind. Eng. Chem. 25, 1116, (1933).

4. Bancroft, W. D., The Electrolytic Theory of Corrosion. J. Phys. Chem. 28, 788, (1924).

5. Bengough, G. D., and Stuart, J. M., Sixth Report of the Corrosion Research Committee of the Institute of Metals. J. Inst. Metals, 28, 31. (1922).

6. Blum, W., and Rawdon, H. S., Electrolytic Studies on Corrosion. J. Electrochem. Soc., 52, 403, (1927).

7. Bogart, L. G., "Combating Corrosion in Industrial Process Piping". Tech. Paper No. 408, May, 1939, Crane Co., Chicago, Ill.

8. Brown, R. H., Roetheli, B.E., and Forrest, H. O., The Initial Corrosion Rates of Metals. Ind. Eng. Chem. 23, 350, (1939).

9. Burns, R. M., The Corrosion of Metals, Mechanism of Corrosion Processes. Bell System Tech. J., 15, 20, (1936), Tech. Pub. B912.

10. Burns, R. M., and Haring, H. E., Determination of the Corrosion Behavior of Painted Iron and the Inhibitors Action of Paints. J. Electrochem. Soc., 69, 169, (1936).

11. Calvert, F. C., Manchester Lit. Phil. Mem. 5, 104 (1871); Dunstan, W. R., Jowett, H. A. D., and Goulding, E., The Rusting of Iron. J. Chem. Soc. 87, 1548, (1905).

12. Chappell, E. L., Roetheli, B. E. and McCarthy, B. Y., The Electrochemical Action of Inhibitors in the Acid Solution of Steel and Iron. Ind. Eng. Chem., 20, 582, (1928).

13. Chappell, E. L., and Ely, P. C., The Pickling of Pipe Using Commercial Inhibitors. Ind. Eng. Chem., 22, 1201, (1930).

14. Deghton, A. L. and Miley, H. A., The Parabolic and Logarithmic Oxidation of Copper. J. Electrochem. Soc., 81, 321, (1942).

15. Dunstan, W. R., Jowett, H. A. D., and Goulding, E., The Rusting of Iron. J. Chem. Soc., 87, 1548, (1905).

16. Dunstan, W. R. and Hill, J. R., The Aerial Oxidation (Rusting) of Metals. J. Chem. Soc., 99, 1835, (1911).

17. Dunstan, W. R. and Hill, J. R., The Passivity of Iron and Certain Other Metals. J. Chem. Soc., 99, 1853, (1911).

18. Evans, U. R., Inhibitors - Safe and Dangerous. J. Electrochem. Soc., 69, 213, (1936).

19. Evans, U. R., "Metallic Corrosion Passivity and Protection". p. 3, Edward Arnold, London, 1938.

20. Forrest, H. O., Roberts, J. K. and Roetheli, B. F., Effect of Inhibitors on Acid Solution of Copper and Copper Alloys. Ind. Eng. Chem. 20, 1369, (1928).

21. Friend, J. A. N. and Vallance, R. H. , The Influence of Protective Colloids on the Corrosion of Metals and on the Velocity of Chemical and Physical Change. J. Chem. Soc., 121, 466, (1922).

22. Friend, N. J., Hammond, J. W. and Trobridge, T. W., Influence of Emulsions on the Rate of Solution of Iron. J. Electrochem. Soc. 46, 283, (1924).

23. Griffen, R. C., The Solubility of Metals in Acids Containing Formaldehyde. J. Ind. Eng. Chem. 12, 1159, (1920).

24. Hackerman, N., and Sudbury, J. D., Effect of the Addition of Amine on the Electrode Potential of Copper in Buffered Acid Solution. J. Electrochem. Soc., 93, 191, (1948).

25. Hodgman, C. D., "Handbook of Chemistry and Physics". p. 1597, Chem. Rubber Publishing Co., Cleveland, Ohio, 1948, 30th ed.

26. Hultin, C. T., A Study of Organic Nitrogen Bases as Inhibitors of Corrosion. Unpublished Thesis, Library, Univ. of Minnesota.

27. Jimeno, E., Grifoil, I., and Morral, F. R., Inhibitors in Pickling. J. Electrochem. Soc., 69, 105, (1936).

28. Knudson, A. A., The Corrosion of Metals by Electrolysis. J. Electrochem. Soc., 3, 195, (1905).

29. Kosting, P. R., and Heins, Jr., C., Corrosion of Metals by Phosphoric Acid. Ind. Eng. Chem., 23, 140, (1931).

30. Lawrence, R. W., and Walton, J. H., The Effect on the Rate of Oxidation of Copper in Phosphoric Acid Solution. J. Phys. Chem., 46, 609, (1942).

31. LeBlanc, M., "A Textbook of Electrochemistry". p.297, The Macmillan Co., New York, 1910, American Translation.

32. McKay, R. J., Corrosion by Electrolyte Concentration Cells. J. Electrochem. Soc., 41, 201, (1922).

33. McKay, R. J., and Worthington, R., "Corrosion Resistance of Metals and Alloys". p. 20, ACS Monograph Series No. 71, Reinhold Publishing Corp., New York, 1936.

34. Ibid, p. 21.

35. Ibid, p. 23.

36. Ibid, p. 411.

37. Ibid, p. 413.

38. Machu, W., The Theory of Inhibitors. Berg. und hoettenmannische jahrbuch (Leoben. Montanistische hochschule), 84, 62, (1936); C. A., 31, 82, (1937).

39. Machu, W., Protective Action of Inorganic and Organic Substances in the Acid Corrosion of Metals. Osterr, Chem. Ztg., 39, 144, (1936); C. A., 31, 3857, (1937).

40. Machu, W., New Inhibitor Theory and A New Method for the Evaluation of the Inhibitors. Korrosion u. Metallschutz, 13, 1, (1937); C. A., 31, 4943, (1937).

41. Machu, W., Critical Discussion of Previous Inhibitor Theories and Explanation of the Function of Organic Inhibitors in the Acid Corrosion of Metals. Korrosion u. Metallschutz., 13, 20, (1937); C. A. 31, 4943, (1937).

42. Machu, W., Inhibiting of Acid Corrosion of Metals by Means of Organic Substances. Anegew. Chem., 51, 853, (1938); C. A., 33, 1255, (1939).

43. Machu, W., Temperature Coefficient of the Acid Corrosion of Iron in the Presence of Organic Materials. Korrosion u. Metallschutz., 14, 324, (1938); C. A., 33, 2466, (1939).

44. Mann, C. A., Organic Inhibitors of Corrosion. J. Electrochem. Soc., 69, 115, (1936).

45. Mann, C. A., Lauer, B. E., and Hultin, C. T., Organic Inhibitors of Corrosion - Aliphatic Amines. Ind. Eng. Chem., 28, 159, (1936).

46. Mann, C. A., Lauer, B. E., and Hultin, C. T., Organic Inhibitors of Corrosion - Aromatic Amines. Ind. Eng. Chem., 28, 1049, (1936).

47. Mann, C. A., and Shih - Jen Ch'iao, Nitrogen Containing Organic Inhibitors of Corrosion. Ind. Eng. Chem., 39, 910, (1947).

48. Marangoni, C., and Stephanelli, P., The Influence of Certain Liquids in Retarding or Arresting the Action of Acids upon Metals. J. Chem. Soc., 25, 116, (1872).

49. Martell, A. E., and Bersworth, F. C., Amino Acids as Chelating Agents. Proc. Scient. Sect. Tiolet Goods Assoc. 10, 1, (1948).

50. Mears, R. B., and Evans, U. R., "Probability" of Corrosion. Trans. Faraday Soc., 31, 534, (1935).

51. Mears, R. B., and Eldredge, G. G., The Use of Inhibitors for Aluminum Chemical Equipment. J. Electrochem. Soc., 83, 403, (1943).

52. Mears, R. B., A Unified Mechanism of Passivity and Inhibition. J. Electrochem. Soc., 95, 1, (1949).

53. "Metals Handbook". p. 1392, Am. Soc. for Metals, Cleveland, Ohio, 1939.

54. Munger, H. P., The Use of Inhibitors in the Pickling of Iron. J. Electrochem. Soc., 69, 85, (1936).

55. Rhodes, F. H., and Kuhn, W. E., Inhibitors in the Action of Acid on Steel. Ind. Eng. Chem., 21, 1066, (1929).

56. Rohrman, F. A., Corrosion of Metals by Phosphoric Acid. Chem. and Met., 42, 368, (1935).

57. Ruisakov, M. V., and Bushmakin, I, N., Corrosion of Metals and Alloys by Phosphoric Acid and Phosphorous. J. Applied Chem. (U.S.S.R.), 5, 715, (1932); C. A., 27, 54, (1933).

58. Speller, F. N., "Corrosion - Causes and Preventions". p. 8, McGraw - Hill Book Co., New York, 1936, 2nd ed.

59. Ibid, p. 51.

60. Speller, F. N., and Chappell, E. L., Inhibitors - Their Behavior in Laboratory and Plant. Trans. Am. Inst. Chem. Eng., 19, 153, (1927).

61. Speller, F. N., and Chappell, E. L., Practical Application of Inhibitors in Pickling Operations. Chem. and Met., 34, 421, (1927).

62. Thompson, J. F., and McKay, R. J., The Control of Motion and Aeration in Corrosion Tests. Ind. Eng. Chem., 15, 1114, (1923).

63. Uhlig, H. H., "Corrosion Handbook", p. 3, John Wiley and Sons, New York, 1948.

64. Ibid, p. 21.

65. Ibid, p. 905.

66. Ibid, p. 906.

67. Ibid, p. 908.

68. Ibid, p. 914.

69. Walker, W. H., The Function of Oxygen in the Corrosion of Metals. J. Electrochem. Soc., 14, 175, (1909).

70. Warner, J. C., Organic Type Inhibitors in Acid Corrosion of Iron. J. Electrochem. Soc., 55, 287, (1929).

71. Watts, O. P., and Whipple, N. D., The Corrosion of Metals by Acids. J. Electrochem. Soc., 32, 257, (1917).

72. Watts, O. P., The Electrochemical Theory of Corrosion. J. Electrochem. Soc., 64, 125, (1933).

73. Whaley, E. P., The Effect of Certain Nitrogen - Containing Organic Compounds on the Corrosion of Copper in Phosphoric Acid. Unpublished Thesis, Library, Virginia Polytechnic Institute, Blacksburg, Virginia, 1948.

74. Whitman, W. G., Russell, R. P., Welling, C. M., and Cockran, J. D., The Effect of Velocity on the Corrosion of Steel in Sulfuric Acid. Ind. Eng. Chem., 15, 672, (1923).

75. Whitman, W. G., and Russell, R. P., Fundamental Factors of Corrosion. Chem. and Met., 30, 671, (1924).

76. Whitman, W. G., and Russell, R. P., The Acid Corrosion of Metals; Effect of Oxygen and Velocity. Ind. Eng. Chem., 17, 348, (1925).

77. Whitney, W. R., Corrosion of Iron. J. Am. Chem. Soc., 25, 394, (1903).

78. Reeves Manufacturing Company, Dover, Ohio. Private Communication, 1949.

The vita has been removed from the scanned document