

# PHOSPHATE COATINGS ON STEEL PART I

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## ABSTRACT

This first report in connection with a study of phosphate coatings for steel to inhibit corrosion comprises two items:

1. Prior to the considerable experimental work to be expected in such a study, an examination was made of technical literature for information that might aid in planning necessary work or in furnishing data directly usable. The literature reveals little fundamental determination of the chemistry involved in phosphate coatings and processes, but abounds in purely empirical data which show very limited agreement in conclusions. This report includes a discussion of pertinent literature, particularly references that include expressions of opinion by authorities in the field.

2. As an initial phase of the experimental investigation of the problem, the solution rate of steel in phosphoric acid was measured in a series of experiments to determine how this rate is affected by differences in the controlling factors - reaction time, acid concentration, and temperature. A rotating cylindrical specimen was used with acid concentrations between 0.01 and 3 N, and temperatures between 32° and 93° C. The solution rate remained substantially constant throughout the experimental period (thirty minutes) and was directly proportional to the logarithm of the acid concentration. The logarithm of the solution rate was directly proportional to the logarithm of the absolute temperature. These functions were evaluated for the experimental conditions of this study.

## PROBLEM STATUS

This is an interim report; work on this problem is continuing.

## AUTHORIZATION

NRL Problem No. C05-11R

## PHOSPHATE COATINGS ON STEEL Part I

### INTRODUCTION

The useful life of painted steel depends to a large extent on the treatment of the metal surface prior to painting. It is generally recognized that the phosphating of steel before painting increases the corrosion resistance of the finished product by providing a good bond between the metal and paint, by inhibiting the spread of rust around chips and scratches in the paint film, and by minimizing the blistering known as alkaline peeling.

Satisfactory phosphating processes are available for many applications, but extraordinary problems are encountered when large structures such as the steel hulls of ships are to be prepared for painting. Relatively little attention has been given to such specialized requirements and it is the purpose of this study to obtain sufficient basic information that may serve ultimately to perfect, standardize, and extend the phosphating processes suitable for use by the U. S. Navy, which is faced with the construction and maintenance of ships and other large structures subjected to the particularly corrosive sea water environment.

Industrial phosphating processes consist of treatment of steel with hot solutions of zinc or manganese phosphates in phosphoric acid containing accelerators. This treatment produces an adherent, uniform coating of crystalline phosphates on the metal surface. The deposition of satisfactory coatings from these solutions demands rigid standards for the preparation of the metal surface prior to treatment, and a careful control of the phosphating solutions.

Such processes are limited by high cost and necessary specialized techniques in their applicability to naval constructions such as the steel hulls of ships which must be treated in drydock. Thus the relatively ineffective phosphoric acid and iron phosphate solutions, virtually eliminated from industry in recent years, are still in use for special applications such as employed by the U. S. Navy for treating hull bottoms prior to painting. As a result processes based on these solutions have been developed to only a limited extent, and no recent investigations have been conducted to adapt them to such special uses.

It is therefore easy to understand why the phosphating methods in actual use by the Navy vary from yard to yard and from boss to boss. An example of the treatment of hulls for painting in drydock is the Mare Island procedure (31)\* which calls for sandblasting of the hull with hard silica sand that has been wet with a water solution of trisodium phosphate and potassium dichromate. The sand and dust are then brushed from the hull with a soft foxtail brush, and the hull is immediately painted. If the painting is not done before light

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\* The numbers in parentheses refer to specific references on page 31.

rusting occurs, the hull is washed down with a ten-percent phosphoric acid solution. By this treatment is formed a nonuniform, powdery deposit that has little resemblance to the phosphate coating produced by industrial processes.

The present study was undertaken to determine the chemical and physical factors that govern the rate and mechanism of formation of the coatings, the identification of the materials present in the coatings, and the mechanism of the protective action of the coating. This initial report includes a study of pertinent technical literature and experimental observations on the solution rate of steel in phosphoric acid as affected by differences in reaction time, acid concentration, and temperature.

## REVIEW OF LITERATURE

The inhibiting of rust may be accomplished by converting the surface of ferrous metals into insoluble phosphate salts which render the metal surface less active chemically, followed by coating with oil, paint, varnish, or lacquer. The combination of phosphate and organic coatings produces an exceptionally rust-resistant finish for many types of service. In addition to the corrosion resistance imparted by phosphate coatings, it has been established that these coatings also increase the wear resistance of iron and steel parts and greatly facilitate the cold drawing of these metals.

Earliest phosphating methods employed dilute phosphoric acid or solutions of iron in phosphoric acid, (21, 23) but modern industrial practice involves the use of phosphoric acid solutions of manganese or zinc salts, usually containing accelerators for decreasing treatment time. All phosphating baths contain iron, either from the chemicals used in making up the solutions or dissolved from the metal during treatment. The industrial phosphating processes are known by several familiar trade names such as Bonderizing, Grandodizing, Parkerizing, and Atramentizing. The first two use zinc ion, the other two use manganese ion, in addition to the phosphoric acid and the chemically diverse materials that act as accelerators.

The remarkable corrosion resistance of steel treated with such industrial phosphating methods prior to painting is evident in Figure 1 - developed by Apesekloof and reported by Macchia (20) - which shows the corrosion resistance of phosphated steel, represented by the solid black lines, in comparison to the corrosion resistance offered by sherardizing and by zinc or nickel plating on steel.

A search of the technical literature reveals little concerning the fundamental chemistry of phosphate coating, even though considerable amounts of empirical data are available. Evaluation and reconciliation of many anomalous reports will remain impossible until the fundamental processes of phosphating are clarified. Among the factors which affect the coating formation, its crystal structure and its corrosion resistance may be listed: composition of the metal; pretreatment of the metal (pickling, degreasing, etc.); composition of phosphating solution; techniques of phosphating including operating temperatures, agitation of the solutions, and treatment time.

The following brief discussion of the literature is largely devoted to pertinent references that contain scientific opinions of authorities in the field. Comparison of empirical data from independent sources is virtually impossible because of the variations in testing methods, personal evaluation of corrosion resistance, and many other factors. The single point of agreement among the many investigators is that uniform fine-grained coatings possess greater corrosion resistance than nonuniform, coarse-grained deposits.

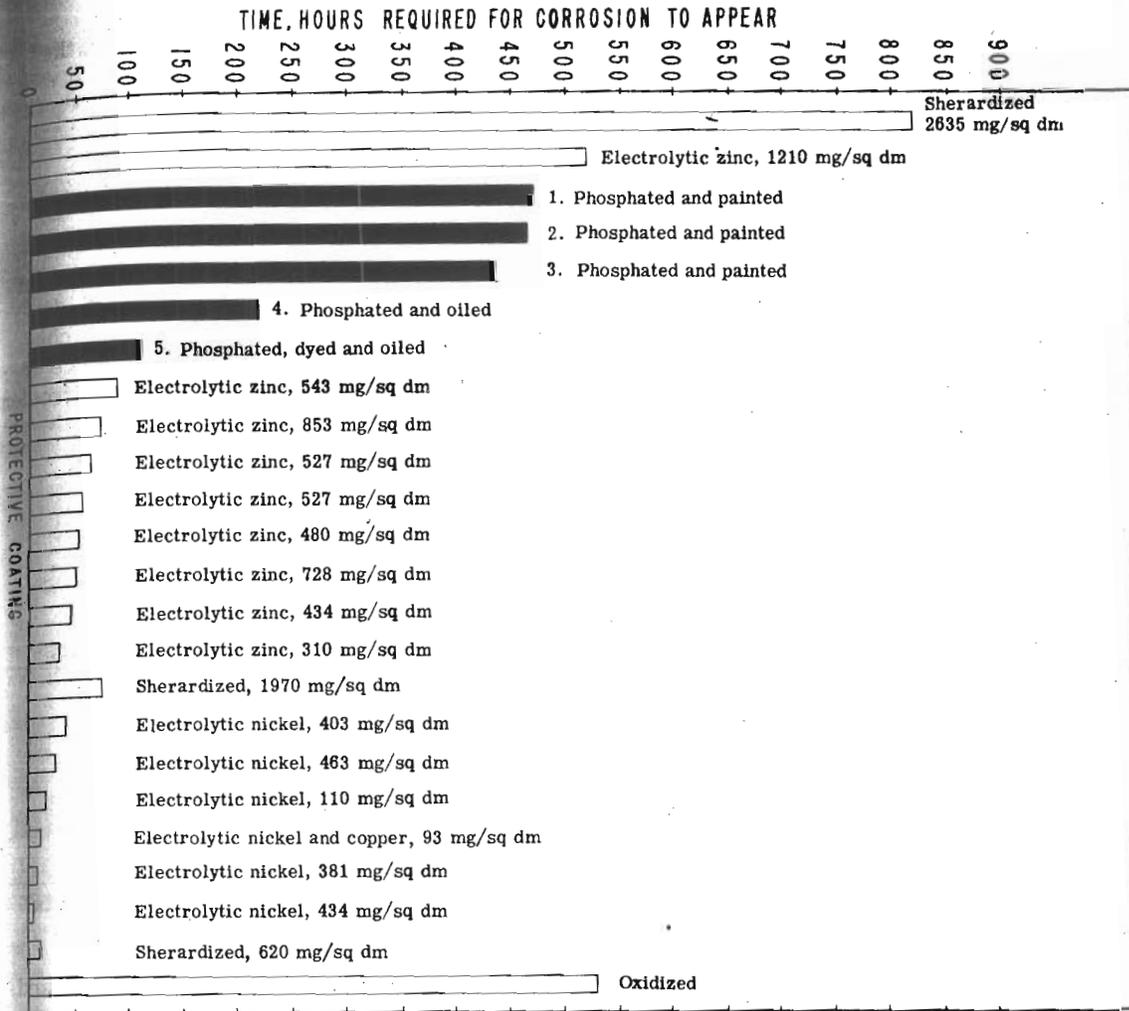


Fig. 1 - Corrosion resistance of coated steel in 20% salt spray (from Macchia (20))

Evaluation of Phosphating Solutions Consisting of Phosphoric Acid Alone

Bigeon (3), Pollard and Porter (34), Macchia (22) and others have reported that although the coating deposited by treating steel with dilute phosphoric acid solutions offers little corrosion resistance and small adhesion for paints, such treatment is better than none prior to painting. The experimental work reported on coatings deposited from straight phosphoric acid baths is very limited and no recent fundamental investigations have been found. Phosphating did not come into wide use until about 1930 after the accelerated zinc and manganese baths were patented, with the result that most of the reported experimental work has been done with these baths.

Mechanism of Phosphate Coating Formation

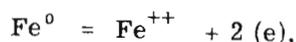
Justh (16), Schuster (35, 40) and others consider that the deposition of phosphate coatings is caused by attack of the metal surface by phosphoric acid, liberating hydrogen gas and thereby raising the pH of the bath solution adjacent to the metal surface. The

solubilities of the metal phosphates are then exceeded, and a deposit is formed on the metal surface, according to the reaction

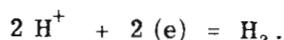


in which Me = metal ion, and is usually iron, zinc, or manganese.

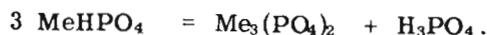
Machu (27) demonstrated the electrochemical nature of the phosphating processes by means of Müller's (33) shielded electrode technique which showed the change in potential of an iron surface throughout the phosphating process. By his extensive studies Machu has modified the original macroscopic concept of phosphate-coating formation. He considers that two electrode processes take place during phosphating under the influence of the local anodes and cathodes present on the metal surface. At the anodic areas corrosion takes place according to the equation



and at the cathodic areas hydrogen is liberated according to the equation

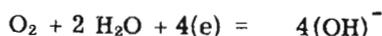
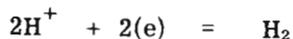


The depletion of hydrogen ion in these areas then causes deposition of the metal phosphates by hydrolysis of the soluble metal salts:



The secondary and tertiary metal phosphates are insoluble, and crystallize on the metal surface at the cathodic areas as the coating.

Müller and Hasner (32) support Machu's concept of phosphate coating formation, and consider that the cathodic reaction is best expressed by the following reactions which supplement those of Machu by introduction of the second reaction, which these authors believe must be included for a complete concept of the mechanism of coating formation:



Macchia (24), and Roesner and Schuster (35) have shown that the absolute as well as the relative concentrations of metal, free acid, and total acid must be carefully controlled for the deposition of satisfactory coatings. If the solution contains an excess of free acid, the deposit will be delayed as well as unsatisfactory because a considerable amount of metal must pass into solution before the pH of the solution adjacent to the metal is raised to the point where deposition can occur. The total acid concentration represents the total phosphate content of the solutions. It is obvious that sufficient material must be present

in the solution to permit deposition to take place. On the other hand excessive concentration of metal salts will lead to excessive deposition of the crystalline phosphates as sludge throughout the bath because of the change in pH of the over-all solution caused by the metal going into solution.

#### Effect of the Composition of Steel on Phosphating

Schuster (41) points out that the formation of phosphate coatings depends upon the attack of the metal surface by phosphoric acid and that, for this reason, acid-resistant steels do not present satisfactory surfaces for phosphating.

Gutman (13) found that while carbon steels were easily phosphated, chromium, vanadium, tungsten, and molybdenum steels were more difficult; and copper-bearing steels were virtually impossible to phosphate.

Machu (29) showed that steels of the compositions, listed in Table 1, were readily phosphated.

TABLE 1  
Compositions of Steels Studied (from Machu (29))

C	Si	Mn	Cu	Cr	Mo	Ni	S	P
(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
.06	.01	.49	.06				.036	.054
.08	.01	.50	.27				.048	.037
.13	.46	.70	.50	.17			.018	.013
.14	.35	1.10	.40	.25	.10			
.30	.25	1.50						
.60	1.90	.60						
.12	.30	.40				3.00		
.25	.25	.60		1.00	.20			

If these opinions appear somewhat in conflict, the contradiction might be resolved by assuming that Gutman referred to steels of higher copper content than those studied by Machu. It may be concluded that the steel which is readily phosphated must have a certain acid solubility.

#### Effect of Pretreatment of Steel on Phosphating

Also coupled with the influence of the composition of the metal is the effect of pretreatment of the metal surface before phosphating. Surfaces must be free of foreign material such as mill scale, rust, soaps, and heavy grease before phosphating. Grease may be removed by treatment with organic solvents or alkali. Mill scale and rust are usually removed by pickling or abrasion.

By means of surface potential measurements, Machu (29) compared the phosphate coatings obtained on steels that were abraded and pickled in hydrochloric acid respectively and found that the pickled surfaces developed more porous phosphate films of lower corrosion resistance than did the abraded surfaces. The same results were obtained when he used electrolytic iron for his test surface. After phosphating, the pickled steels had an area remaining uncoated more than twice as great as that remaining on the abraded samples. For these reasons Machu concluded that pretreatment was of more importance in developing satisfactory phosphate coatings than the composition of the steel; and that the deleterious effect of pickling was not due to enrichment of the surface in acid resistant components of the metal, since pure electrolytic iron would not contain such materials.

Schuster (41) found that the roughness of the surface is of great importance in phosphate-coating formation. When treated in slow phosphating baths, polished surfaces gave rise to nonuniform layers of large crystals, while surfaces sandblasted or abraded with emery, produced uniform fine-grained coatings owing to the numerous points where crystallization might take place. This was demonstrated by sandblasting deep-drawn steel plates on only one-half of their surface and then phosphating in nitrated zinc baths. Fine-grained coatings were developed on the sandblasted portion, and coarse-grained coatings on the untreated portion. The hardness of the surface is also of importance since Schuster has shown that fine-grained coatings develop on case-hardened steels and coarse deposits on nonhardened steels.

Nonmetallic contaminants on the metal surface - such as scale, rust, grease, oils, or soaps - will also interfere with phosphate deposition. Mechanical cleaning processes admittedly produce surfaces that are readily subject to phosphating, but these treatments are inconvenient or uneconomical for industrial use. In industry, chemical treatment for the removal of the oxide layer with mineral acid is usually preferred.

In many instances coarser phosphate coatings develop on pickled than on unpickled steel surfaces, but by using nitrated zinc baths Schuster was able to obtain satisfactory coatings on pickled steel. He concluded that a generalization could not be made concerning the influence of pickling on phosphating.

Pickle inhibitors are additives which act to hinder the solution of metal in acid, but the deposition of phosphate coatings depends upon the attack of the metal surface by the acid. Thus if a pickle inhibitor is present on the metal surface in large amounts when the metal is placed in the phosphating bath, it will inhibit the action of the phosphoric acid; if, on the other hand, the phosphating bath contains an oxidizing agent as accelerator, the pickle inhibitor will be removed from the surface by oxidation and its effect minimized.

Schuster also suggests that the film developed in pickling may be evenly distributed over the surface in those cases where pickled steel yields fine-grained coatings, and that the composition of the pickle residue depends upon the composition of the steel. Conflicting results were obtained from vapor and alkali degreasing methods; beneficial effects were noted at one time and detrimental effects at others.

Schuster believes that a thin oil film (vaseline, mineral oil) inhibits the growth of the phosphate coating in an outwardly direction but promotes the spread of the coating across the surface, producing fine-grained phosphate deposits.

Copper salts act on the iron to form the cell Fe/Cu, which hastens the solution of the iron in the acid and in turn increases the rate of coating formation, thereby producing fine-grained deposits. Similar effects are noted when the surface is pretreated with nitrite solutions, because the nitrous acid formed on the surface when the steel is placed in the

phating bath rapidly removes the hydrogen and increases the rate of solution of the steel in the acid.

Schuster used two types of hot-rolled steel sheet in these experiments: Siemens-Stahlgüte (designated by SM), and Thomas Stahlgüte (designated by T). Samples were selected from the plates so that differences due to manufacture, surface roughness, etc. were at a minimum.

Schuster demonstrated the effect of annealing of these steels on subsequent phosphating as shown in Table 2.

TABLE 2  
Effect of Annealing Steel Prior to Phosphating from Schuster (41)

Steel	Annealing Treatment	Phosphate Coating
SM normalized, pickled, polished	Twice annealed, cooled in inert gas	Fine-grained, uniform thickness
SM normalized, pickled, polished	Twice annealed, cooled without inert gas	Nonuniform, larger crystals, thin coating
SM normalized, pickled, polished	Not annealed	Nonuniform, larger crystals, thin coating
T, normalized, pickled, polished	Twice annealed, cooled in inert gas	Fine-grained, uniform thickness
T, normalized, pickled, polished	Twice annealed, cooled without inert gas	Nonuniform, larger crystals, thin coating
T, normalized, pickled, polished	Not annealed	Nonuniform, larger crystals, thin coating

When these plates were examined metallographically after phosphating, the photomicrographs showed that the surface structure of the steel had not been altered by the annealing or phosphating treatments.

The differences in the phosphate coatings - in spite of identical chemical composition of the metal specimens, their apparent surface roughnesses, and their structures - show that after pickling there is a film left on the metal surface with chemical and physical properties dependent upon the annealing treatment. This film thereby greatly influences either favorably or otherwise the formation of a phosphate coating. These experiments also show that the heat treatment of the steel may or may not favorably influence the coating formation.

Schuster claims that the contamination on the metal surface, the surface potential, and the troublesome "surface films" are less important when accelerated baths are used for phosphating than when slow processes are employed. Schuster also claims that some steels which are completely passive in a slow phosphating bath are covered with films which are not attacked by phosphoric acid. He believes that these films are probably destroyed by the oxidizing agents present in the accelerated processes where the phosphating readily takes place. It is possible that these films may be a particular modification of iron, but they are more likely to consist of iron oxide of a low acid solubility.

Schuster also points out that the presence of a surface film influences the coatings obtained in galvanizing, plating, and in fact, in the coating of any material.

Dyrmont and Goldenberg (11) considered the influence of surface pretreatment on phosphating. These investigators used steel of the following compositions

C	0.19 - 0.25%
Mn	.40 - .50
Cu	.10 - .15
Si	.20 - .30
S	.02
P	.02,

and employed Parker Powder for phosphating (Mn-Fe bath). All phosphating was carried out under identical conditions, only the pretreatment of the steel being varied. The samples were Parkerized one hour at 100° C, rinsed in hot distilled water, dried at 70° C, and cooled in a desiccator. Prior to phosphating, all samples were degreased in a three-per-cent soda solution, and given the pretreatments shown in Table 3.

TABLE 3  
Pretreatments for Steel Used by Dyrmont and Goldenberg (11)

Experiment Number	Pretreatment
1	Abraded with emery, degreased in soda solution, rinsed in hot water, pickled 5 minutes in 5 percent H <sub>2</sub> SO <sub>4</sub> at 70° C, rinsed.
2	Abraded with emery, degreased in soda solution, rinsed in hot water, pickled 5 minutes in 15 percent H <sub>2</sub> SO <sub>4</sub> at 70° C, rinsed.
3	Abraded with emery, degreased in soda solution, rinsed in hot water, pickled 5 minutes in 5 percent H <sub>3</sub> PO <sub>4</sub> at 70° C, rinsed.
4	Abraded with emery, degreased in soda solution, rinsed in hot water, pickled 5 minutes in 15 percent H <sub>3</sub> PO <sub>4</sub> at 70° C, rinsed.
5	Abraded with emery, degreased in soda solution, rinsed.
6	Twice abraded with emery, degreased in soda solution, rinsed.

The corrosion test methods employed for evaluating these pretreatments are listed in Table 4, and the results are summarized in Table 5.

TABLE 4  
Corrosion Test Methods Used by Dyrmont and Goldenberg (11)

Method	Description
A	Water spray at room temperature in wooden vat. Distilled water atomized at 2 to 3 atmospheres.
B	Same as above with spray containing 20 percent salt.
C	Immersion in water containing 3 percent salt.

Experiment Number *	Corrosion Tests			Nature of the Phosphate Coating
	Time (hrs.)	Appearance of Visible Corrosion		
	A†	B†	C†	
1	17-20	17	17	Nonuniform mixture of large and small crystals -
2	40-50	40	46	Fine crystals with inclusions of large crystals.
3	2	2-5	2-4	Irregular mixture of large and small crystals.
4	4	6	10	Fine crystals with inclusions of large crystals.
5	60	25	168	Uniform, very fine crystals.
6	72	65	310-334	Very fine crystals.

From Table 3.

From Table 4.

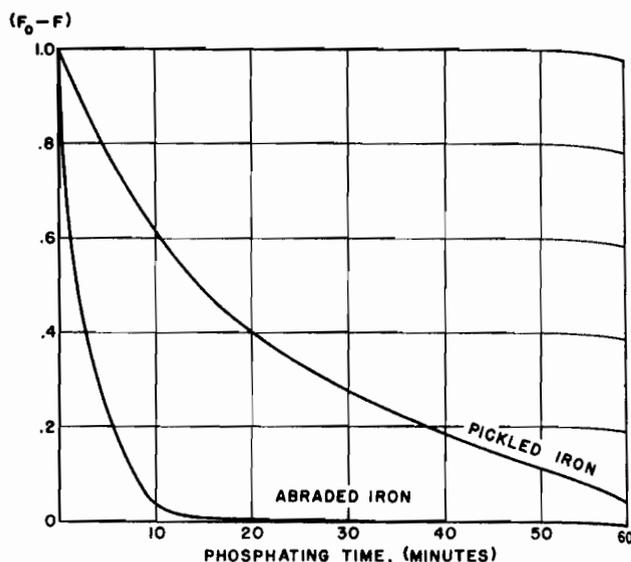
From these observations Dyrmont and Goldenberg concluded that:

1. The surface preparation is of great importance in phosphating.
2. By comparison, mechanical cleaning is better than chemical.
3. Of the chemical treatments, that with  $H_3PO_4$  is least beneficial, but is improved slightly with increase from 5 to 15 percent  $H_3PO_4$ .

Domnitsch and Dubrowsky (8) claimed that the quality of the phosphate coating depends upon the cleanliness of the metal surface. Abrasion with finer grade emery paper gave finer-grained phosphate coatings than abrasion with coarser papers. They also reported that a thin coating of vaseline promoted the formation of fine-grained, uniform phosphate coatings. In addition, they found that coarser-grained coatings were deposited on surfaces that had been degreased in hot lye solution than on electrolytically degreased surfaces. In this case the finer-grained coatings had twenty times the corrosion resistance of the coarse-grained deposits.

Machu (26) compared the effect of abrasion and pickling on the phosphate coating, by use of the shielded-electrode technique on electrolytic iron. He measured the free-pore area ( $F_0 - F$ ), that is, the area of the sample not covered by the coating, for surfaces that had been abraded with 2/0 emery, or pickled in hydrochloric acid (1:2) at 25°C for two minutes prior to phosphating and obtained the curves shown in Figure 2 when he plotted  $F_0 - F$  values against length of phosphating time. The greater length of phosphating time required for pickled steel is obvious from the plot and, in addition, the coatings were rougher and made up of very large crystals.

Fig. 2 - Free pore-area vs length of phosphating time for abraded and pickled iron - from Machu (26)



#### Effect of Bath Composition on Phosphate Coatings

Machu (26, 27, and 28), using electrochemical measurements, has made extensive studies of phosphating baths and has attempted to correlate free-pore-area determinations with results from corrosion tests. In these studies Machu used a shielded electrode of specially prepared vacuum-fused iron, degreased and abraded with emery. The free-pore-area studies were correlated with corrosion tests run on 60 x 40 mm plates subjected to a sodium chloride solution.

It was found that those test pieces having low free-pore areas had high corrosion resistance. Based on these studies Machu claimed that the corrosion resistance of phosphated metal may be predicted from a knowledge of the value of the free-pore areas. Test pieces were weighed before and after phosphating and the ratio of the weight gain per unit area to the specific gravity of the coatings was taken as a measure of the thickness of the coating, on the assumption that the weight loss in phosphating was negligible.

When the bath temperature was lowered from the usual 98° to 20° C, Machu found that the free-pore area, even after 70 hours treatment time, was 0.10 or, in other words, that only 90 percent of the surface was coated. For such coatings the corrosion resistance was very low.

The addition of accelerators (nitrates, nitrites, dichromates, copper salts, quinoline, etc.) to the phosphating solution caused a decrease in the free-pore area of the phosphate deposits. Since some accelerated baths inhibit the evolution of hydrogen gas, the free-pore-area measurement may be used to determine the required treatment time for the commercial use of such baths.

Excessive addition of accelerator to phosphate baths may hinder or prevent coating formation because of the passivation of the metal surface. Since phosphates are deposited at the local cathodes, Machu postulates that any extension of the cathodic area would stimulate coating formation. Inhibiting the anodic attack would have the same effect. The action of chemically diverse accelerators may therefore be explained on the basis of their adsorption at electrode surfaces, thereby polarizing the surface and promoting the cathodic deposition.

TABLE 6

Free-Pore Area of Phosphated Steel Vs Area of Steel Treated (From Machu (28))

Area of Steel Processed	Free-Pore Area ( $F_0 - F$ ) of Treated Steel* ( $F_0 - F$ ) $\times 10^3$ / $\text{cm}^2 / \text{cm}^2$	
	Nitrated Bath	Nitrate Free Bath
0	5.41	5.45
1000		2.83
2000	1.16	49.9
3000		127.6
4000	2.72	549.0
6000	1.03	447.0
8000	1.59	683.0

\*Average values from duplicate experiments.

Using his shielded-electrode technique, Machu has attempted to determine the effect of the phosphate coating of aging and of enrichment of the baths in iron. These baths were processed by processing deep-drawn steel plates. Using both nitrated and nitrate-free zinc baths to process various areas of steel, and measuring  $F_0 - F$  in the usual manner, Machu (28) obtained the data shown in Table 6. It can be seen that the free-pore areas of the samples treated in the nitrated zinc bath remain essentially constant throughout the aging cycle; but in the case of the nitrate-free bath the free-pore-area measurements vary by a factor of one hundred for a corresponding aging cycle.

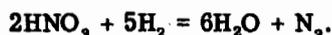
These free-pore-area measurements were correlated with corrosion tests run in sodium chloride solution. Greater corrosion resistance was obtained throughout the bath life from the nitrated zinc bath, although the fresh baths gave coatings of the same corrosion resistance. Thus Machu concludes that the corrosion tests are a direct reflection of the free-pore-area measurements.

In corresponding measurements on manganese baths, the free-pore area of the coating obtained from nitrate-free baths is fairly constant over a long life, but the corrosion resistance was not as great at the end of the series as in the earlier cycles. Machu claims that as such a bath ages the coating deposited from it becomes enriched in iron phosphate and this compound is gradually oxidized to ferric phosphate, which causes rupture of the coating and failure in corrosion tests. In the nitrated baths the soluble ferrous salts are oxidized and precipitate out as sludge, but not in the coating, and therefore give coatings of greater corrosion resistance over a longer period of time.

In nitrate-free baths the ratio of iron to manganese or zinc in the respective baths was determined as a function of the area of metal treated and it was found that the amount of iron increased in the zinc bath to a far greater extent than in the manganese bath - so much so that at the end of the aging cycles the zinc bath was actually a ferrous phosphate bath.

Ferrous phosphate baths, Machu found, require about the same treatment time as manganese baths. Thus when an aged nitrate-free zinc bath is allowed the normal short zinc treatment time, the coatings have very large free-pore areas. If given proper length of reaction time, ferrous phosphate baths deposit coatings of small free-pore areas. However the tendency of ferrous compounds to oxidize to ferric salts, which in turn may hydrolyze to form the nonprotective iron rust, makes the ferrous phosphate coatings unsatisfactory for protection against corrosion. All of Machu's corrosion resistance measurements were made on samples having no further protective coating.

Schuster et al. (35, 36, 40, 42, 43, and 44) investigated the phosphating baths in common use in industry, and evaluated the corrosion resistance of the coatings by salt spray and by atmospheric exposure tests. It was shown that nitrated zinc baths produce the most consistently satisfactory results. By comparing analyses of fresh phosphating baths with those of used and regenerated baths, it was shown that nitrated zinc solutions undergo the least change during use. This they attributed to the presence of nitrates, which react with the hydrogen liberated at the cathodic areas to depolarize the surface. It is believed that the hydrogen absorbed on the metal surface prevents contact with fresh solution. The hydrogen is replaced by nitrogen (since nitrogen does not act in this manner) by the reaction



Nitrate-free phosphating baths liberate gas containing about 90 percent hydrogen; in nitrated baths the gas evolved is about 75 percent nitrogen. As a nitrated bath is used it becomes enriched in iron; and the gas liberated from a used bath contains oxides of nitrogen, hydrogen, and oxygen. The total volume of gas liberated from nitrated baths is less than that liberated from nitrate-free baths. This may be due to the rapid action of nitrated baths, in which the attack on the metal surface is less.

An interesting technique which was employed by Schuster and Krause (43) for determining by gravimetric methods the weight loss and corrosion resistance of the coatings is outlined as follows:

1. Weight of untreated sample

$$A = a$$

2. Weight of phosphated sample

$$B = a - n + b$$

in which

$$\begin{aligned} n &= \text{weight of iron lost in phosphating} \\ b &= \text{weight of phosphate coating} \end{aligned}$$

3. Weight of sample after corrosion in NaCl

$$R = (a - n + b) - m + r$$

in which

$$\begin{aligned} m &= \text{weight loss of metal in corrosion} \\ r &= \text{weight of corrosion product adhering to sample} \end{aligned}$$

4. Weight of sample after removal of corrosion products and phosphate coating

$$C = a - n - m$$

5. Weight of sample after removal of phosphate coating (this is not the same sample as used in the corrosion test numbers 3 and 4 above)

$$D = a - n$$

Algebraically

$$\text{Iron lost in phosphating } n = A - D$$

$$\text{Iron lost in corrosion } m = D - C$$

$$\text{Weight of phosphate coating } b = B - D$$

$$\text{Weight of corrosion product } r = R - B + D - C$$

At least ten identical samples must be run to eliminate experimental error and establish a statistical average.

Schuster measured the thicknesses of these coatings with a Zeiss optical instrument and found that normal and accelerated baths gave coatings of  $13.5 \times 10^{-4}$  cm and  $1.1 \times 10^{-4}$  cm respectively. Schuster criticizes Machu's thickness determinations on the basis that he neglected the weight of iron dissolved by the phosphating bath.

Macchia and Boggio (25) have reported a series of experiments using zinc, manganese, and iron phosphate solutions, singly and in combination, as phosphating baths. These investigators exposed the phosphated steel samples to the outdoor atmosphere and made periodic inspections of the progress of corrosion. The corrosion resistance was rated on an arbitrary scale of 100 percent representing no corrosion, and 0 to 25 percent representing complete rusting. The tests were discontinued after 100 hours exposure and Table 7 shows their evaluation of the corrosion resistance of the coated steel panels.

#### Composition of Phosphate Coatings

Durer, Schmid, and v. Schweinitz (9, 10) published pictures of X-ray diffraction patterns from phosphate coatings from zinc and manganese baths and concluded that the coatings were made up of  $Zn_3(PO_4)_2 \cdot 4H_2O$  and  $Mn_3H_2(PO_4)_4 \cdot 5\frac{1}{2} H_2O$  respectively; however, no X-ray diffraction data for either of these compounds were presented, and there is little information in the literature on the latter material.

Schuster and Krause (42) analyzed the coatings deposited by zinc and manganese baths with and without nitrates and found that as the bath ages the coating becomes richer in iron when nitrate-free baths are used. This enrichment in iron caused these coatings to have a lower corrosion resistance. When nitrated baths were employed, the coating was of a more uniform composition throughout the life of the bath, and the lower content of iron contributed to the higher corrosion resistance of these coatings.

Roesner, Schuster, and Krause (36) believe that the phosphate coating consists of insoluble secondary and tertiary phosphates of zinc, manganese, and iron - the relative amounts of each depending on the conditions of phosphating, including the type of bath used, the pretreatment of the metal surface, and the age of the bath.

Roesner and Schuster (35, 41) picture the phosphate coating as made up of three layers: ferrous phosphate adjacent to the metal surface, followed by a layer of mixed zinc or manganese and iron phosphates and finally a layer of zinc or manganese phosphate.

TABLE 7  
Corrosion Resistance of Steel Panels Phosphated in Various Baths  
After 100 Hours of Atmospheric Exposure (%)  
(From Macchia and Boggio (25))

Relative Concentration of the Metal Phosphate in Solution		Evaluation When Total Concentration of Metal Phosphates in Solution is			
		3%	3.5%	4%	
100% Fe (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> 100% Mn (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> 100% Zn (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>		15%	*75%	40%	
		30	85	50	
		95	60	35	
Mn (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	{ 10% 20 30 40 50 60 70 80 90	Zn (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> { 90% 80 70 60 50 40 30 20 10	95	45	80
			85	55	73
			50	30	65
			70	5	65
			85	65	90
			50	95	55
			70	60	75
			10	55	70
			20	100	90
			90		
Fe (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	{ 10% 20 30 40 50 60 70 80 90	Mn (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> { 90% 80 70 60 50 40 30 20 10	75	100	70
			60	100	75
			60	97	75
			70	100	73
			40	93	70
			70	96	63
			50	85	55
			25	75	65
			3	35	55
			90		
Fe (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	{ 10% 20 30 40 50 60 70 80 90	Zn (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> { 90% 80 70 60 50 40 30 20 10	50	90	65
			90	60	80
			95	85	60
			93	95	70
			98	50	95
			98	70	93
			98	95	90
			96	75	85
			93	10	75
			90		

\* Attention is called to the high rating obtained from the 100 percent ferrous phosphate bath when used at 3.5 percent concentration, and the low ratings at the other two concentrations.

Macchia (20) claims that the phosphate coating is made up of a "basic ferrous phosphate," but presents no further information concerning this compound.

Justh (16) states that the phosphate coating is made up of basic iron phosphate or ferrosferric phosphates but later in the same reference claims the coating consists of insoluble secondary and tertiary phosphates of iron.

Brich (19) states that the coating developed on iron in cold phosphoric acid is iron phosphate, but when hot acid is used, secondary and tertiary iron phosphates are deposited.

Chemical Treatment of Phosphated Steel

There are many patent claims for increased corrosion resistance imparted by special treatments following phosphating. Such treatments usually involve the application of a solution of a hydrolyzable metal salt, such as those of aluminum or chromium, to produce a "water coat" in the pores of the phosphate coating. Machu (30) showed by means of pore-area measurements that hot sodium chromate solution does seal the pores of phosphate coating and increases its corrosion resistance.

COMMENTS ON THE LITERATURE REVIEW

It is readily seen from the foregoing brief review of the literature that many questions remain to be answered in the problem of phosphating. Evaluation of the phosphating solutions containing phosphoric acid alone has been almost completely neglected owing to more recent developments reflected in the patents covering the use of metal ions in phosphoric acid solution. The possibility of the formation of satisfactory phosphate deposits by the use of phosphoric acid alone should not be overlooked in a complete investigation of the problem. As far as is known no attempt has been made to accelerate the reaction of phosphoric acid and steel so that deposition of the insoluble ferrous phosphates would occur at a practical rate.

The concept of the mechanism of the formation of phosphate coatings has followed chronologically the development of the theories of corrosion based upon studies of metals and their reaction with their environments. Early concepts of the mechanism of phosphating were macroscopic in approach. The deposition was thought to be due solely to the change in pH of the solution adjacent to the metal surface caused by the solution of the metal in acid. This deposition resulted in supersaturation and consequent deposition of the metal phosphates from solution. However, the work of Thornhill and Evans (46), Agar (1), and Evans and Hoar (12, 14) among others has demonstrated beyond argument that most corrosion processes are electrochemical in nature. The solution of metals in acids is believed to be due to the electrochemical action of the local cathodes and anodes present on the metal surface. Therefore the acceptance of the electrochemical theory of corrosion processes, including the solution of metals in acids, leads directly to the acceptance of the mechanism of phosphating proposed by Machu and Müller and Hasner. This view is further supported by the work of Akimov and Paleolog (2) who showed by direct observation that the surface of phosphated steel is made up of neutral, anodic, and cathodic areas and that the cathodic points outnumber the anodic. There can be little doubt in the light of these recent developments that the electrochemical mechanism best expresses the essential processes taking place during phosphating.

The treatment of the metal surface prior to phosphating is of primary importance in determining the size of the crystals that make up the phosphate coating, and there appears to be no doubt that fine-grained, uniform phosphate coatings have the highest corrosion resistance. But the basic factors controlling the crystal size have not been defined although trial and error methods have led to commercially practical techniques.

The pretreatments of metal surfaces for phosphating include annealing, degreasing, pickling, abrading, sensitizing, or any treatment given the metal before phosphating. All the specific treatments mentioned are known to affect the deposition of phosphate coatings

Concentration of Solution is	4%
	40%
	50
	35
	80
	73
	65
	65
	90
	55
	75
	70
	90
	70
	75
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although there is lack of consistency in some of the effects. Schuster has shown that when steel is cooled in an inert gas after annealing, followed by phosphating, the coating will be uniform and fine-grained, but that cooling in air leads to large-grained, unsatisfactory coatings. The formation of an oxide film has been suggested as a cause; however it is possible that some other factor may be responsible. If the oxide film formed on the metal surface during annealing permanently prevented the formation of fine-grained phosphate coatings, it would be virtually impossible to obtain satisfactory coatings under the usual conditions in industry. Most steel objects have been subjected to high temperatures in rolling and drawing before they arrive at the phosphating bath, yet satisfactory phosphate deposits are readily applied. It may well be that the particular condition of the oxide film present on the samples examined by Schuster was the cause of their resistance to satisfactory phosphating. It has been shown by Lewis (18) that at high temperatures the oxide or mill scale formed on steel is made up of three layers: ferric oxide, magnetic oxide, and ferrous oxide. The layer of ferrous oxide is oxidized upon exposure to air and fissure occurs in the scale providing many points where corrosion may take place. The thickness of the ferrous oxide layer is dependent upon the conditions of annealing and subsequent cooling, and oxide layers that are intact are known to be protective. Thus in Schuster's experiments, insufficient time may have elapsed between the annealing and phosphating to be representative of the conditions prevailing in industry, and the oxide films present on the surfaces he used may have been virtually intact. If this were the case, the oxide films would offer marked protection to the steel, and the phosphating process would, as he reported, have been unsuccessful. But had the samples been aged prior to phosphating, permitting oxidation of the ferrous oxide layer adjacent to the metal, or had the scale been loosened by some other treatment, it appears likely that phosphating would have taken place readily.

For the deposition of satisfactory phosphate coatings the surface of the steel must be free of scale, rust, and soaps. In order to clean the surface, the steel is usually pickled, but this often produces a surface that is not readily phosphated. Many investigators have attempted to solve this problem, but it is admitted that a generalization can not be made concerning the effect of pickling on phosphating.

Dickens (7) claims that there are residues of iron salts and portions of the steel insoluble in acids left on the steel surface after pickling, which must be removed prior to further treatment. Schumacher (39) examined residues remaining on steel after pickling in sulfuric and hydrochloric acids and found by chemical analysis that the residues had the compositions shown in Table 8.

TABLE 8  
Analyses of Steel and Pickle Residues from Schumacher (39) (%)

Residues	C	Si	Mn	P	S	Cu	Ni	As	Fe
Steel	0.035	0.0	0.32	0.026	0.012	0.18	0.08	0.043	
Pickle from H <sub>2</sub> SO <sub>4</sub>	4.7		0.27	0.88	1.08	20.4	2.36	3.81	49.56
Pickle from HCL	5.0		0.28	1.44	0.18	20.16	7.23	6.73	41.1

It is not possible to determine in what form the iron occurs in the pickle residue, since the oxidation effect is present even when the pickling is carried out in carbon dioxide

sphere. The residue from sulfuric acid is firmly adherent to the metal surface and rubbing is required to remove it. Pickling in HCl produces less residue so loosely adhered to the metal surface that most of it floats off in the pickling bath. The remarkable increase in the copper and nickel content on the surface layers after pickling does lend weight to the contention of Schuster and others that the surface of the steel after pickling has a lower acid solubility than an untreated surface; and, since the phosphating process depends upon the attack of the metal by the acid, such residues would render the surface more difficult to phosphate. It has also been pointed out that pickle inhibitors are adsorbed on the metal surface and hinder the attack of the acid on the metal itself; when such materials are present on the metal surface when it is introduced into the phosphating bath, they inhibit or prevent phosphating from taking place. But on the other hand Machus has shown that pickling pure vacuum-fused iron in acid containing no inhibitor also produces a surface that is not easily phosphated. In this case there could be no increase of adsorbed resistant materials on the iron surface, and no inhibitor adsorbed on the surface; therefore the effect of pickling prior to phosphating must be due at least partially to some other factor.

In contrast to the effect of pickling on phosphating, abrasion with emery or by sand-blasting gives rise to uniform fine-grained phosphate coatings. The effect of abrasion has been attributed to the formation of numerous centers where crystallization may take place.

It is interesting to note that in galvanizing steel, exactly the opposite effects are noted when the surface is pickled or abraded. Burns and Schuh (5) state that the cleanliness of the metal surface is most imperative prior to galvanizing and it has been noted that pickled surfaces give rise to fine-grained zinc coatings but a spangled coating is produced when the metal is first abraded. The fine-grained coating on pickled iron is attributed to the numerous centers where crystallization may take place, but when an iron surface is cleaned by abrading with emery and then dipped in molten zinc, a poor coating is formed because of the presence of an air-formed oxide film. Although the mechanisms of crystallization in the galvanizing and phosphating processes may not be the same, it is obvious that the true conditions prevailing on the surfaces during the coating processes are not understood and demand clarification.

This is further borne out by the fact that although it had been repeatedly stated that the surface of the metal prior to phosphating should be free of grease and oils, many investigators have noted the beneficial effect of treating the cleaned surface with mineral oil or vaseline before phosphating. Jernstedt (15) has conducted lengthy experiments with certain pretreatment solutions to determine their effect on the phosphating process, and has offered the "wiping effect" as an explanation of the action of certain materials which are colloidal in nature, and probably deposit a film of adsorbed lyophilic micelles on the metal surface. The term "wiping effect" was chosen because as reported by Schuster and others, vigorous wiping of the metal surface after pickling gives rise to satisfactory phosphate coatings.

The beneficial effects of pretreatment with solutions of nitrite and copper ions have been attributed by Schuster to an increased solution rate of the metal in the phosphoric acid, thus causing a more rapid change in the pH of the solution adjacent to the metal surface, more rapid nucleation and growth of the coating crystals, and hence a deposit of many small crystals rather than fewer large crystals.

From these studies it appears most likely that the factors which determine the crystal size and uniformity of the phosphate coating are both physical and chemical in nature. The effect of films of vaseline, oil, and lyophilic colloids is probably physical

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whereas the effect of pretreatment with nitrite or copper ion may be chemical. Further investigations using the methods described in the experimental section of this report would determine what effect, if any, these pretreatment methods have on the solution rate of the steel in phosphoric acid, and perhaps lead to a better understanding of the mechanism of the action of these pretreatment processes.

The composition of the phosphate coatings deposited by the several types of baths has not been fully established although extensive chemical analyses of the coatings have been reported by Roesner, Schuster, and Krause. These workers have reported the variation in chemical composition of the coatings during bath life, but it has not been established whether a change in the crystal structure accompanies these changes in composition. Chemical analysis alone can not furnish such information, and further work is being conducted at this Laboratory using X-ray diffraction to establish the patterns for the pure metal phosphates and for certain mixtures. The results of this work will be the subject of another report in the near future.

Some work of this type has been reported by Durer, Schmid, and v. Schweinitz, but they published only a limited amount of information and presented no data concerning the X-ray studies of the phosphate coatings. Until such information is available, it is impossible to identify fully the materials present in the coatings, although many opinions have been offered in the literature, as has been pointed out in the foregoing brief review.

Machu and Schuster and co-workers have reported that as a phosphate bath becomes aged, the coatings obtained from it become enriched in iron, and the corrosion resistance of the coatings decreases. These conclusions were based on tests run on samples having no further protective coating such as oil or paint. The work of Macchia and Boggio with solutions of iron, zinc, and manganese phosphates - singly and in combination - clearly indicates that no such unqualified statement is justified. The work of these latter investigators shows that under the proper conditions very satisfactory protective coatings may be obtained from solutions containing ferrous phosphate alone or in several combinations with the other metal phosphates. Since these workers found that the treatment time required for the various solutions does vary their results were obtained on samples that were exposed to the solutions until completion of the hydrogen evolution, rather than for a predetermined arbitrary interval. Burkhardt and Sachs (4) also state that satisfactory corrosion resistance may be obtained from ferrous phosphate coatings, but that these are not now commercially used because of the excessive sludging of the ferrous phosphate baths caused by the oxidation of the ferrous ion in solution.

The problem of sludging is peculiar to batch operation in industry and would not necessarily be detrimental under drydock conditions. Thus it is possible that uniform, fine-grained ferrous phosphate coatings of satisfactory corrosion resistance may be obtained by controlling the reaction of steel and phosphoric acid through the addition of accelerators or other modifications. The work that has been done in the field of accelerators for zinc and manganese baths may prove to be of great value in developing a special process for the particular application of interest to the U. S. Navy.

In particular the problems presented by phosphating large structures at the time of construction or for maintenance are remarkable by the lack of attention they have received. Treatments are now in use by the U. S. Navy involving phosphoric acid. The resultant coatings, however, are not comparable to those deposited with the zinc and manganese processes which have not been adapted for drydock application. The present problem was established to study the fundamentals of present day phosphating to gain a better understanding of the mechanism of the deposition of these coatings. The literature survey has revealed that the mechanism of the formation of fine-grained uniform coatings is not well understood nor the compounds that constitute these

completely identified. The causes of the anomalous effects of the treatments to the steel before phosphating have not been determined, nor has there been any study of the fundamental reaction upon which the whole process of phosphating is based, namely, the reaction of steel with phosphoric acid. Most of the published reports concerning this reaction deal with the corrosion testing of construction materials for use in the acid in plant processes. Two examples of such articles are the papers by Rasmussen (37) and Kosting and Heins (17) describing a series of accelerated tests on a large number of metals and alloys placed in phosphoric acid solutions. Thus it became necessary as a first step in this investigation to study the kinetics of this reaction in order to establish a basis for study of the phosphating process itself.

## SOLUTION RATE OF STEEL IN PHOSPHORIC ACID

### Experimental Methods and Apparatus

**Materials** - Standardized solutions of Baker's C. P. Phosphoric Acid were used in making up the acid solutions.

The specimens were random cuts from ten-foot lengths of a single batch of half-inch-diameter cold-rolled steel rod of the following composition:

C	Si	Mn	P	S	Cr	Ni	Mo
.15%	.01	.44	.011	.055	.015	.063	.001

The shaft designed for specimen rotation was turned from paper-base Bakelite fitted with a cap nut of the same material.

**Preparation of the Specimens** - The steel rod used in the study was cut into two-inch cylinders, drilled to fit on the Bakelite shaft, and turned down on a lathe to remove the shop-scarred surface and establish a fairly uniform cross section.

Immediately prior to each run the specimen was abraded with a sequence of dry emery papers and cloths ranging from No. 100 to 3/0 grits. No lubricant was employed during polishing, and the emery papers were dried in an oven at about 60°C immediately before use. The dimensions of the specimens were measured with vernier calipers and micrometers.

**Apparatus** - The experiments were carried out in a water bath equipped with immersion heaters, a mercury thermoregulator, a thermometer, and a motor-driven stirrer. The temperature of the bath was regulated within  $\pm 0.2^\circ\text{C}$ . The phosphoric acid was placed in a constant-head reservoir connected to a flow control constructed of capillary pyrex glass tubing with a by-pass of large-diameter tubing. The acid flow rate was controlled by manipulation of stopcocks in the flow control. Distilled water for washing was contained in a second reservoir.

The reaction cell, Figure 3, was designed for use with a rotating specimen. A coil for preheating the acid solution and the reaction cell were constructed as a single unit from pyrex glass. The overflow port from the reaction cell was attached through a series of traps to an aspirator. All connections were made with rubber tubing. A schematic diagram of the apparatus appears in Figure 4.

**Methods** - In this investigation the solution rate of steel in phosphoric acid was measured by rotating cylindrical specimens in a flowing acid solution under controlled conditions.

apparent area of the specimen is only a fraction of the true area, but if a standard finish is applied to the specimen this factor should be constant and without effect on the observed reaction rates. This assumption was supported by the results from a brief series of experiments in which the specimen areas were varied while all other factors remained constant and the weight loss varied directly as the area.

After polishing, and immediately preceding each run, the steel had a bright silvery luster, and was readily wetted by water. The surface became dark gray and dull immediately upon exposure to the acid solution. After acid attack the surface of the specimen was examined under a microscope and no evidence of an adherent surface film was visible. The dark surface was probably due to etching and possibly to the enrichment of the surface layer of the metal in carbon and other acid-insoluble materials. In the longer runs in normal and 3 normal acid at 93°C, the surface of the sample became somewhat etched with shallow microscopic pits distributed fairly uniformly over the surface. There was also an accumulation of a nonadherent dark material on the metal surface which was readily removed during rinsing. This material resembled that described by Whitman, Russell, Welling, and Cochrane (47) in experiments with steel and sulfuric acid.

There was a vigorous evolution of hydrogen during most runs, markedly less in the 0.01 N acid solutions and at the lower temperatures than in the stronger solutions and at higher temperatures. Gas evolution began immediately upon contact of the specimen with the acid solution with no evidence of an induction period.

The specimens were selected at random and the weight-loss figures are average values obtained from duplicate runs on several random samples. A single specimen could be used repeatedly but was used only once under a particular set of conditions. The method of selecting the specimens probably caused some scatter in the results, but this did not exceed 5 percent variation from the average in most cases except with very dilute acid solutions and short reaction times. Since random samples were used, it is believed that the observed solution rates are fairly representative of the steel as a whole.

**Solution Rate and Time** - Figure 5 and Table 9 present the experimental results obtained in establishing the relation between time and the solution rate of steel in .01, 1, and 3 N phosphoric acid at 93°C. The total reaction time of thirty minutes was selected because it was believed that this interval certainly covers that of greatest interest from a practical viewpoint and that during this period the area of the specimen would probably not be altered by etching to such a degree that it would become the controlling factor in the rates. The temperature 93°C, is in the range employed in commercial phosphating.

The amounts of steel dissolved are plotted against the time of exposure to the acid solution in Figure 5 and show essentially a straight line for each of the acid concentrations. The linearity of the curves suggests that probably no change occurs in the mechanism of solution during the course of the reaction up to 30 minutes nor between the acid concentrations of .01, 1, and 3 N. This relation between the solution rate and time may be expressed by the equation:

$$\frac{dr}{dt} = k_t \quad (1)$$

The constant  $k_t$  can be evaluated from the slopes of the curves for each acid concentration. In the present study, where  $k_t$  has the dimensions of grams per square centimeter per minute, the values shown in Table 10 were observed.

**Solution Rate and Acid Concentration** - The acid solution was allowed to flow through the reaction cell throughout the reaction period. This technique was adopted to minimize

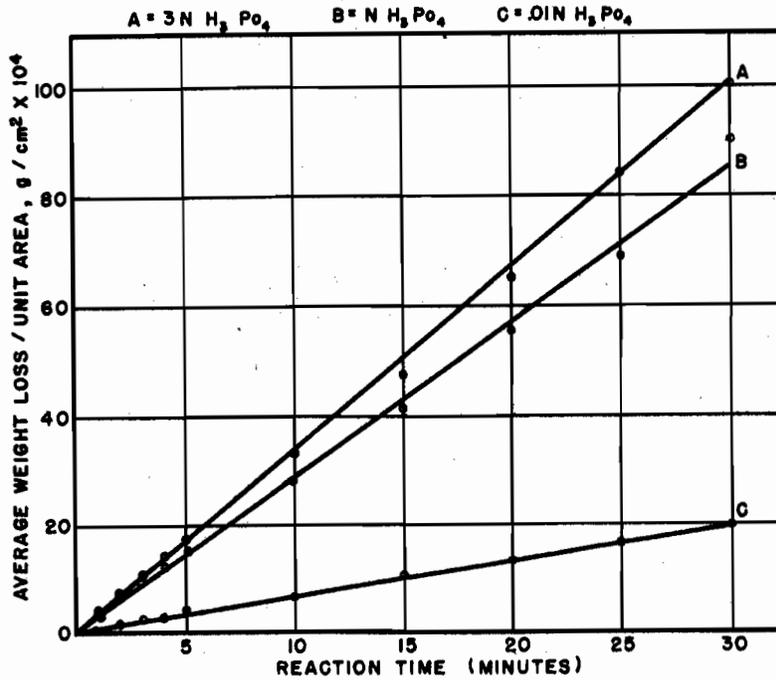


Fig. 5 - Weight loss of steel in 3, 1, and 0.01 N H<sub>3</sub>PO<sub>4</sub> vs reaction time

TABLE 9  
Weight Loss of Steel in 3, 1, and .01 N Phosphoric Acid After Various Time Intervals up to 30 Minutes (Temperature 93° C)

Time of Run (minutes)	Average Weight Loss* g/sq. cm. x 10 <sup>4</sup>		
	3 N H <sub>3</sub> PO <sub>4</sub>	1 N H <sub>3</sub> PO <sub>4</sub>	.01 N H <sub>3</sub> PO <sub>4</sub>
1	4.09	3.46	0.877
2	7.55	6.38	1.95
3	10.80	9.18	2.52
4	14.20	12.33	2.72
5	17.02	15.18	4.19
10	33.15	28.18	6.88
15	47.62	41.65	10.99
20	65.34	56.8	13.26
25	84.12	69.2	16.68
30	100.85	90.4	19.72

\*Each weight loss value represents the average of several measurements obtained from random samples.

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TABLE 10  
Solution Rate of Steel in Phosphoric Acid

Normality of Phosphoric Acid	$k_t \times 10^4$
3	3.4
1	2.8
0.01	0.66

the accumulation of insoluble reaction products on the surface of the specimens and to insure a constant acid concentration throughout the reaction period. The rate of 35 cc per minute was more than adequate as shown by preliminary experiments. By using this technique the observed weight loss of the specimen was considered to be a direct measure of the reaction rate.

Figure 6 and Table 11 show the variation in the solution rate of steel in phosphoric acid at 93°C with the concentration of the acid. These data represent average values obtained from duplicate determinations in ten-minute runs. From this graph it can be seen that the amount of steel going into solution increases rapidly with increasing acid concentration up to about 1 N; above this value the effect of increasing acid concentration is less pronounced.

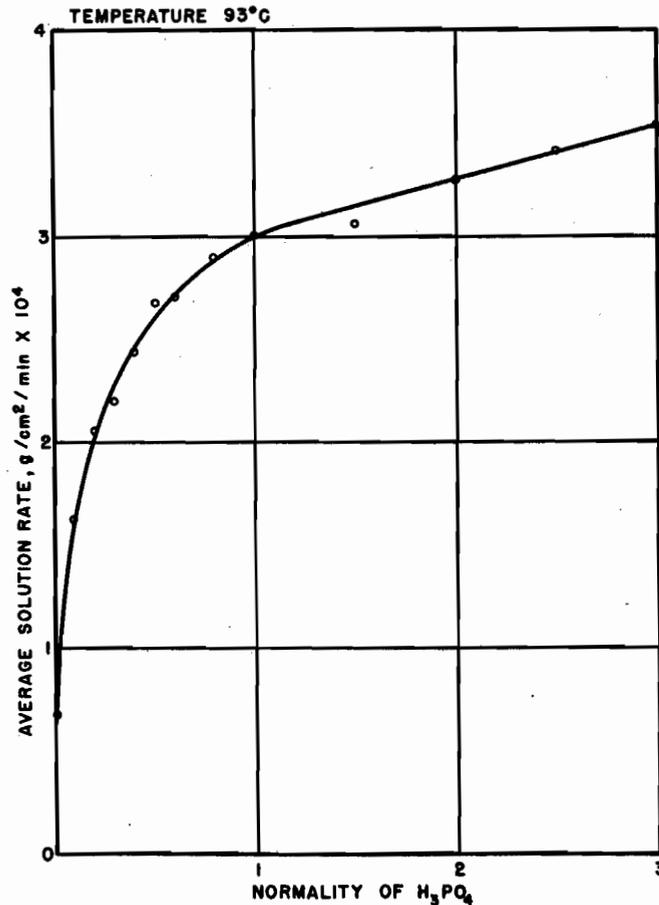


Fig. 6 - Solution rate of steel vs H<sub>3</sub>PO<sub>4</sub> concentration

TABLE 11  
Solution Rate of Steel in Phosphoric Acid  
of Various Concentrations

(Temperature 93° C)		(Rpm 1000)
Acid Concentration (N)	Average Solution Rate* (g/sq. cm./min x 10 <sup>4</sup> )	
0.1	1.64	
0.2	2.07	
0.3	2.20	
0.4	2.45	
0.5	2.69	
0.6	2.72	
0.8	2.91	
1.0	3.01	
1.5	3.07	
2.0	3.29	
2.5	3.43	
3.0	3.54	

\*Each value represents the average of two determinations on separate specimens.

The evolution of hydrogen first became vigorous at an acid concentration of 0.4 N; below this value there was little gassing.

If the solution rate is plotted against the logarithm of the acid concentration, the best probable curve through the experimental points, approximates a straight line, curve A, Figure 7. This is indicative of a first-order reaction, or,

$$dr = 2.303 k d \log C \quad (2)$$

$$r = 2.303 k \log C + \text{constant.} \quad (3)$$

Under the specific experimental conditions employed in this study, these constants have been evaluated approximately, giving the expression,

$$r = 2.303 (5.38 \times 10^{-5}) \log C + 2.99 \times 10^{-5} \quad (4)$$

where C is expressed in normality.

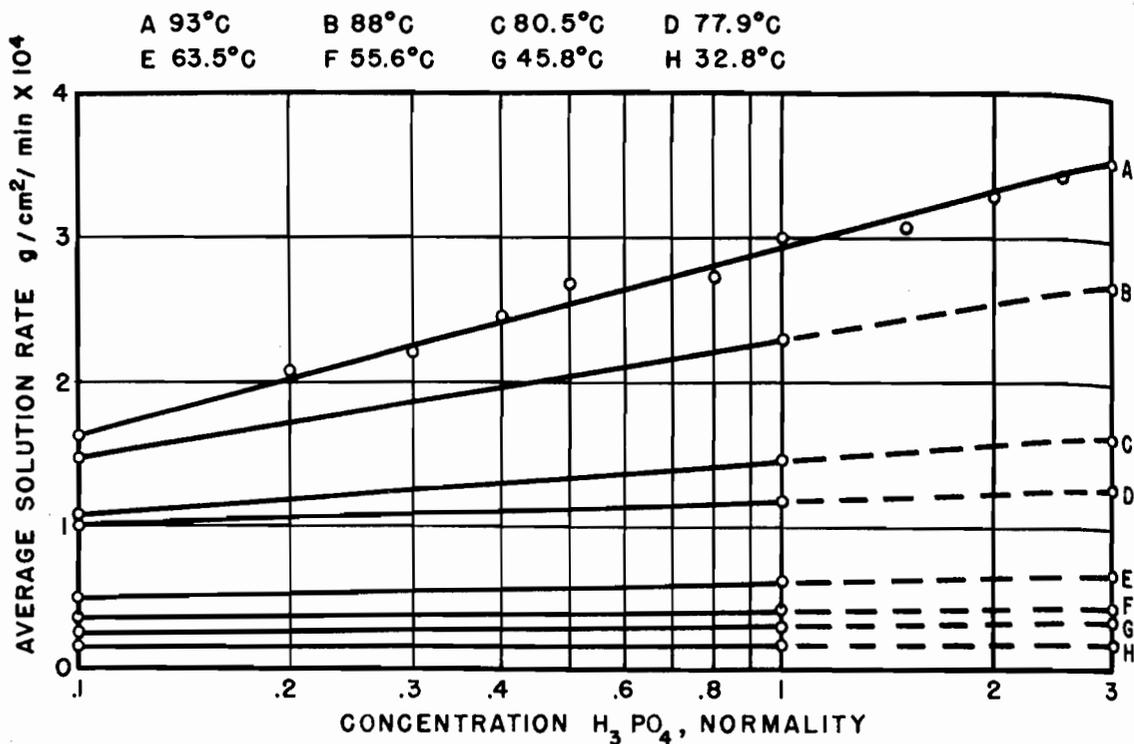


Fig. 7 - Solution rate of steel vs concentration of  $H_3PO_4$

Solution Rate and Temperature - In Table 12, columns 2 and 3 show the average experimental values for the solution rates of steel in 1 and 0.1 N phosphoric acid solutions at several temperatures. These data are shown graphically in Figure 8 and when replotted on logarithmic coordinates, Figure 9, a and b, produce curves which approximate straight lines, indicating a relationship of the following character:

$$\ln r = k \ln T + \text{constant} \quad (5)$$

for 0.1 N acid

$$\ln r = 12.84 \ln T - 84.57 \quad (6)$$

for 1 N acid

$$\ln r = 16.45 \ln T - 105.31. \quad (7)$$

The ratio of the reaction rates at two temperatures ten degrees apart is the temperature coefficient of a reaction. Table 13 shows the temperature coefficient of the reaction of steel and phosphoric acid for several ten-degree intervals. The value of this ratio has been used as an indication of the mechanism of chemical reactions (45) even though the correct interpretation is still a matter of controversy. It has been considered that temperature coefficients below 1.8 or so are indicative of a diffusion-controlled reaction. From this it would appear that the reaction of steel in 1 N phosphoric acid might possibly be chemically controlled over a portion of the temperature range, but the temperature coefficient of the 0.1 N acid solution rate would indicate a diffusion-controlled reaction throughout the temperature range. However, the curves shown in Figure 5 indicate that the

TABLE 12  
Solution Rate of Steel in 1, 0.1, and 3 Normal Phosphoric Acid  
at Various Temperatures - (Rpm 1000)

Temperature (°A) (1)	Solution Rate (g/sq cm/min x 10 <sup>4</sup> )		
	N H <sub>3</sub> PO <sub>4</sub> * (2)	0.1 N H <sub>3</sub> PO <sub>4</sub> * (3)	3N H <sub>3</sub> PO <sub>4</sub> † (4)
305.98	0.177	0.167	0.182
318.98	0.286	0.266	0.296
328.78	0.408	0.361	0.430
336.68	0.615	0.522	0.659
351.08	1.179	1.015	1.257
353.68	1.455	1.099	1.635
361.18	2.302	1.483	2.690
366.18	3.01	1.642	3.662

\* Experimental observations - average values from two duplicate runs on separate specimens.

† Extrapolated values obtained by equation 2.

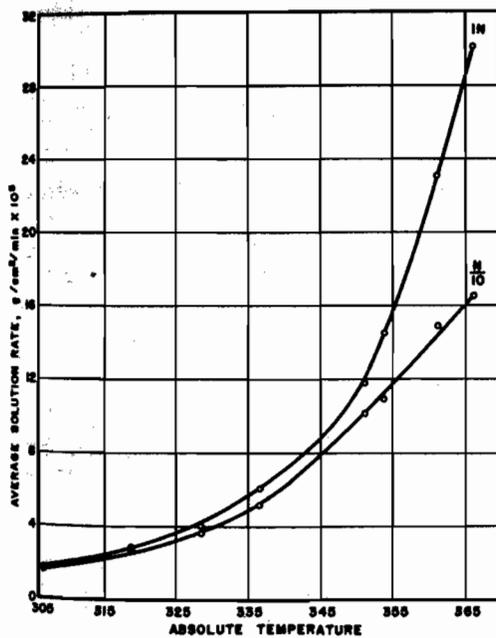


Fig. 8 - Solution rate of steel in 1N and 0.1 N H<sub>3</sub>PO<sub>4</sub> vs temperature

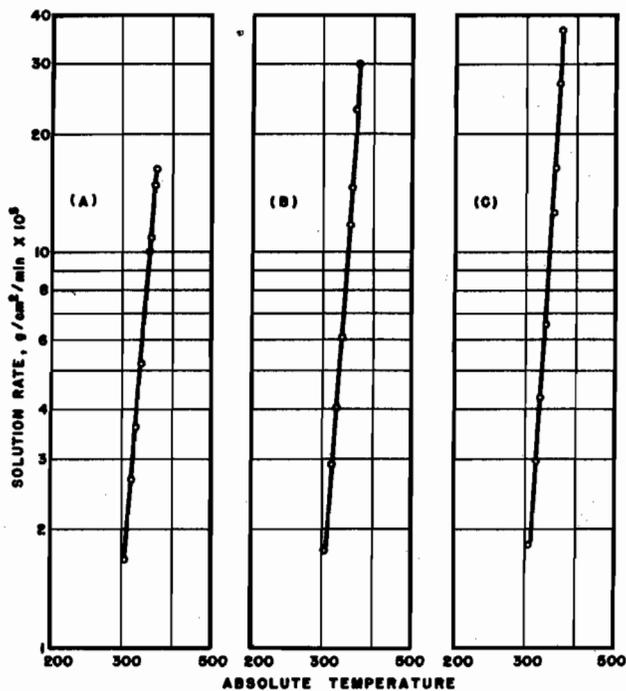


Fig. 9 - Solution rate of steel vs absolute temperature - logarithmic coordinates

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(6)

(7)

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must be investigated before any final recommendations may be made concerning actual phosphating practice.

#### RECOMMENDATIONS FOR FUTURE WORK

It is suggested that studies analogous to those described in this report be carried out using commercial phosphating compositions in place of the phosphoric acid. Direct comparison of results would be possible if the same experimental conditions and materials are employed. The work should include similar studies on phosphoric acid containing additional agents at various concentrations. With these data available, it would be possible to determine whether the solution rate of steel in the commercially proved phosphating solution is markedly different from that reported here for straight phosphoric acid solution. Subsequent work on the problem could then be directed more definitely toward determination of optimum conditions for deposition of satisfactory phosphate coatings under the conditions usually prevailing in drydock.

It is suggested that work be carried out concurrently on further study of the crystalline compounds occurring in the phosphate coatings. Some work on this phase of the problem has been done at this Laboratory and will be the subject of another report in the near future.

It is suggested that surface area measurements by gas adsorption methods such as employed by Burwell, Smudski and May (6) in studying anodic films on aluminum might prove of interest in determining the causes of the anomalous reports on the effects of pickling and abrasion reported in the technical literature. Such studies comparing the areas of untreated, abraded, pickled, and phosphated steel surfaces would probably also lead to a clearer understanding of the mechanism of paint adhesion to phosphated steel.

The review of literature at the beginning of this report indicates the many phases of work that must be investigated and correlated to bring the problem of phosphate coatings to final conclusions; however, it is the intention of this study to limit the investigation to points of interest to the U. S. Navy. Some of the problems of immediate interest suggested by the literature survey include a further investigation of iron phosphate solutions; phosphoric acid solutions containing depolarizers; the effect of pretreatment solutions; the identification of compounds that constitute the phosphate coatings produced by the various baths; the factors that control the crystal size of the coatings; and development of an economical procedure for drydock application of satisfactory phosphate coatings.

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Dr. T. P. May, Engineer of the International Nickel Company, has continued to furnish occasional advice in connection with this and related problems since terminating his employment as Head of the Corrosion Section, Chemistry Division, Naval Research Laboratory.

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\* \* \*

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