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ELECTROCHEMICAL STUDIES OF INHIBITIVE PIGMENTS

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ABSTRACT

This report covers the results obtained from electrochemical studies of selected pigments and the mechanism by which they may protect steel in the presence of electrolytes. The work involved potential and polarization tests with steel in solutions containing pigments in dissolved and suspended states and as pastes. Known soluble inhibitors were included for comparison.

The potential tests gave qualitative information on the electrochemical effects of the more soluble inhibitors but failed to indicate whether such behavior was exhibited by the much less soluble pigments. Polarization studies gave quantitative information on the electrochemical behavior of suspended pigments when differential aeration cells were employed.

Red lead, zinc chromate, zinc tetroxychromate, chromated red lead, basic lead sulphate and blue lead were found to inhibit the corrosion of steel by increased polarization in both sulphate and chloride solutions. Iron oxide and mica pigment showed no inhibition while ferrous ammonium phosphate accelerated the corrosion of steel. The mechanism of such effects is explained on the basis of polarization of local cell elements.

PROBLEM STATUS

This is a final report on one phase of the problem; work on other phases has been discontinued and the problem is closed.

AUTHORIZATION

NRL Problem C05-12R
NR 405-120

ELECTROCHEMICAL STUDIES OF INHIBITIVE PIGMENTS

INTRODUCTION

A large proportion of exposed metal used by the U. S. Navy is protected by organic protective coatings familiarly known as paint. Such coatings are composed of pigments and vehicles. They are not perfect insulators against corrosive attack from the weather and sea and consequently require continual and periodic maintenance and renewal. This in itself is a costly item. Gradual improvement in the life of these coatings has been made over the years through a better understanding of the mechanisms of organic film formation and protection and the application of these principles to practical painting procedures. However, additional information on this subject is still needed.

For a long time, many have believed that certain pigments exhibit electrochemical properties which, when incorporated in paint films, confer increased life to the films under exposure to moisture conditions. Others contest this assertion and believe that physical conditions predominate.

A large amount of experimental work has been carried out with pigments and vehicles, both singly and in combination as paint films, in efforts to increase their ultimate protective effects when applied on iron or steel. This has mostly included work on their physical and chemical characteristics with some emphasis on the electrochemical properties.

Organic coatings protect steel by serving primarily as mechanical barriers to the passage of corrosive electrolyte to the metal surface. In addition to this physical protection, some investigators believe that certain pigments may dissolve in any liquid which permeates the paint film and that this solution then inhibits corrosion of the underlying metal through the mechanism of passivity(1,2,3,4,5). Others, while admitting the possibility of such mechanisms, suggest that electrochemical effects are probably of minor importance when the pigments are incorporated in paint films. Physical and chemical characteristics are then thought to predominate (6,7,8,9). These include such properties as pigment solubility, moisture permeability, osmosis, adhesion, blistering, and size and distribution of pigment particles.

The types of tests employed in evaluating the electrochemical effect of pigments have included such studies as potentials (2,10,11,12,13,14,15), electrical resistance (3,9,16,17), and polarization (18,19,20).

It appears that the difficulties encountered in elucidating the mechanism of pigment behavior have resulted from the sole use either of accelerated methods or of exposure panels as a means of obtaining results. One or more factors are exaggerated in most accelerated tests, thus not reproducing environmental conditions and making it difficult

or impossible to apply the results obtained to service behavior of the material. The use of paint films on metal exposure panels involves the simultaneous operation of all the chemical, physical, and electrochemical factors previously mentioned. An accurate evaluation of any single factor is thus difficult because its influence is frequently masked by others. Both accelerated and actual exposure tests fail to indicate what is occurring under the paint film during exposure and thus the factors controlling breakdown or protection can not be evaluated. Visual examination of failed films neither indicates the speed of failure nor permits a quantitative study of the mechanism of protection.

The work herein reported was instituted at the request of the Bureau of Ships (21) in an effort to obtain a better understanding of the role of paint pigments in the protection of iron and steel. It was desired to know the factors which determine the inhibitive behavior of paint pigments and how these properties may be utilized for the protection of steel surfaces.

The first phase of the project covers studies of the electrochemical behavior of steel and the mechanism by which it may be protected in dilute salt solutions (NaCl and other salts) containing various selected pigments in either a dissolved or suspended state or as pastes. The work involves time-potential and polarization tests. Future work contemplates an extension of these tests to actual paint films (pigments combined with vehicles to form paint films) and to actual conditions of exposure, since the protective behavior of organic coatings depends on the combined properties of the film, characteristics of the substrate, and the environment.

TIME-POTENTIAL STUDIES

General

Time-potential studies have been used by many investigators in studying corrosion processes. In general, a cathodic potential or a trend of potential in this direction is believed to indicate passivity or corrosion resistance of a metal while a trend of potential in an anodic direction indicates activity or corrosion. However, exceptions to this statement have been noted and there may be some question as to the exact interpretation of time-potential data.

Time-potential relationships for various metals have been discussed by several investigators (22,23,24,25). In general, it is believed that cathodic trends are associated with film formation, passivity, and absence of corrosion, while anodic trends indicate film removal, activity, and general corrosion (2, 22, 26). However, others have pointed out that precautions should be exercised in the interpretation of these phenomena (10,27,28). Mears (29) notes that when passivity is a function of time and is caused by anodic polarization, the potential of a freshly immersed metal electrode will move in a cathodic direction with time of exposure. He considers that such shifts in potential are not characteristic of all passivity since cases have been noted where the potential of a metal moved in an anodic direction even though the corrosion rate diminished with time.

Considerable work on the time-potential relationship of steel in a wide variety of solutions was carried out in the initial phases of this project since it was anticipated that this relationship would be used as the principal electrochemical test in the latter phases involving painted steel panels.

The general outline of the apparatus used for conducting these tests is shown in Figure 1. The quartz cell, A, contained steel electrode B, gas inlet C, solution inlet D, and a gas exit tube. The rest of the equipment was of glass. The standard reference electrode was inserted in reservoir E. The electrolyte was stored in reservoir F where

means were provided for saturating it with nitrogen prior to admitting it to cell A for the potential measurements. The electrode consisted of a small strip of cold-rolled steel, polished by hand, degreased, and attached inside of cell A. The cell was evacuated of air, filled with purified hydrogen, and heated in an electric furnace at 950°C for approximately two hours. After being removed from the furnace and cooled, it was assembled to the two reservoirs, the whole apparatus filled with nitrogen, and the particular solution under investigation transferred to the cell.

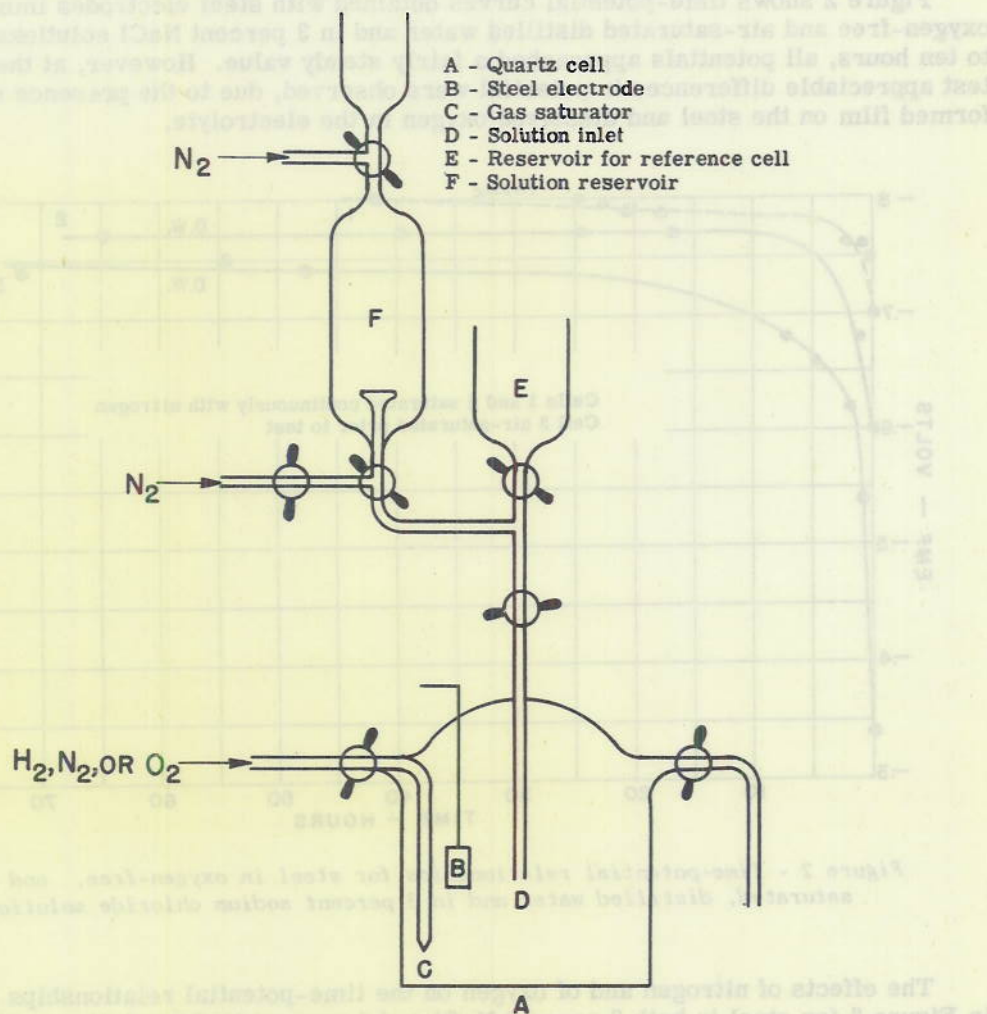


Figure 1 - Sketch of apparatus used for time-potential tests

In most cases nitrogen gas was passed into the cell during test and served both to saturate and to agitate the solution. Under these conditions, the potential between the steel electrode and a saturated calomel reference electrode was determined at frequent intervals for a period of 20 to 24 hours. A fairly steady potential* was observed in most cases at

* All potentials given in this report refer to the saturated calomel cell as a reference electrode.

the end of the period using both a Beckman pH meter and a vacuum-tube voltmeter. The solution was then saturated with oxygen and potential readings made as before. Decided shifts in potential were observed for many of the solutions when the oxygen was substituted, a fairly steady potential being obtained within a few hours. The potentials obtained under these conditions of gas saturation were classified as steady nitrogen and oxygen potentials, respectively.

Figure 2 shows time-potential curves obtained with steel electrodes immersed in both oxygen-free and air-saturated distilled water and in 3 percent NaCl solutions. After five to ten hours, all potentials approached a fairly steady value. However, at the start of the test appreciable differences in potential were observed, due to the presence of both an air-formed film on the steel and dissolved oxygen in the electrolyte.

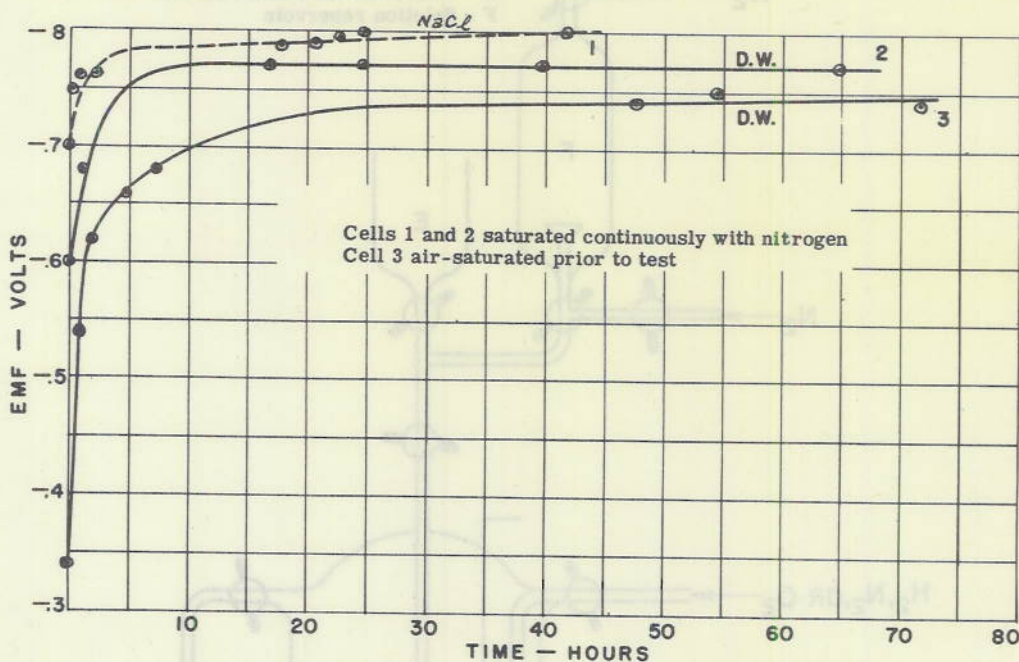


Figure 2 - Time-potential relationships for steel in oxygen-free, and air-saturated, distilled water and in 3 percent sodium chloride solutions

The effects of nitrogen and of oxygen on the time-potential relationships are shown in Figure 3 for steel in both 3 percent NaCl and 4 percent NaOH solutions. Under nitrogen saturation, steel maintains a fairly high anodic potential since there is no oxygen to form an oxide film on the metal. However, in the presence of oxygen the potential shifts rapidly in a cathodic direction. Introduction of nitrogen following saturation with oxygen results in a rather slow rise of potential in an anodic direction. Dissolved oxygen inhibits the corrosion of iron at sufficiently high concentrations and accelerates corrosion at lower concentrations (30,31). The existence of pre-immersion oxide films has a considerable influence on the initial potential behavior of steel, but this effect gradually decreases as the period of immersion is increased. Probably the two electrodes would ultimately reach a "steady-state" which might correspond to the electrode potential of the system iron-ferrous hydroxide-saturated solution. The length of time required to attain such an equilibrium would depend on such factors as solution rate, film repair and stability, agitation

of solution, etc. The effect of pre-immersion films on the steel electrodes was eliminated by using film-free surfaces.

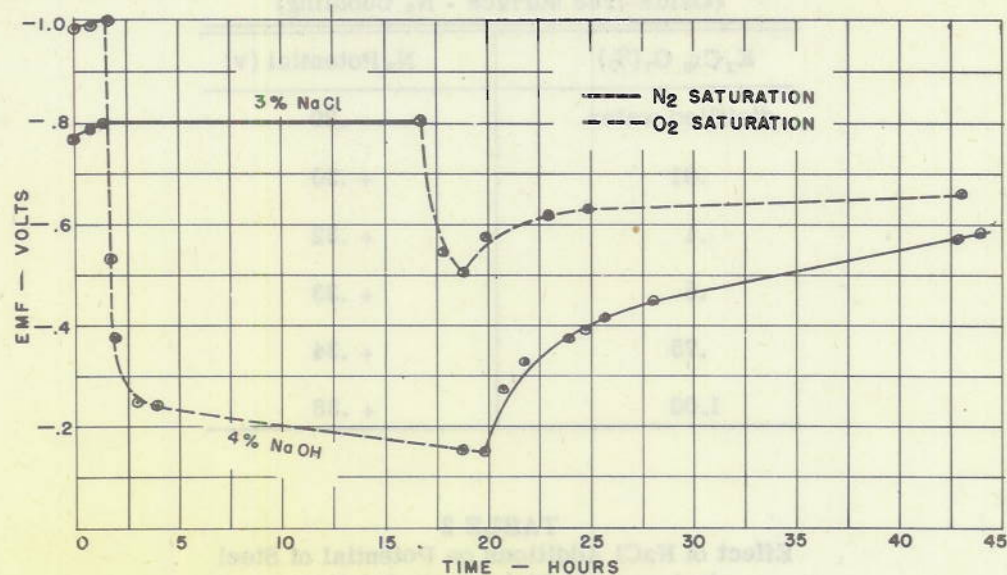


Figure 3 - Time-potential relationships for steel in 3 percent sodium chloride and 4 percent sodium hydroxide solutions under oxygen and nitrogen saturation (oxide-free surface at the start)

Solutions

A variety of solutions were used. In every case, the introduction of oxygen made the potential more cathodic; most oxidizing solutions caused large drops, in the cathodic direction, from the nitrogen potentials. As shown in Figure 4, little or no effect of dissolved gases was observed in the case of chromate solutions, particularly where appreciable amounts of chromate ion were present. The rate of supply of dissolved oxygen to the metal had a negligible influence on the film present. The film formed under these conditions promotes anodic polarization, reduces the local cell current, and makes the electrode potential more cathodic. Corrosion is reduced but, unless it is entirely eliminated, a severe localized type may result (10).

Steady nitrogen potentials obtained with various dichromate solutions are shown in Table 1. A cathodic potential was observed on the steel when even a small amount (.01%) of dichromate was present. The effect of chloride ion on the potential of steel in dichromate solutions is shown in Table 2 and Figure 5. Great sensitivity of the steel electrode to slight changes in chloride ion concentration is shown. Also, as shown in Figure 4, the electrode potential of steel in chromate solutions is but little affected by the presence of either oxygen or nitrogen, the reaction between chromate ion and steel largely determining the potential.

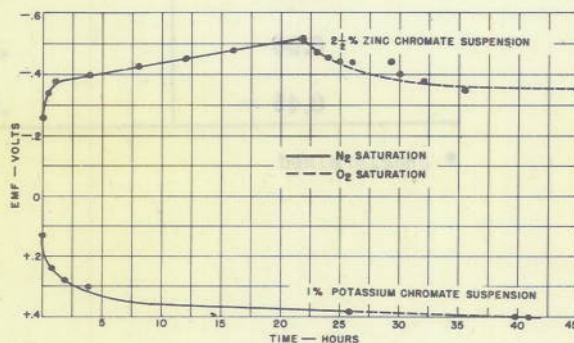


Figure 4 - Time-potential relationships of steel in chromate solutions under nitrogen and oxygen saturation

TABLE 1
Effect of Dichromate on the Potential of Steel
(Oxide-free surface - N₂ bubbling)

K ₂ Cr ₂ O ₇ (%)	N ₂ Potential (v)
distilled water	- .80
.01	+ .30
.1	+ .32
.5	+ .33
.75	+ .34
1.00	+ .38

TABLE 2
Effect of NaCl Additions on Potential of Steel
in 1 percent Dichromate Solutions
(N₂ - O₂ bubbling)

NaCl (%)	Dichromate (%)	Potential (v)	
		in O ₂	in N ₂
0.0	1.00	+ .40	+ .38
0.01	1.00	+ .20	+ .22
0.04	1.00	+ .17	- - *
0.06	.98	+ .10	- - *
0.11	.96	- .14	- - *
0.19	.94	- .41	- - *
0.36	.88	- .48	- - *
0.45	.85	- .53	- .62

* Undetermined

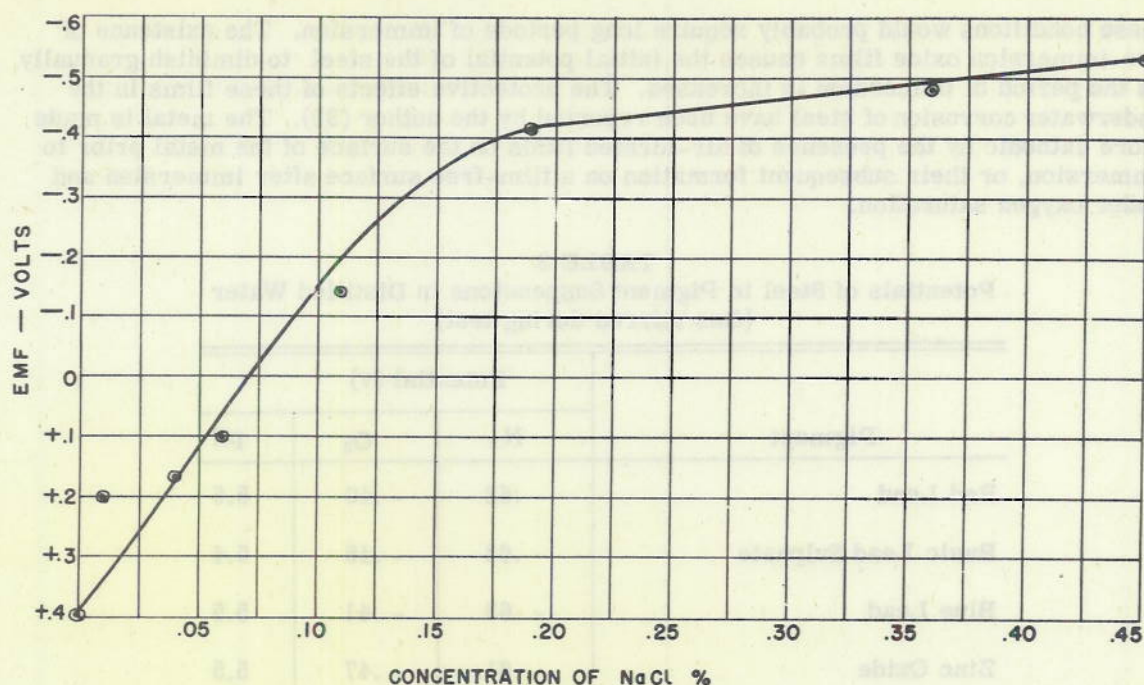


Figure 5 - Effect of NaCl on the oxygen potential of steel in 1 percent potassium dichromate solutions

Pigment Suspensions

Steady potentials of oxide-free steel electrodes immersed in 2½ percent, by weight, suspensions in distilled water were determined for some common paint pigments. Nitrogen was bubbled for approximately 20 hours after which time a fairly steady potential was obtained; then oxygen was bubbled for several hours until steady values were again observed. The bubbling also served to maintain a suspension of the pigments in solution. The electrode potentials obtained in these tests are shown in Table 3. The time-potential curves obtained for red lead and zinc chromate pigments are shown in Figure 6. Under a nitrogen environment, steel in zinc chromate was cathodic to that in red lead, though they tend to approach identical values as the time of immersion is increased. Under oxygen saturation, steel is initially more cathodic in red lead than in zinc chromate. However, again, with increased immersion time, little difference in electrode behavior was observed for the two pigments.

The effect of oxygen saturation as compared to nitrogen saturation was to make the potential of steel in any of the pigment suspensions cathodic by 0.15 to 0.25 volt. Steel electrodes in any of the pigment suspensions show characteristic time-potential relationships similar to those of Figure 6. These relationships fail to differentiate a marked electrochemical behavior of steel in any of the pigment suspensions in distilled water.

Discussion

Steady potentials were reached in a much shorter time under oxygen saturation than under nitrogen saturation. The formation of ferrous ions, under the latter conditions, proceeds at a relatively slow rate, thus accounting for the long time required for the electrode potentials to reach relatively steady value. The attainment of equilibrium potentials under

these conditions would probably require long periods of immersion. The existence of pre-immersion oxide films causes the initial potential of the steel to diminish gradually as the period of immersion is increased. The protective effects of these films in the underwater corrosion of steel have been reported by the author (32). The metal is made more cathodic by the presence of air-formed films on the surface of the metal prior to immersion, or their subsequent formation on a film-free surface after immersion and under oxygen saturation.

TABLE 3
Potentials of Steel in Pigment Suspensions in Distilled Water
(Gas stirred during test)

Pigment	Potential (v)		
	N ₂	O ₂	pH
Red Lead	- .62	- .40	5.5
Basic Lead Sulphate	- .63	- .46	5.4
Blue Lead	- .63	- .41	5.5
Zinc Oxide	- .61	- .47	5.5
Zinc Chromate	- .52	- .36	6.2
Amm. Ferrous Phosphate	- .70	- .46	6.8
75% Iron Oxide	- .84	- .59	5.5

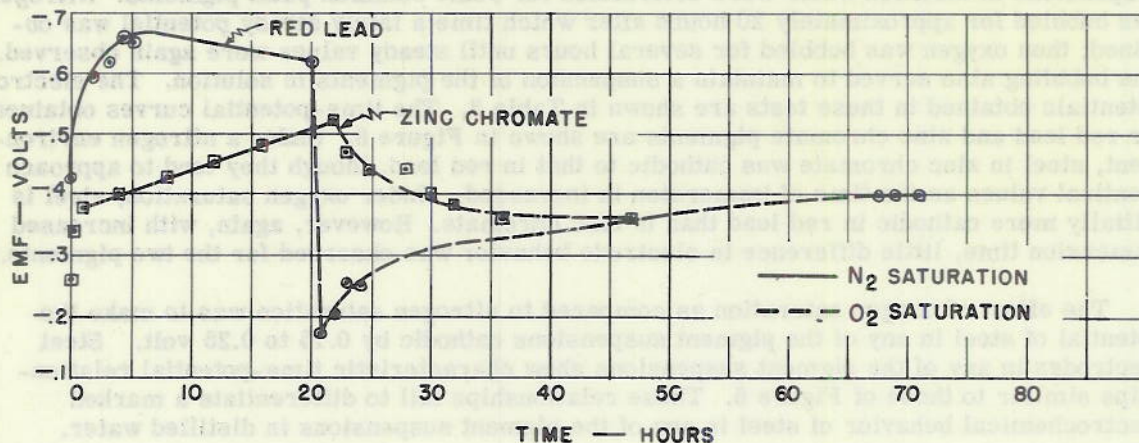


Figure 6 - Time-potential relationships of steel in pigment suspensions under nitrogen and oxygen saturation

Determination of the time-potential relationship for steel in a variety of solutions and in pigment suspensions, under both nitrogen and oxygen saturation, indicated that the actual value depends upon many factors, such as type of reaction taking place at the metal surface, degree of polarization of local anodes and cathodes, and presence and stability

of both passive and corrosive films. Strong oxidizers tended to produce passive films irrespective of the presence of dissolved nitrogen or oxygen.

Under the two types of gas saturation no significant differences were observed in the steady electrode potentials of steel in various pigment suspensions. In addition to the potential value, other important electrochemical characteristics must be known in order to determine fully the corrosion reaction. The time-potential test was not found sensitive enough to describe completely the mechanism by which pigments might inhibit corrosion.

POLARIZATION STUDIES

General

The relationship between potential and current density has been used by many investigators (8,18,19,20,23,33,34) as a means of obtaining quantitative information on the mechanism of the electrochemical process taking place on a metal undergoing corrosion. In this method an attempt is made to isolate and control the anodic and cathodic areas of a metal so as to determine the relative role of each in the corrosion process. Since corrosion of metals is assumed to be electrochemical, it is best measured by determining local cell current, itself a direct measure of the rate of corrosion. The tapping of all or a large part of the local cell current is difficult and necessitates the separation of anodic and cathodic areas (33,35). The mechanism and quantitative effect of local cell action may be more fully understood from polarization studies.

The method utilizes application of given controlled current densities from either an internal or external potential source to electrodes of the same metal and observation of the resulting anodic or cathodic potentials (or possibly of different metals if galvanic corrosion is being studied). The potential measurements can be made, either on open or closed circuit, though the usual interruptions in making the former are of such duration as to introduce considerable errors.

The tendency for metal to dissolve in the liquid film surrounding the anode surface is less than it would be if the solution were uniform throughout (36)—a difference known as anode polarization. Similarly, the decrease in hydrogen concentration at the cathode and the accumulation of discharged hydrogen at its surface gives rise to cathodic polarization, which must increase with current density and, to a lesser extent, with time. Manifesting itself as a counter potential invariably opposing the causative voltage, polarization can be considered as the accumulation of various irreversible electrode effects which oppose the direction of current flow and which cause the potential of anodic areas to become more cathodic and that of cathodic areas to become more anodic. The current density necessary to make these areas equipotential is known as the "corrosion current" and is believed to measure the accumulated effect of all the current flowing in local cells. The effective voltage of corrosion cells may be reduced by polarization to virtually zero, in which case the rate of corrosion is limited to that required to maintain this polarization. The rate of corrosion may be controlled by the extent of anodic or cathodic polarization or both (29).

Equipotential Electrode Cells

Method. Work on the first phase of the problem involved the study of potential-current relationships of steel electrodes in air-saturated stagnant solutions. The two electrodes were of the same material and were approximately at the same potential after immersion in the electrolyte and before any current was applied. They consisted of short lengths of

steel wire, approximately 5/64 inch in diameter, immersed to a depth of approximately two inches in several hundred ml of electrolyte. Beckman-type, saturated calomel reference electrodes were placed close to the steel electrodes. The wire electrodes were selected since they were to be used also with pigment pastes contained in a cylindrical glass filter placed within a beaker.

Constant small currents were obtained from a high external voltage (100 volts) applied through a large resistance to the two electrodes. Since the voltage used is large relative to any potential changes occurring within the cell and the resistance very high compared to that of the cell, the current remained constant with changes taking place within the cell. In actual corrosion processes the metal provides its own current but it is extremely difficult to obtain constant values where this method is utilized. The mechanism of corrosion is the same for a current-producing cell and a cell supplied with current from an external source.

Increasing increments of current were applied between the two electrodes until a sufficient range in current density had been obtained to show the polarization effect. The current was maintained at each point for at least ten minutes or until a fairly steady potential value was observed between each electrode and its respective reference cell. All potentials were obtained by the "direct method" with current flowing. Errors resulting from these measurements were reduced to a minimum through the use of fairly high-conducting solutions and careful location of the reference electrode.

The current-potential curves never intersected since both electrodes were at the same open-circuit potential at the start. In this respect, the corrosion current, usually determined from the intersection of the potential curves where an initial difference in potential exists in conventional polarization curves, could not be observed. However, the curves that were obtained are believed to show the reaction at the anodes and cathodes under the given conditions of exposure. The work is of a more qualitative nature as compared with the more quantitative effects observed in the work described in a succeeding section of this report.

Solutions. Polarization curves for steel in solutions of various concentrations of potassium chromate in distilled water are shown in Figure 7. The two most dilute solutions have such high electrolytic resistance that their potential measurements include appreciable IR. Chromates exert little inhibition at the cathode but polarize the anodes very markedly even at concentrations as low as 0.001 M. Anodic polarization is usually attributed to the formation of oxide films. Figure 8 shows the large effect of time on the anode potential which moves in a cathodic direction with the flow of a very small current. The current-potential relationships are given in Figure 9 for steel in 4 percent NaCl solutions containing various amounts of potassium chromate. Under these conditions, chromates have little or no effect upon cathodic polarization; they show slight polarization at the anodes. The results obtained by adding alkali to 0.001 M chromate in 4 percent NaCl solutions are shown in Figure 10. Here again, no effect was observed at the cathode, but there was a slightly increased polarization at the anode resulting from alkalinity. These tests show that chromates are powerful anodic polarizers in the absence of chloride ions, but that they lose most of this effect if appreciable amounts of chloride ion are present. The chloride ion reduces anodic polarization by interfering with the formation of protective anodic films. Increasing the alkalinity of the saline solutions had but slight effect upon this anodic behavior of the steel.

Pigment Pastes. Thick pastes were made up with several pigments and 4 percent NaCl. These pastes were placed in a cylindrical glass tube with sintered glass filter at the bottom and immersed in a beaker containing 4 percent NaCl solution and a reference electrode. The

two steel electrodes were placed in this paste, current applied, and potentials determined. The results obtained are shown in Figure 11.

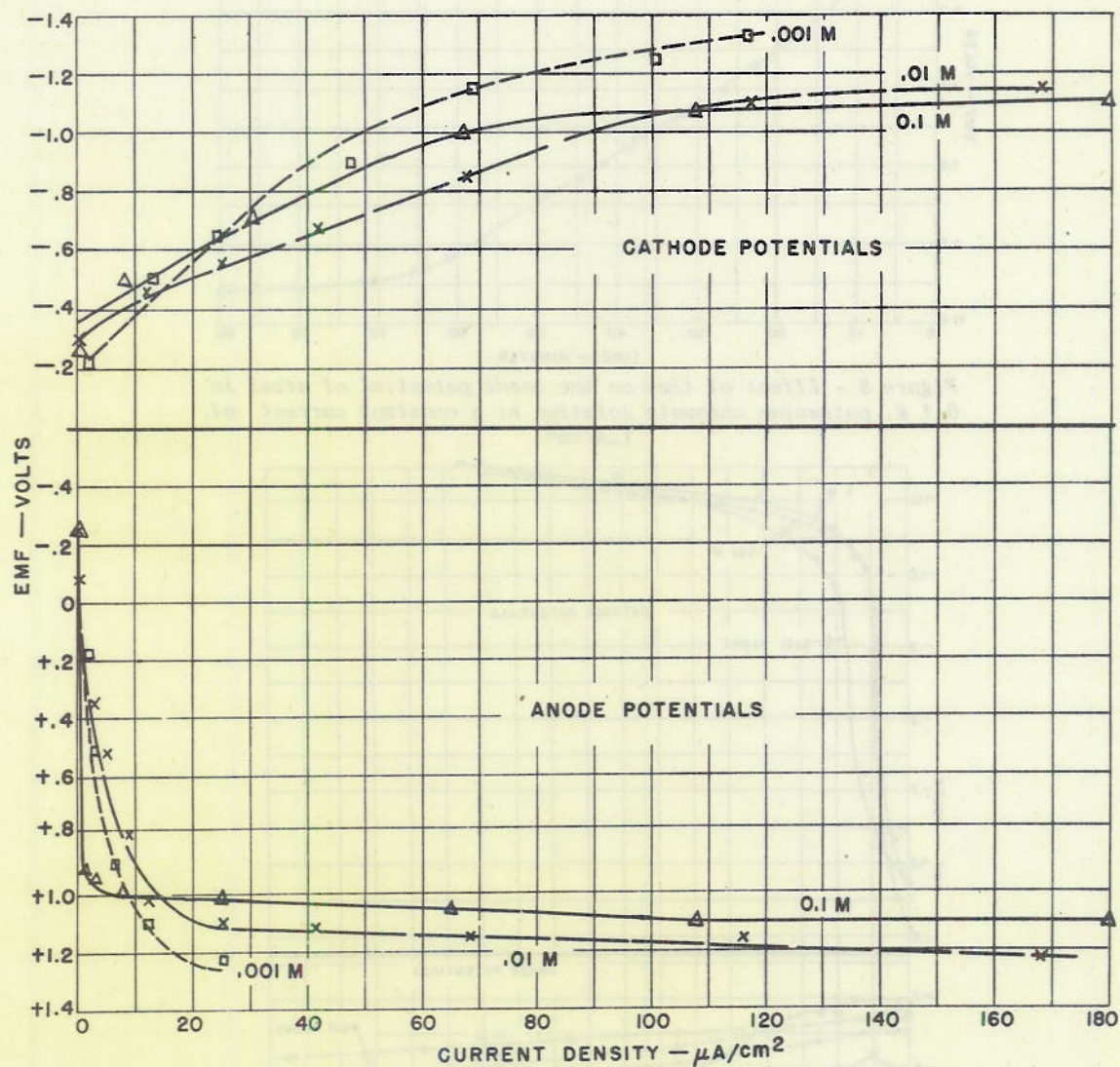


Figure 7 - Anodic and cathodic polarization of steel in potassium chromate solutions (air saturated)

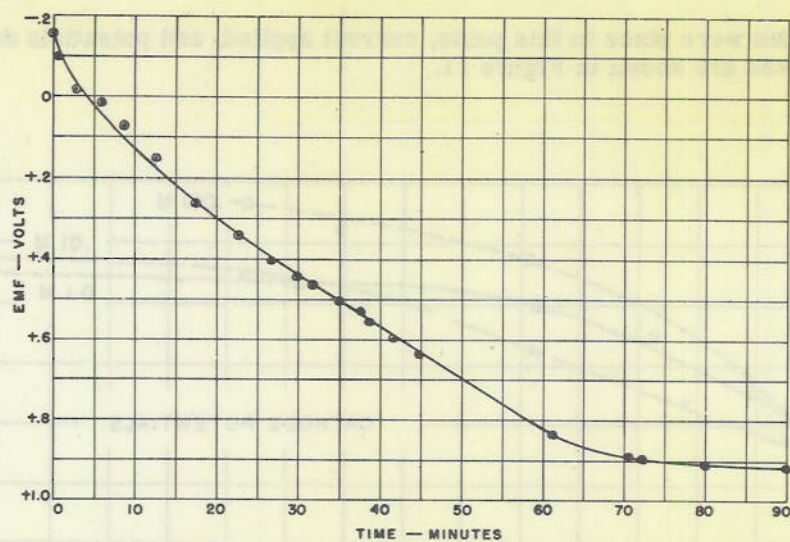


Figure 8 - Effect of time on the anode potential of steel in 0.1 M. potassium chromate solution at a constant current of $1 \mu A/cm^2$

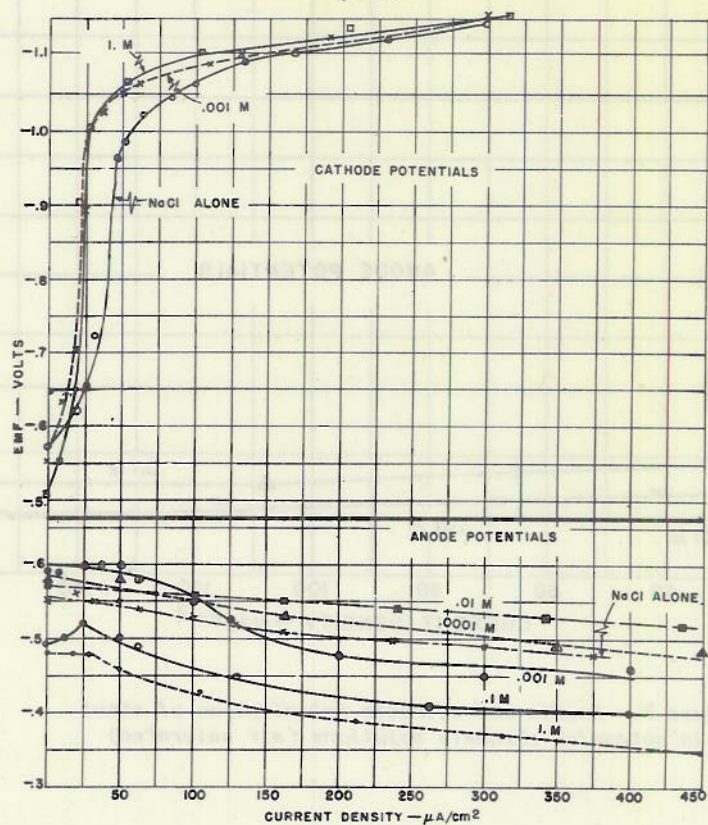


Figure 9 - Effect of chromates upon the polarization of steel in 4 percent NaCl solutions (air saturated). Cathodic potentials of other concentrations of chromates not shown fall within the curves that are given

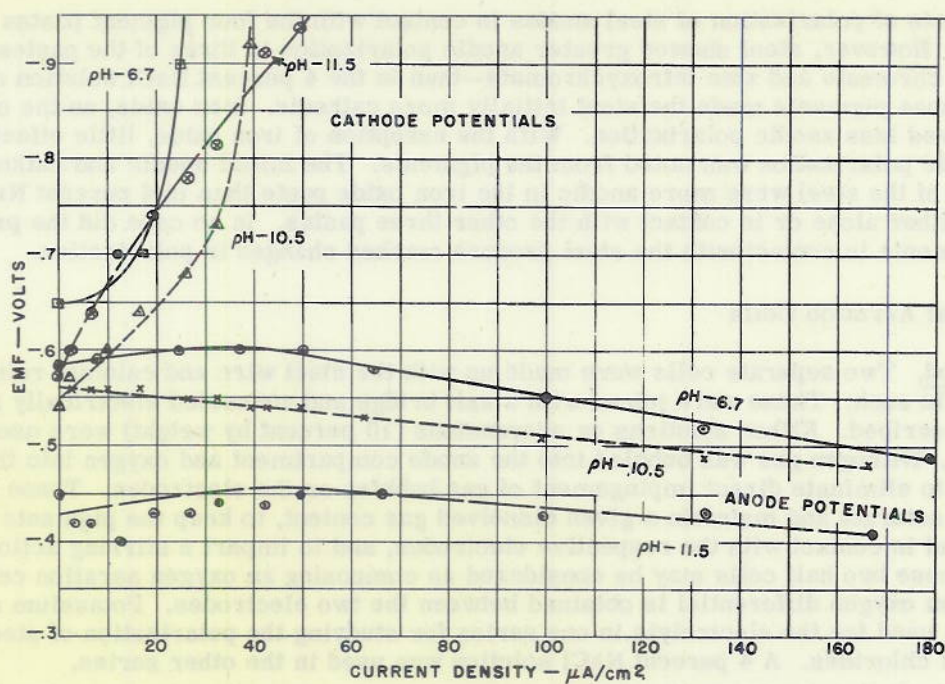


Figure 10 - Effect of alkali on the polarization of steel in 4 percent NaCl solutions containing 0.001 M. potassium chromate

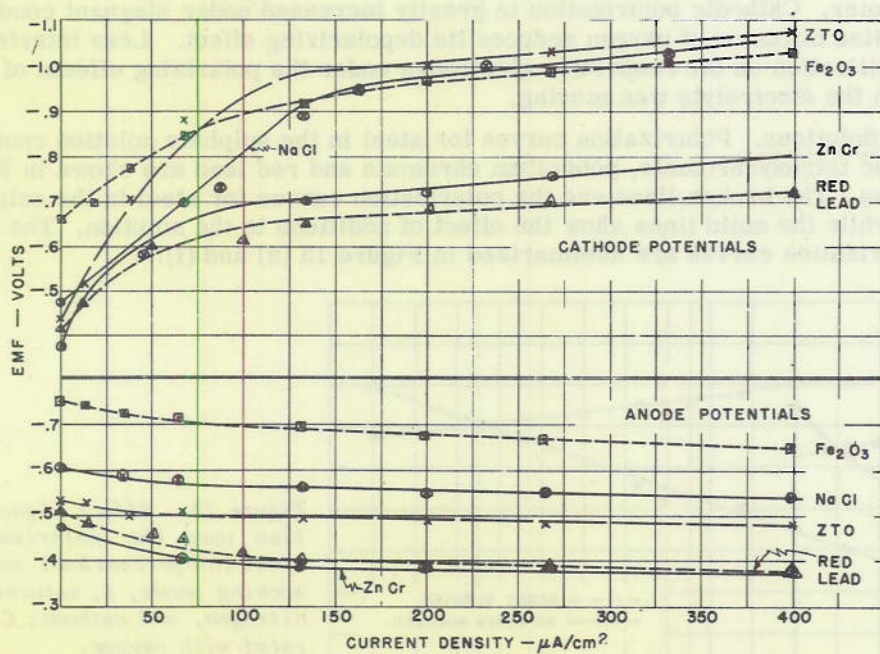


Figure 11 - Polarization of steel in pigment pastes in 4 percent NaCl solutions

The rate of polarization of steel anodes in contact with the four pigment pastes was the same. However, steel showed greater anodic polarization in three of the pastes—red lead, zinc chromate and zinc tetroxychromate—than in the 4 percent NaCl solution alone, because these pigments made the steel initially more cathodic. Iron oxide, on the other hand, showed less anodic polarization. With the exception of iron oxide, little effect upon the cathodic polarization was noted from the pigments. The initial anodic and cathodic potentials of the steel were more anodic in the iron oxide paste than in 4 percent NaCl solution either alone or in contact with the other three pastes. In no case did the presence of the pigments in contact with the steel produce marked changes in polarization.

Differential Aeration Cells

Method. Two separate cells were made up with the steel wire and calomel reference electrode in each. These were joined with a salt bridge and connected electrically as previously described. Either solutions or suspensions (10 percent by weight) were used in both cells. Nitrogen gas was bubbled into the anode compartment and oxygen into the cathode with care to eliminate direct impingement of gas bubbles on the electrodes. These gases served to saturate and maintain a given dissolved gas content, to keep the pigments in suspension and in contact with the respective electrodes, and to impart a stirring action to the liquid. These two half cells may be considered as composing an oxygen aeration cell where a maximum oxygen differential is obtained between the two electrodes. Potassium sulphate (.1 N) was used for the electrolyte in one series for studying the polarization of steel in the absence of chlorides. A 4 percent NaCl solution was used in the other series.

Figure 12 shows polarization curves for steel electrodes under nitrogen and oxygen saturation in both moving and quiescent salt solutions. The results obtained with moving solutions were found to be much more reproducible than those obtained when the solutions were stagnant since the diffusion of oxygen to the cathode is much more closely controlled under the former. Cathodic polarization is greatly increased under stagnant conditions since the limited diffusion of oxygen reduces its depolarizing effect. Less interference from local cell action on the respective electrodes under the polarizing effects of current resulted when the electrolyte was moving.

Sulphate Solutions. Polarization curves for steel in the sulphate solution containing zinc chromate, zinc tetroxychromate, potassium chromate and red lead are shown in Figure 13 (a) to (d) inclusive. The broken lines are the polarization curves for steel in the sulphate solution alone while the solid lines show the effect of additions to the solution. The anodic and cathodic polarization curves are summarized in Figure 13 (e) and (f).

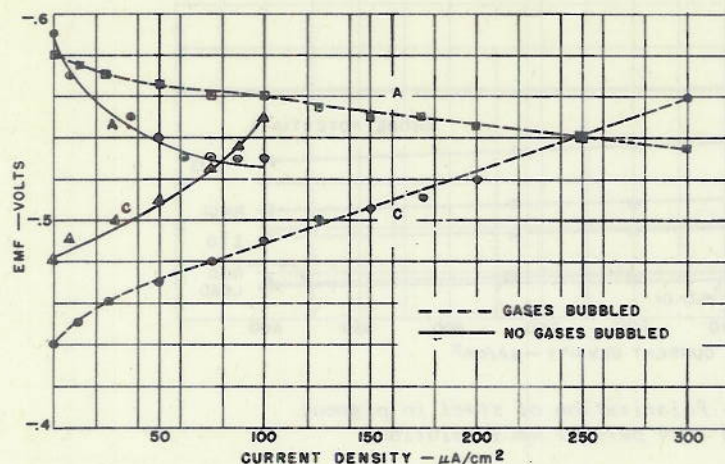
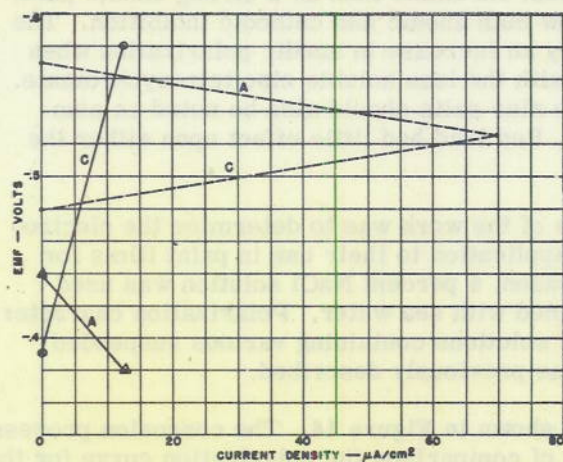
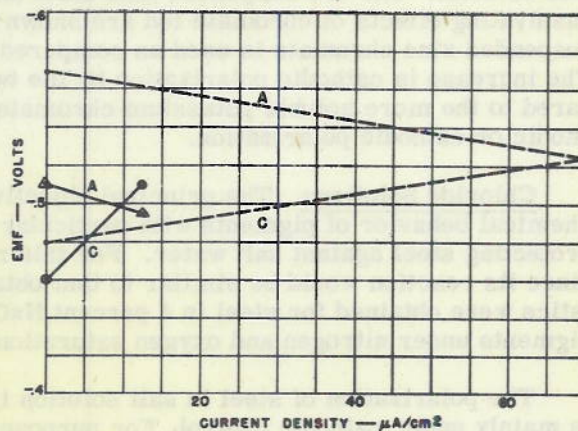


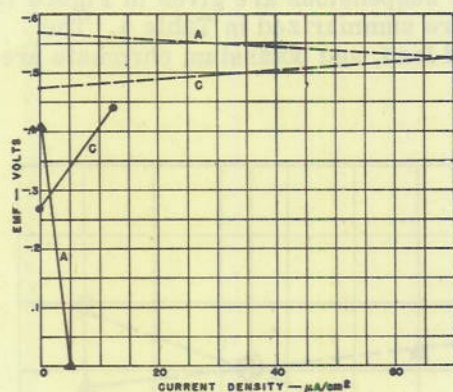
Figure 12 - Effect of gas agitation upon the polarization of steel in 4 percent NaCl solution, showing anode, A, saturated with nitrogen, and cathode, C, saturated with oxygen.



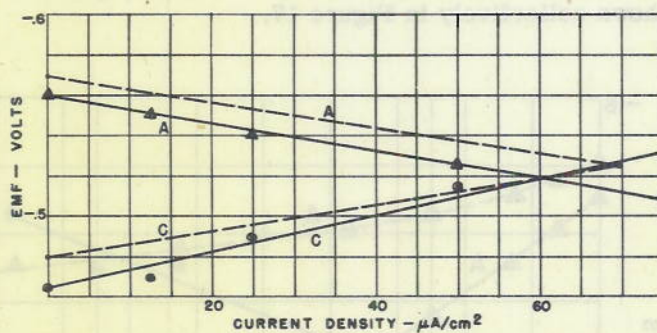
a. Zinc chromate



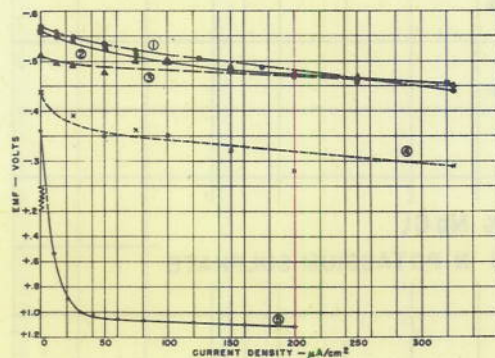
b. Zinc tetroxy chromate



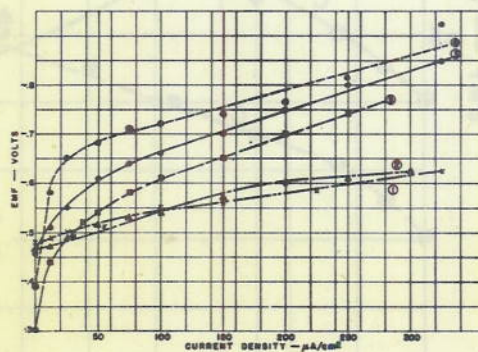
c. 0.1 N potassium chromate



d. Red lead



e. Comparison of anode polarization curves



f. Comparison of cathode polarization curves

-Figure 13 - Polarization of steel in 0.1 N potassium sulphate solutions containing pigment suspensions

a,b,c,d - Broken lines represent sulphate solution alone; solid lines represent solution with pigment additions; A represents anode polarization; C represents cathode polarization.
e,f - Numbered lines represent: 1, potassium sulphate solution alone; 2, with red lead; 3, with zinc tetroxychromate; 4, with zinc chromate; 5, with 0.1 N potassium chromate.

Under the conditions of these tests, potassium chromate acts as a strong anodic polarizer to steel. The two suspended zinc salts show both anodic and cathodic inhibition. The passivating effects of chromate ion are shown by an increase in anodic polarization when suspended zinc chromate is used as compared with the less soluble zinc tetroxochromate. The increase in cathodic polarization by the two zinc salts should also be noted as compared to the more soluble potassium chromate. Red lead had little effect upon either the anodic or cathodic polarization.

Chloride Solutions. The principal objective of the work was to determine the electrochemical behavior of pigments with particular application to their use in paint films for protecting steel against salt water. For this reason, 4 percent NaCl solution was used since its reaction would be similar to that obtained with sea water. Polarization characteristics were obtained for steel in 4 percent NaCl solutions containing various suspended pigments under nitrogen and oxygen saturation as previously described.

The polarization of steel in salt solution is shown in Figure 14. The corrosion process is mainly under cathodic control. For purposes of comparison the polarization curve for the sulphate solution is also given. Polarization is much greater in the presence of sulphates than with chlorides. The effects of the various pigment suspensions are given in Figure 15, and Figure 16. The essential data from these curves are summarized in Table 4. The cathodic and anodic curves for three zinc pigments, red lead, and potassium chromate are shown collectively in Figure 17.

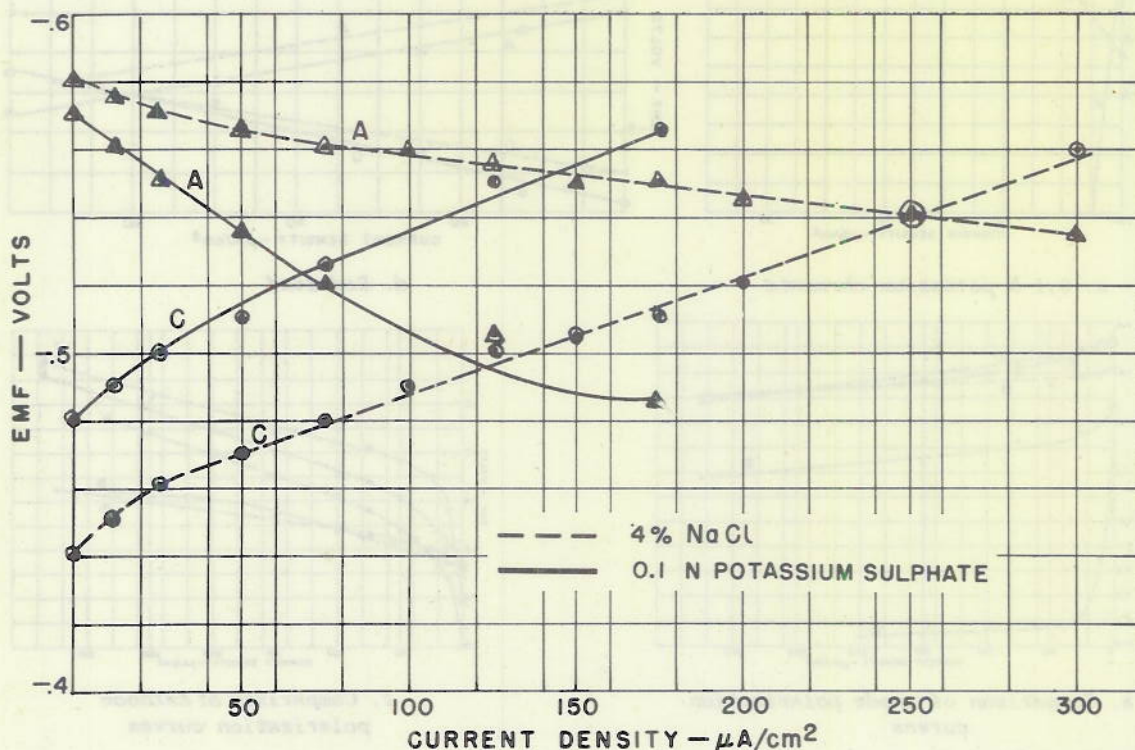
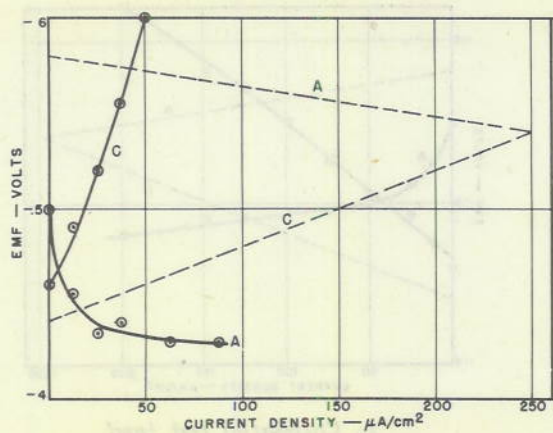
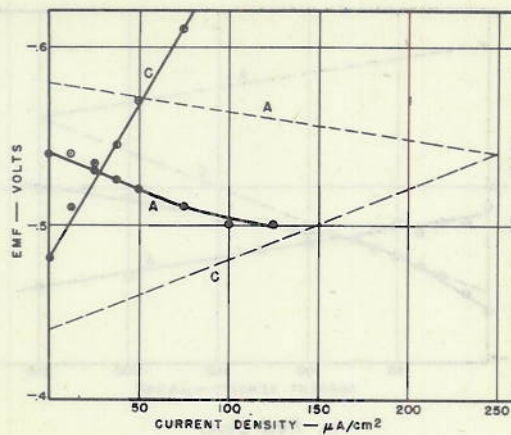


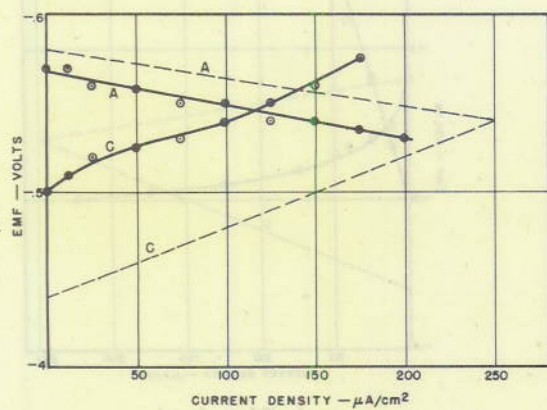
Figure 14 - Comparison of polarization of steel in chloride and sulphate solutions



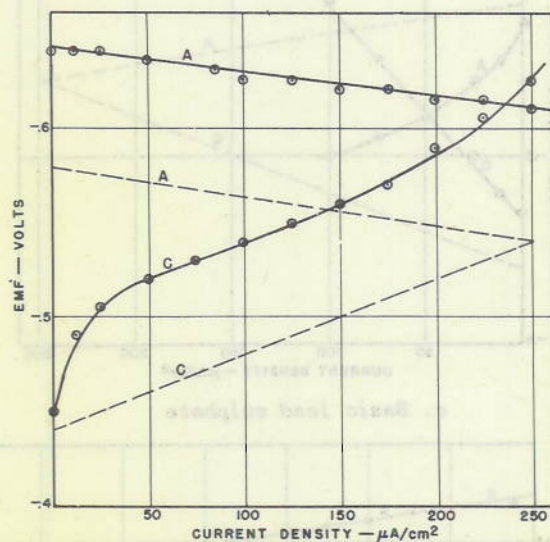
a. Zinc chromate



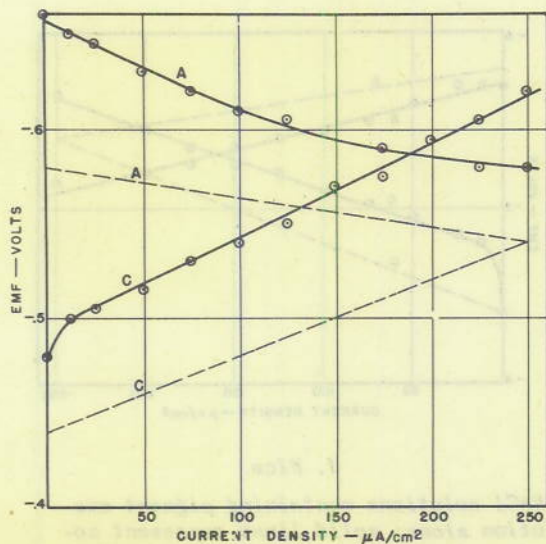
b. Zinc tetroxochromate



c. Zinc oxide

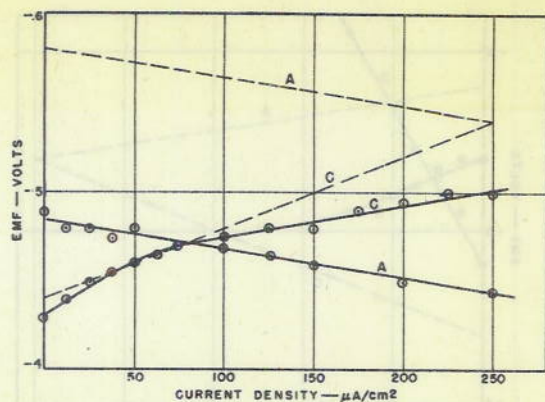


d. 75 percent iron oxide

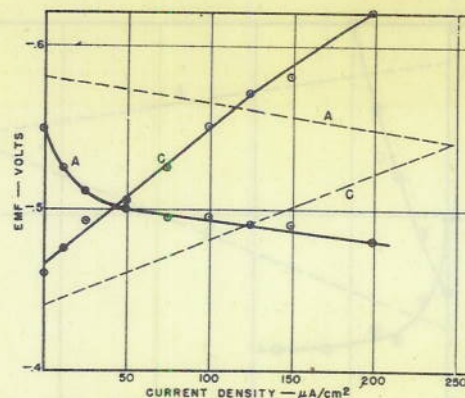


e. 98 percent iron oxide

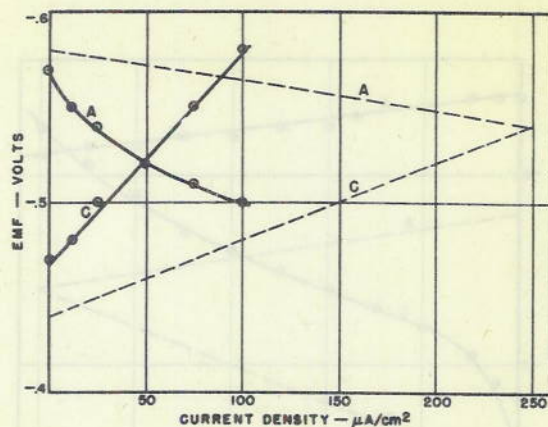
Figure 15 - Polarization of steel in 4 percent NaCl solutions containing pigment suspensions. Broken lines represent chloride solution alone; solid lines represent solution with pigment additions; A represents anode polarization; C represents cathode polarization.



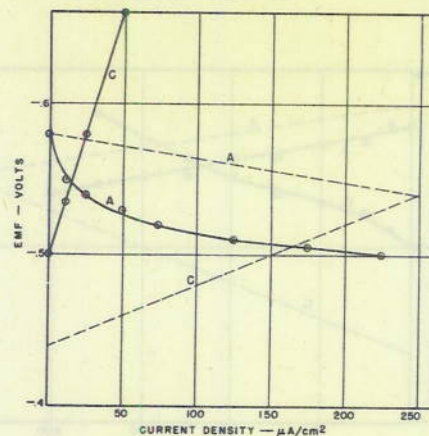
a. Red lead



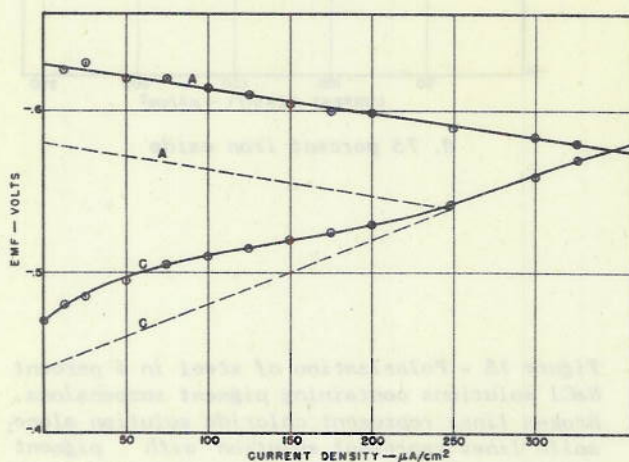
b. Chromated red lead



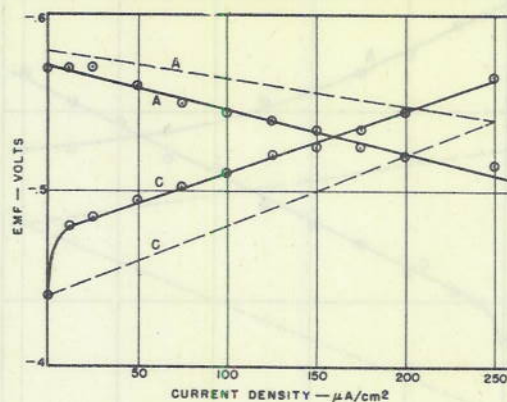
c. Basic lead sulphate



d. Blue lead

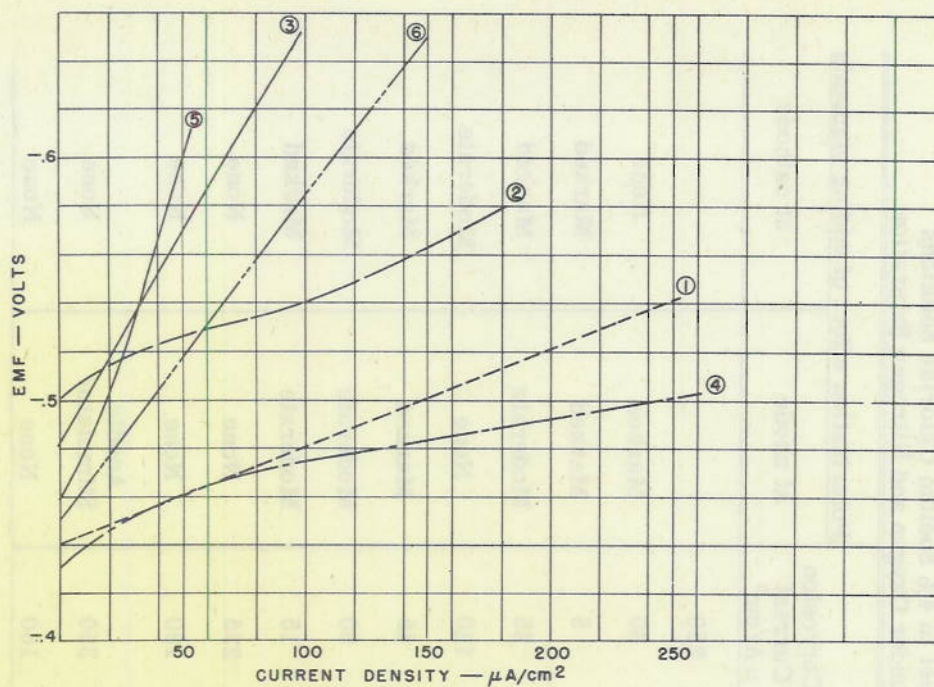


e. Ferrous ammonium phosphate

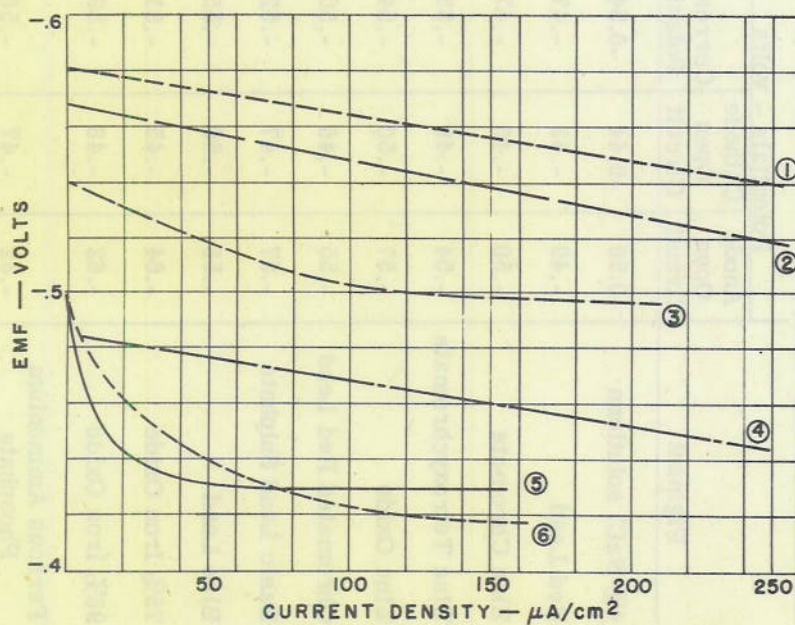


f. Mica

Figure 16 - Polarization of steel in 4 percent NaCl solutions containing pigment suspensions. Broken lines represent chloride solution alone; solid lines represent solution with pigment additions; A represents anode polarization; C represents cathode polarization.



a. Comparison of cathode polarization curves



b. Comparison of anode polarization curves

Figure 17 - Polarization of steel in 4 percent NaCl solutions. Numbered lines represent 1, NaCl alone; 2, zinc oxide; 3, zinc tetroxychromate; 4, red lead; 5, zinc chromate; 6, 1.0 M. potassium chromate.

TABLE 4
Summary of Results for the Polarization of Steel in 4% Sodium Chloride Solutions
with Various Pigment Suspensions as Obtained under Oxygen and Nitrogen Saturation

Pigment	Potentials - volts		Corrosion Current $\mu\text{A}/\text{cm}^2$	Polarization effect of adding pigments	
	Anode Open Circuit	Cathode Open Circuit		at anode	at cathode
4% NaCl solutions	-0.58	-0.44	250		
Red Lead	-.49	-.43	80	Marked	None
Zinc Chromate	-.50	-.46	5	Marked	Marked
Zinc Tetraoxochromate	-.54	-.48	25	Moderate	Marked
Zinc Oxide	-.57	-.50	120	None	Moderate
Chromated Red Lead	-.55	-.46	45	Marked	Marked
Basic Lead Sulphate	-.57	-.47	50	Moderate	Moderate
Blue Lead	-.58	-.50	15	Moderate	Marked
75% Iron Oxide	-.64	-.45	235	None	None
98% Iron Oxide	-.62	-.48	190	None	None
Ferrous Ammonium Phosphate	-.62	-.47	350	Anodic Stimulator	None
Mica	-.57	-.44	160	None	None

The results of these tests permit classification of the pigments as follows:

- (1) Those which show inhibiting properties through anodic polarization—red lead, zinc chromate, and chromated red lead;
- (2) Those which show inhibiting properties through cathodic polarization—zinc chromate, zinc tetroxychromate, chromated red lead, and blue lead (containing approximately 75 percent basic lead sulphate and other lead compounds);
- (3) Those showing no inhibition—75 and 98 percent iron oxide and mica pigment; and
- (4) Ferrous ammonium phosphate which acts as a corrosion accelerator by stimulating the anodic reaction through decreased polarization.

Discussion

Polarization studies offer a method for determining the electrochemical behavior of steel in contact with given electrolytes. The information obtained with a system using two electrodes at the same potential prior to application of the polarizing current is qualitative in nature. The conditions of immersion are the same for both electrodes and as such do not represent the true conditions found in most natural corrosion processes where environmental conditions largely determine the existence of areas with potential differences.

Utilization of a system employing electrodes (of the same material) under immersed conditions which simulate normal corrosion processes offers greater possibilities for obtaining quantitative information on the mechanism of corrosion and the electrochemical behavior of inhibitors or other addition agents. The application of the results of such studies to interpretation of normal corrosion processes is dependent largely upon the degree to which the conditions favoring local cell action in the latter are reproduced in the cells used in polarization studies.

The corrosion of steel in natural or sea water is believed to be controlled largely by differential aeration. Consequently, the use of concentration cells by oxygen and nitrogen saturation, as carried out in the work reported here, should give results representative of the normal corrosion of the steel in either natural or sea water. Saturation of the electrolyte with the two gases probably produces slightly accelerated conditions since the oxygen differential concentrations so produced are somewhat greater than those normally encountered with air-saturated solutions. However, the mechanism of polarization should be the same.

Most of the pigments covered in the polarization studies exhibited electrochemical behavior toward steel. Corrosion of the steel was inhibited in suspensions of the pigments by the following basic polarization effects (as compared with steel in the solutions without pigments):

- (1) An increase in anodic polarization,
- (2) an increase in cathodic polarization,
- (3) the open circuit potential of the anode becoming more noble, or
- (4) the open circuit potential of the cathode becoming less noble.

More than one of these reactions may occur simultaneously and thereby still further reduce corrosion through their cumulative effect.

Iron oxide and mica pigments showed no electrochemical inhibition. The open-circuit potentials of steel with the iron oxide were more anodic. This condition may be due to surface effects. Corrosion of the steel was increased with ferrous ammonium phosphate. Here the rate of both anodic and cathodic polarization remains unchanged but the open-circuit potential of the anode was considerably more anodic (Figure 16 (e)). Similar results would be obtained in cases where there was no change in the rate of polarization but where the open-circuit potential of the cathode was more cathodic. None of the pigments exhibited this characteristic.

Corrosion may be reduced by either of two effects: increasing anodic or cathodic polarization or increasing both, and secondly, decreasing the open-circuit potential difference between the two electrodes. The rate of polarization depends on the distribution of local cells on the electrodes. The nature and concentration of the electrolyte and the type of electrode reaction determine the open-circuit potential difference. Corrosion processes are often complicated and their mechanism usually involves the combination of several of the effects just discussed.

The polarization effects observed in this work are not great enough to classify any of the pigments as strong inhibitors of the corrosion of steel in either sulphate or chloride solutions. None of the pigments exhibited the effects of passivation observed with potassium chromate in solutions with chlorides absent. Less inhibition would probably be shown if these pigments were incorporated with vehicles into paint films since some of the factors favoring inhibition in these tests would be either absent or reduced considerably in effectiveness.

The polarization characteristics of steel in a solution of zinc chromate or zinc tetroxychromate in comparison with that of potassium chromate should be pointed out. In the absence of chlorides, the more soluble potassium chromate exhibits strong anodic polarization with practically no change in cathodic polarization (over that observed in the same solution with no chromates). The presence of chlorides reduces markedly this anodic polarization. In chloride-free solutions, zinc chromate shows some increase in anodic polarization with an appreciable increase in cathodic polarization. The less soluble tetroxy variety shows these effects to a lesser degree. Under these conditions the effectiveness of the chromate ion as a corrosion inhibitor has been reduced through decreased solubility. In chloride solutions both forms of the zinc chromate show increased cathodic polarization over that observed with potassium chromate. Thus, the zinc chromates exhibit electrochemical inhibition through polarization of both anodic and cathodic areas. The zinc ion probably acts as a cathodic inhibitor through the formation of a film of zinc hydroxide which interferes with the transfer of oxygen to the cathode (37).

SUMMARY AND CONCLUSIONS

1. A complete understanding of the mechanism by which organic coatings protect steel against corrosion is necessary if improvements in their durability are to be made. The characteristics of pigments are an important consideration in this mechanism. The role of certain pigments in the electrochemical inhibition of the corrosion of steel has been the subject of much speculation. The work herein reported only covered studies of selected pigments in the presence of electrolytes, and thus is only applicable where similar conditions might prevail. Some of the pigments are capable of exhibiting electrochemical behavior under specific conditions.

2. The electrochemical studies involved the use of time-potential and polarization tests with steel in both chloride-free and saline solutions containing pigments as pastes and suspensions. Known soluble inhibitors were also included for comparison.

3. Special techniques were developed for preparing an oxide film-free surface on steel electrodes and then immersing them in either nitrogen- or oxygen-saturated solutions until steady potentials were reached. The introduction of dissolved oxygen made the potential of steel more cathodic in most of the solutions. Little or no effect of dissolved oxygen was observed with chromate and strong oxidizing solutions. The cathodic effect of chromate ion was reduced markedly by the presence of chloride ion. No appreciable differences were observed in the steady electrode potential of steel in most of the pigment suspensions with the two types of gas saturation. In addition to the potential value, other important electrochemical characteristics must be known to determine fully the corrosion reaction.

4. The information obtained in polarization studies using two electrodes at the same potential prior to the application of current was qualitative in nature. The presence of several of the pigments in the form of pastes with NaCl solution did not produce apparent changes in the polarization of the steel.

5. Utilization of a cell employing steel electrodes under immersed conditions of differential aeration closely simulated normal corrosion processes and gave quantitative information on the electrochemical behavior of suspended pigments. The potential difference of such a cell is at a maximum and probably greater than would occur normally in local corrosion cells with air-saturated solutions.

6. Most of the pigments covered in the polarization studies exhibited electrochemical inhibition to the corrosion of steel. This was found to be due to an increase in either anodic or cathodic polarization or in both, and by a decrease in the open-circuit potential difference between the two electrodes. This was true for zinc chromate, zinc tetroxochromate, red lead, blue lead, basic lead sulphate, and chromated red lead. Iron oxide and mica pigments showed no chemical inhibition. Ferrous ammonium phosphate increased the corrosion of steel.

Incorporation of the inhibitive pigments into paint films could result in decreased corrosion of steel surfaces if the conditions met with in these tests were found to exist—namely, maximum solubility and occurrence of differential aeration cells. In salt solutions, none of the pigments exhibited the marked polarization found with the soluble chromates in solutions with chlorides absent. Undoubtedly the electrochemical effects of inhibitive pigments will be decreased when they are incorporated into paint film because of the impermeability of moisture to the metal. Physical characteristics of the film may then exert control over the protective effects.

7. In the absence of chlorides, the presence of the more soluble chromates results in a marked increase in anodic polarization with little change in cathodic polarization. The two zinc chromates showed similar anodic trends but to a less marked degree because of their limited solubility. However, they exhibit an appreciable increase in cathodic polarization due to the formation of zinc hydroxide which interferes with the transfer of oxygen to the cathode. Solubility thus limits the full utilization of corrosion-inhibiting properties of the chromate ion. Greater solubility might result in decreased durability of the film.

8. Red lead showed no increase in cathodic polarization with a slight increase in anodic polarization. If conditions similar to those existing in these tests prevailed in a paint film, red lead would not be expected to be as effective an inhibitor as zinc chromate. The satisfactory performance of red-lead paint may be due to predominating physical characteristics

of the film, to reactions with fatty oils to produce anodic absorption inhibitors, or to both. The importance of such additional reactions was not investigated in this work.

Chromated red lead showed a mechanism of inhibition involving a combination of the factors just described for both red lead and zinc chromate.

9. Basic lead sulphate and blue lead exhibited inhibition through increased anodic and cathodic polarization, the latter being the most effective inhibitor. Zinc oxide showed increased cathodic polarization, possibly due to formation of zinc hydroxide.

10. Iron oxide and mica pigment showed no electrochemical inhibition though the open-circuit potentials with the former were more anodic. Corrosion was increased with ferrous ammonium phosphate by an increase in the open-circuit potential difference of the two electrodes.

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