

FR-3510

PHOSPHATE COATINGS ON STEEL

PART II - AN X-RAY DIFFRACTION STUDY OF THE PHOSPHATES OF ZINC, IRON, AND MANGANESE

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ABSTRACT

Available X-ray diffraction data are extended to include the zinc, iron, and manganese phosphates most likely to be encountered in phosphating processes and coatings. Ten phosphates have been synthesized—3 of zinc, 3 of manganese, and 4 of iron—and their X-ray diffraction patterns established. These patterns, together with those previously established and available in the literature, constitute a comprehensive series of data for the neutral and acid phosphates of these metals.

Such reference patterns were used to identify the materials present on the surface of phosphated steel, and to identify the products resulting from several reactions.

Phosphate coatings of normal appearance and texture were deposited on steel from a gelatinous medium at room temperature.

PROBLEM STATUS

This is a final report on one phase of the problem. Work on the problem has been suspended.

AUTHORIZATION

NRL Problem C05-11R

PHOSPHATE COATINGS ON STEEL
PART II - AN X-RAY DIFFRACTION STUDY
OF THE PHOSPHATES OF ZINC, IRON, AND MANGANESE

STATEMENT OF THE PROBLEM

The value of the phosphate coating of steel prior to painting, the desirability of determining the phosphating process most suitable for use by the U. S. Navy, and the need of basic information regarding phosphating processes and coatings were discussed generally in a first partial report (1).*

The information required includes a more complete knowledge of the composition of phosphate coatings. Although various phosphating processes are in common use, the composition of the coatings deposited by these methods has not been fully established. Chemical analysis (2) has shown the relative amounts of metal and phosphate ions present in such coatings, but invaluable as this information is, it does not show exactly what compounds are present.

The use of X-ray diffraction patterns to supplement the analytical data offers a particularly suitable technique for studying the metal phosphates. For this reason an X-ray diffraction study of zinc, iron, and manganese phosphates was undertaken as an element of the whole problem and is the subject of this report.

Special techniques will be required for the application of phosphate coatings to ships' hulls. One of the methods that suggests itself is the incorporation of the phosphating chemicals in a viscous medium similar to a paint base. Since it was not known whether phosphate coatings could be obtained from such mixtures, a beginning was made in exploring this question, and the tentative results of these experiments are reported herein.

BACKGROUND

In the earlier report (1) it was pointed out that suggested compositions for the phosphate coatings include many different metal phosphate compounds.

The recent X-ray diffraction work of Durer, Schmid, and v. Schweinitz (3, 4) indicated that tertiary zinc phosphate ($Zn_3(PO_4)_2 \cdot 4H_2O$) and ditrimanganous phosphate ($Mn_3H_2(PO_4)_4 \cdot 5\frac{1}{2}H_2O$) were deposited as coatings from zinc and manganese phosphating baths respectively. These conclusions were offered together with photographs of the X-ray diffraction patterns, but without the necessary related data, leaving these conclusions subject to verification.

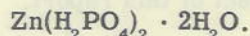
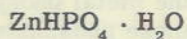
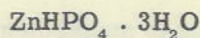
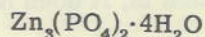
A more general survey of the neutral and acid phosphates of zinc, iron, and manganese reveals relatively little work on the establishment of the X-ray diffraction patterns of

*References appear at end of report.

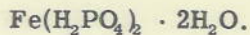
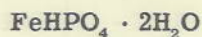
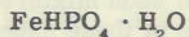
these compounds. Only the following appear in the ASTM Card File of X-Ray Diffraction Data (5):

| <u>Formula</u> | <u>Name</u> | <u>Card Number</u> |
|----------------------------|---|--------------------|
| Not stated | Zinc phosphate | 2347 |
| $Zn_3(PO_4)_2$ | Tertiary zinc phosphate anhydrous | 1324 |
| $Zn_3(PO_4)_2 \cdot 2H_2O$ | Tertiary zinc phosphate, dihydrate | 3580 |
| $Zn_3(PO_4)_2 \cdot 4H_2O$ | Tertiary zinc phosphate, tetrahydrate | 2346 2373 |
| $FePO_4 \cdot 2H_2O$ | Tertiary ferric phosphate dihydrate | II - 515 |
| $Mn_3(PO_4)_2 \cdot 7H_2O$ | Tertiary manganous phosphate heptahydrate | 2723 |
| $MnHPO_4 \cdot 3H_2O$ | Secondary manganous phosphate trihydrate | 680 |

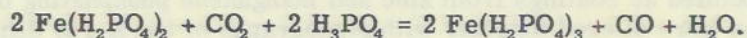
Other phosphates of these metals are known to exist and the phase diagrams at certain temperatures have been established. The excellent work of Eberly, Gross, and Crowell (6) has shown that in the system $ZnO:P_2O_5:H_2O$ the following well-defined compounds occur:



In the ferrous system $FeO:P_2O_5:H_2O$, Carter and Hartshorne (7) identified the following compounds:

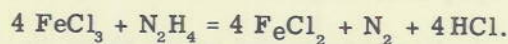


The latter pointed out that some oxidation was encountered in their work on the ferrous phosphates although the preparations were carried out in a carbon dioxide atmosphere. However Kukuschkin (8) has reported that monoferrous phosphate is oxidized by carbon dioxide in the presence of light according to the reaction

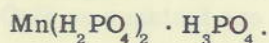
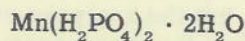
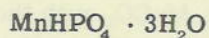


Although no further information was given concerning the conditions under which this reaction takes place, it indicates that a carbon dioxide atmosphere as employed by Carter and Hartshorne is probably not the best choice for preventing oxidation of the ferrous phosphates.

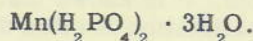
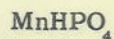
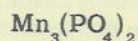
By employing hydrazine salts to maintain the ferrous state, the iron phosphates were successfully prepared in the present study without resorting to the complicated techniques involved in the use of an inert atmosphere. The use of this material was based on a report by Bray, Simpson, and MacKenzie (9) who showed that hydrazine reduces ferric ion quantitatively in acid solution according to the reaction



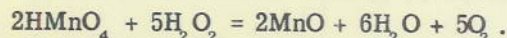
In the system $\text{MnO}:\text{P}_2\text{O}_5:\text{H}_2\text{O}$ Amadori (10) reported the following compounds:



In addition to these he prepared ditrimanganous phosphate to which he assigned the formula $\text{Mn}_3\text{H}_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$. Grube and Staesche (11) also studied the manganese system under the same experimental conditions as used by Amadori, but reported different compounds,



In the present study, the manganese compounds used in preparing the phosphates frequently appeared to contain traces of permanganates. These were converted to the divalent form by use of hydrogen peroxide which reduces permanganate ion in acid solution according to the reaction



It was the purpose of the present study to extend the available X-ray diffraction data to include all of the zinc and iron phosphates mentioned above; to resolve the conflicts shown, and establish the X-ray diffraction patterns for the manganous phosphates; and to identify the compounds present in the phosphate coatings on steel by X-ray diffraction methods.

EXPERIMENTAL METHODS

Preparation of the Pure Metal Phosphates

The pure zinc, iron, and manganese phosphates of interest in this study are not readily available from chemical supply houses, and it was necessary to synthesize them in crystalline form for the X-ray diffraction studies. The acid salts have been reported in phase studies of the systems represented by $\text{MeO}:\text{P}_2\text{O}_5:\text{H}_2\text{O}$ in which Me represents zinc, iron, or manganese. In preparing these compounds the concentrations of the components were

selected by choosing points lying within the phase areas indicated on the diagrams of Figure 1. The mixtures corresponding to the selected points were made by treating weighed quantities of metal salts with phosphoric acid solutions of known composition, and then adding distilled water to the mixtures in measured amounts. In one case, the preparation of the salt $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_3\text{PO}_4$, the 85% C.P. phosphoric acid solution did not contain sufficient P_2O_5 to produce the desired concentration, and solid P_2O_5 was added to the reaction mixture in order to bring the total P_2O_5 concentration to the desired value.

The metal oxide concentration represented by the phase diagrams may be realized by several means, in the zinc system, C.P. ZnO was used as the raw material; in the iron system a quantity of C.P. iron powder corresponding to the required amount of FeO was used in the preparations; and, in the manganese system, the desired amount of manganese was added to the reaction mixtures by treating C.P. MnCO_3 with the acid solution and then expelling the CO_2 . In preparing such mixtures it is not necessary to use the chemical species shown at the three vertices of the phase diagrams, but the analyses of the final mixtures must be represented by these three components. Thus the manganese system, reported in two papers (10, 11), was appropriately presented in one instance as $\text{MnO}:\text{P}_2\text{O}_5:\text{H}_2\text{O}$, and in the other case as $\text{Mn}_3(\text{PO}_4)_2:\text{H}_3\text{PO}_4:\text{H}_2\text{O}$.

The quantities represented by the phase diagrams are weight percent, and the mixtures are most readily prepared by gravimetric methods. The composition of aqueous phosphoric acid solutions may be expressed on a basis of H_3PO_4 content and with equal correctness on the basis of P_2O_5 content. Thus, in the present study, the mixtures were made by weighing out C.P. phosphoric acid solutions of known composition. Sufficient water was added as required to each reaction mixture to produce the desired composition by weight.

In preparing the neutral ferrous phosphate, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, several methods other than that reported in detail here, were tried. It is known that some neutral phosphates tend to precipitate in amorphous form and crystallization is often difficult. Usually prolonged digestion at elevated temperatures is required to convert from the amorphous to the crystalline state. Attempts to obtain the neutral ferrous salt by metathesis in aqueous solution were not entirely satisfactory because of the oxidation of the ferrous ion, which takes place most readily in neutral and alkaline solutions. Former experience with crystallization in gel medium had demonstrated advantages in such techniques, and the crystalline neutral ferrous phosphate was prepared in the present study by reaction in such medium.

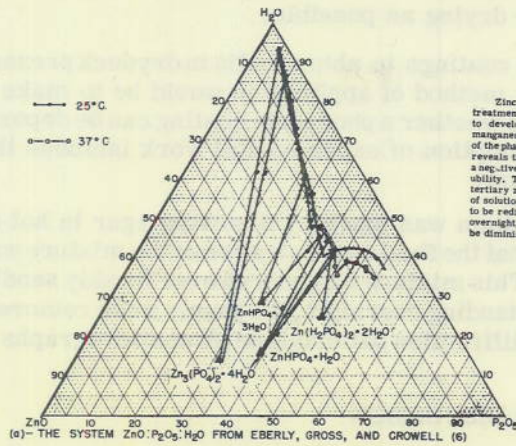
The details of the individual preparations of the ten phosphates included in this study are given in Appendix I. Immediately after preparation the X-ray diffraction pattern of each of these compounds was recorded, and the compounds were analyzed chemically where necessary. The X-ray diffraction apparatus and techniques are described in Appendix II, and Appendix III gives the analytical methods and results. Several photomicrographs were made of the crystals prepared in this study.

Phosphate Coatings

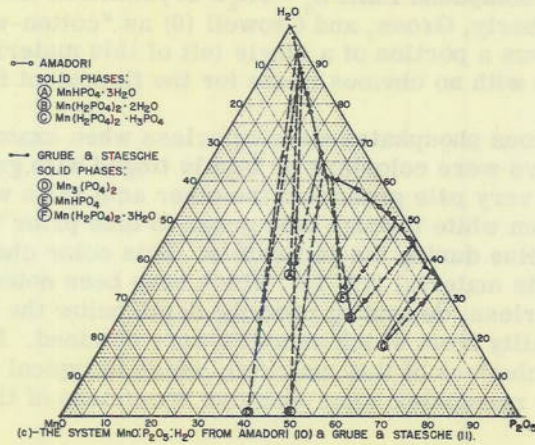
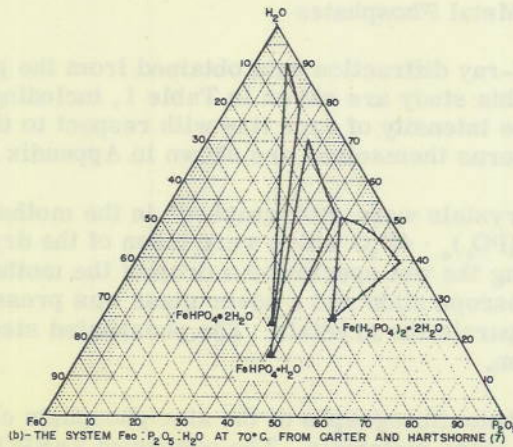
Phosphate coatings are normally applied by treating metal surfaces with hot solutions of manganese or zinc phosphates in phosphoric acid. In the present study the X-ray diffraction patterns were recorded of steel surfaces treated by such solutions.

A manganous phosphating bath (2) was heated by submerging the container in a boiling water bath. Freshly sandblasted steel panels were treated in the phosphating bath after it had come up to temperature, and were removed from the solution after completion of the hydrogen evolution, rinsed with water, dried, and the X-ray diffraction pattern recorded.

A zinc phosphating composition (2) was heated by submerging the container in a boiling water bath. Steel panels, sandblasted immediately before use, were placed in the bath after



Zinc phosphating baths for the pre-treatment of steel for painting are known to develop markedly less sludge than manganese baths (2,32). An examination of the phase diagram shown in Figure 1(a) reveals that tertiary zinc phosphate has a negative temperature coefficient of solubility. Thus in actual use in phosphating, tertiary zinc phosphate crystallizing out of solution during phosphating would tend to be redissolved as the bath cooled down overnight, and the amount of sludge would be diminished.



- AMADORI
SOLID PHASES:
A) MnHPO₄·3H₂O
B) Mn(H₂PO₄)₂·2H₂O
C) Mn(H₂PO₄)₂·H₃PO₄
- GRUBE & STAESCHE
SOLID PHASES:
D) Mn₃(PO₄)₂
E) MnHPO₄
F) Mn(H₂PO₄)₂·3H₂O

*For clarity several solid phase tie-lines have been omitted from the diagrams.

Figure 1 - Phase diagrams

it had come up to temperature, and were allowed to remain as long as there was any visible evolution of hydrogen. After completion of the hydrogen evolution they were removed from the bath, rinsed with water, and dried. An X-ray diffraction pattern and a photomicrograph were made as soon after drying as possible.

The application of phosphate coatings to ships' hulls in drydock presents unusual problems in technique. One possible method of application would be to make use of a viscous medium such as a paint base. As to whether a phosphate coating can be deposited on steel from such a mixture the following description of experimental work includes the work done on phosphating in a gelatinous medium.

A gelatinous phosphating medium was made by dissolving agar in hot distilled water and adding phosphating chemicals so that the final concentration of the mixture was equal to that of a liquid zinc phosphating bath (2). This mixture was poured over freshly sandblasted steel panels and allowed to set to a gel. After standing overnight, the panels were removed from the gel, rinsed in hot water, dried, and the X-ray diffraction patterns and photomicrographs recorded.

EXPERIMENTAL RESULTS AND DISCUSSION

The Pure Metal Phosphates

The X-ray diffraction data obtained from the patterns of the pure metal phosphates included in this study are shown in Table 1, including interplanar spacings or "d" values and the relative intensity of each line with respect to the strongest line of each pattern. The X-ray patterns themselves are shown in Appendix IV.

The crystals were photographed* in the mother liquors except those of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{Mn}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ which were taken of the dry salts sprinkled on a microscope slide. In preparing the wet specimens a drop of the mother liquor containing crystals was placed on a microscope slide and a cover glass was pressed over the drop causing it to spread out and separate the crystals. The phosphated steel panels were photographed by oblique illumination.

The photomicrographs of the zinc phosphate crystals, shown in Figure 2, are characteristic of these materials. The compound $\text{ZnHPO}_4 \cdot 3\text{H}_2\text{O}$ crystallizes from solution in small knots aptly described by Eberly, Gross, and Crowell (6) as "cotton-wool-like masses." The photograph, Figure 2(a), shows a portion of a single tuft of this material, and appears to be made up of individual crystals with no obvious cause for the flocculent formation.

The crystals of the acid ferrous phosphates were colorless when examined under the microscope and the mother liquors were colorless or faintly tinged with green. In bulk the secondary salt $\text{FeHPO}_4 \cdot 2\text{H}_2\text{O}$ was very pale green and the other acid salts white. The neutral ferrous phosphate varied from white through pale green to blue prior to separation from the gels, and became deep blue during the separation. This color change is characteristic of mineral deposits of this material (12, 13), which have been noted in many shades of green and blue as well as colorless, depending upon the depth below the surface of the earth when observed and the locality from which samples were obtained. Figure 3 shows a photomicrograph of one of the clusters of this material, which is typical of the crystals grown in gel medium and greatly resembles some massive specimens of the mineral.

*The photomicrographs were made by Mr. A. C. Simon of the Electrochemistry Branch of this Laboratory with a Spencer Research Microscope No. 3 having a binocular body No. 1, equipped with a Palo Vertical Photomicrographic Camera, and a 4" x 5" adapter. Reflected or transmitted illumination was used from an unfiltered tungsten-filament microscope lamp.

TABLE I
X-Ray Diffraction Data of the Pure Metal Phosphates

| Zinc Phosphates | | | | Ferrous Phosphates | | | | Manganese Phosphates | | | | | | | |
|-----------------------|------------------|----------------------|--------------------|----------------------------|------------------|-----------------------|------------------|-----------------------------|------------------|-----------------------------|------------------|-----------------------------|------------------|-------------------------------|------------------|
| $ZnHPO_4 \cdot 3H_2O$ | | $ZnHPO_4 \cdot H_2O$ | | $Fe_2(PO_4)_3 \cdot 8H_2O$ | | $FeHPO_4 \cdot 2H_2O$ | | $Fe(H_2PO_4)_2 \cdot 2H_2O$ | | $Mn(H_2PO_4)_2 \cdot 4H_2O$ | | $Mn(H_2PO_4)_2 \cdot 2H_2O$ | | $Mn(H_2PO_4)_2 \cdot H_2PO_4$ | |
| d | 1/λ ₀ | d | 1/λ ₀ * | d | 1/λ ₀ | d | 1/λ ₀ | d | 1/λ ₀ | d | 1/λ ₀ | d | 1/λ ₀ | d | 1/λ ₀ |
| 6.5 | .20 | 7.4 | .10 | 7.5 | .10 | 7.1 | .08 | 8.5 | .50 | 9.1 | .20 | 5.97 | .85 | 9.15 | .64 |
| 5.6 | 1.00 | 5.8 | .14 | 6.7 | .23 | 6.5 | 1.00 | 5.7 | .92 | 8.27 | 1.00 | 5.10 | .55 | 6.80 | .04 |
| 4.39 | .10 | 5.35 | .16 | 4.86 | .20 | 4.41 | .08 | 5.4 | .11 | 7.30 | .11 | 4.76 | .08 | 6.53 | .04 |
| 4.04 | .20 | 5.21 | .10 | 4.11 | .09 | 4.47 | .02 | 4.97 | .11 | 6.83 | .13 | 4.53 | 1.00 | 5.93 | .09 |
| 3.77 | .25 | 4.39 | .06 | 4.08 | .10 | 3.96 | .04 | 4.60 | .11 | 5.85 | .11 | 4.25 | .05 | 5.78 | .04 |
| 3.71 | .20 | 4.04 | .06 | 3.85 | .02 | 3.41 | .06 | 4.41 | .46 | 5.24 | .07 | 4.16 | .09 | 5.50 | .04 |
| 3.39 | 1.00 | 3.80 | .24 | 3.34 | .22 | 3.25 | .53 | 3.00 | .15 | 4.13 | .13 | 4.13 | .05 | 4.79 | .05 |
| 3.19 | .23 | 3.71 | .08 | 3.19 | .25 | 2.94 | .04 | 2.94 | .27 | 3.70 | .23 | 3.93 | .02 | 4.53 | .09 |
| 3.06 | .25 | 3.60 | .20 | 3.20 | .08 | 2.84 | .02 | 2.78 | .11 | 4.42 | .06 | 3.84 | .02 | 4.00 | 1.00 |
| 2.82 | .75 | 3.56 | .34 | 3.11 | .02 | 2.80 | .06 | 3.38 | 1.00 | 4.32 | .04 | 3.68 | .02 | 3.88 | .11 |
| 2.70 | .30 | 3.45 | .20 | 2.95 | .05 | 2.87 | .15 | 3.31 | .07 | 4.10 | .32 | 3.42 | .45 | 3.68 | .04 |
| 2.59 | .12 | 3.19 | .24 | 2.76 | .03 | 2.59 | .06 | 3.14 | .27 | 4.05 | .07 | 3.39 | .07 | 3.54 | .04 |
| 2.55 | .07 | 3.12 | .28 | 2.64 | .03 | 2.54 | .04 | 2.79 | .06 | 3.80 | .06 | 3.31 | .02 | 3.42 | .09 |
| 2.44 | .25 | 3.02 | .46 | 2.54 | .08 | 2.63 | .03 | 2.50 | .08 | 3.74 | .06 | 3.23 | .24 | 3.36 | .06 |
| 2.31 | .12 | 2.94 | .54 | 2.58 | .08 | 2.43 | .02 | 1.98 | .19 | 3.69 | .09 | 3.09 | .38 | 3.31 | .02 |
| 2.24 | .23 | 2.81 | 1.00 | 2.52 | .50 | 2.38 | .04 | 1.66 | .07 | 3.63 | .06 | 2.99 | .05 | 3.23 | .16 |
| 2.19 | .15 | 2.78 | .20 | 2.46 | .05 | 2.34 | .02 | 1.62 | .07 | 3.30 | .06 | 2.96 | .05 | 3.07 | .06 |
| 2.11 | .25 | 2.72 | .08 | 2.41 | .03 | 2.20 | .02 | 1.55 | .07 | 3.21 | .13 | 2.85 | .02 | 2.99 | .04 |
| 2.01 | 1.0b | 2.65 | .34 | 2.37 | .02 | 2.16 | .02 | 1.53 | .04 | 3.20 | .40 | 2.78 | .05 | 2.89 | .13 |
| 1.94 | .10 | 2.56 | .08 | 2.30 | .03 | 2.13 | .02 | 1.53 | .15 | 3.12 | .06 | 2.67 | .05 | 2.82 | .26 |
| 1.82 | .38 | 2.52 | .08 | 2.18 | .02 | 2.08 | .01 | 2.23 | .15 | 3.08 | .07 | 2.41 | .24 | 2.77 | .26 |
| 1.78 | .18b | 2.49 | .08 | 2.06 | .05 | 2.04 | .02 | 2.20 | .11 | 3.03 | .22 | 2.36 | .05 | 2.68 | .02 |
| 1.72 | .07 | 2.42 | .60 | 1.92 | .04 | 1.94 | .02 | 2.18 | .07 | 2.92 | .07 | 2.33 | .02 | 2.66 | .02 |
| 1.67 | .12 | 2.39 | .50 | 1.87 | .02 | 1.92 | .04 | 2.16 | .19 | 2.89 | .07 | 2.25 | .11 | 2.62 | .02 |
| 1.60 | .12b | 2.28 | .14 | 1.85 | .02 | 1.89 | .06 | 2.13 | .11 | 2.74 | .06 | 2.19 | .05 | 2.57 | .02 |
| 1.57 | .15 | 2.26 | .14 | 1.81 | .02 | 1.86 | .02 | 2.10 | .07 | 2.71 | .11 | 2.08 | .07 | 2.54 | .02 |
| 1.52 | .25b | 1.96 | .52 | 1.77 | .02 | 1.82 | .01 | 2.08 | .04 | 2.65 | .11 | 1.97 | .11 | 2.38 | .04 |
| 1.487 | .10 | 1.78 | .22 | 1.67 | .03 | 1.77 | .01 | 2.06 | .04 | 2.57 | .07 | 1.95 | .02 | 2.29 | .02 |
| 1.446 | .12 | 1.74 | .08 | 1.62 | .04 | 1.62 | .02b | 2.04 | .04 | 2.44 | .09 | 1.87 | .02 | 2.27 | .02 |
| 1.411 | .05 | 1.73 | .06 | 1.57 | .02b | 1.70 | .01 | 2.02 | .04 | 2.40 | .07 | 1.85 | .02 | 2.23 | .02 |
| 1.330 | .07 | 1.68 | .06 | 1.47 | .03 | 1.65 | .01 | 1.94 | .19 | 2.33 | .07 | 1.84 | .02 | 2.20 | .04 |
| 1.280 | .05 | 1.67 | .10 | 1.45 | .02 | 1.62 | .02b | 1.73 | .07 | 2.30 | .09 | 1.81 | .02 | 2.18 | .04 |
| 1.254 | .07 | 1.62 | .14 | 1.311 | .03b | 1.57 | .02b | 1.70 | .19 | 2.28 | .09 | 1.78 | .02 | 2.07 | .06 |
| 1.246 | .07 | 1.60 | .06 | 1.286 | .06 | 1.489 | .01 | 1.53 | .11 | 2.20 | .09 | 1.75 | .02 | 2.05 | .04 |
| 1.196 | .05 | 1.57 | .06 | 1.201 | .03 | 1.474 | .04 | 1.47 | .07 | 2.15 | .06b | 1.74 | .02 | 2.02 | .34 |
| 1.141 | .05 | 1.55 | .22 | 1.195 | .03 | | | 1.43 | .07 | 2.02 | .09 | 1.71 | .02 | 2.01 | .04 |
| | | 1.54 | .10 | 1.168 | .03 | | | | | 1.75 | .09 | 1.70 | .07 | 1.96 | .07 |
| | | 1.51 | .10 | | | | | | | 1.64 | .04 | 1.69 | .33 | 1.69 | .04 |
| | | 1.50 | .08 | | | | | | | 1.58 | .03 | 1.66 | .02 | 1.67 | .02 |
| | | 1.471 | .06 | | | | | | | 1.58 | .05 | 1.64 | .02 | 1.63 | .02 |
| | | 1.442 | .04 | | | | | | | 1.52 | .02 | 1.61 | .02 | 1.61 | .02 |
| | | 1.434 | .04 | | | | | | | 1.477 | .03 | 1.60 | .02 | 1.60 | .02 |
| | | 1.426 | .04 | | | | | | | 1.55 | .02 | 1.55 | .02 | 1.55 | .02 |
| | | 1.415 | .04 | | | | | | | 1.477 | .02 | 1.477 | .02 | 1.52 | .02 |
| | | 1.396 | .12 | | | | | | | 1.436 | | 1.436 | | | |
| | | 1.357 | .10 | | | | | | | | | | | | |
| | | 1.357 | .10 | | | | | | | | | | | | |
| | | 1.330 | .04 | | | | | | | | | | | | |
| | | 1.249 | .06 | | | | | | | | | | | | |
| | | 1.224 | .06 | | | | | | | | | | | | |
| | | 1.197 | .04 | | | | | | | | | | | | |

b - denotes a broad or fuzzy band.

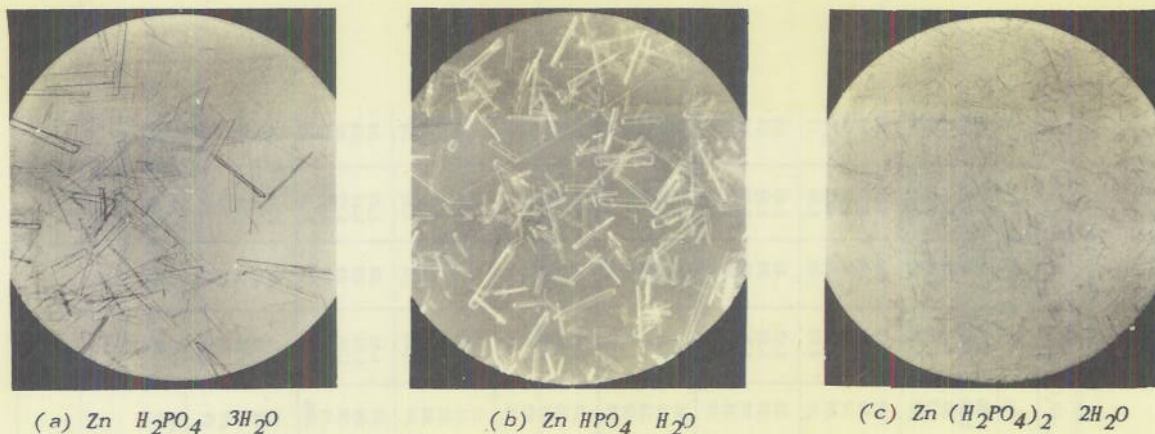


Figure 2 - Photomicrographs of the zinc phosphates (50X)



Figure 3 - Photomicrograph of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ crystals grown in gel medium

Photomicrographs of the manganese phosphates prepared in this study are shown in Figure 4. The ditrimanganous phosphate was very pale pink and the more acid salts appeared colorless. The mother liquors were pink except that in the case of the salt $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_3\text{PO}_4$ it was colorless. The crystals of the ditrimanganous phosphate were usually very small and had a marked tendency to cluster, both when wet with the mother liquor and after drying. There was no obvious cause for this behavior, but great difficulty was encountered in trying to obtain an area relatively free of these clusters in order to obtain a clear photomicrograph.

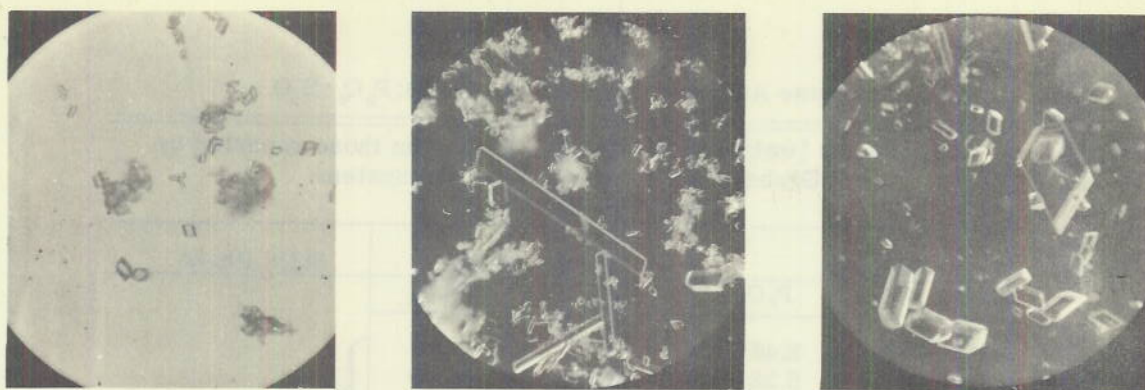
(a) $Mn_5 H_2 (PO_4)_4 \cdot 4H_2O$ (b) $Mn (H_2PO_4)_2 \cdot 2H_2O$ (c) $Mn (H_2PO_4)_2 \cdot H_3PO_4$

Figure 4 - Photomicrographs of the Manganese Phosphates (50X)

The work done at this Laboratory on the acid manganese phosphates supports that reported by Amadori (10) rather than that by Grube and Staesche (11), who reported the system $Mn_3(PO_4)_2 : H_3PO_4 : H_2O$. A recalculation of their data to the same basis as reported by Amadori appears in Table 2 together with the data of Amadori, and both are plotted in Figure 1(c). For clarity several of the solid phase tie-lines are omitted from the diagram. It is seen that the two solubility curves are identical, but there are discrepancies in the solid phases reported.

Amadori reported the use of well-established gravimetric methods in his analytical work. Grube and Staesche did not describe the methods employed in their analyses of the solid phases; but they reported that the liquid phases were analyzed by titration with sodium hydroxide. The agreement in the solubility curves in the two papers indicates that either analytical method may be employed in this concentration range, but if the solid phases reported by Grube and Staesche were analyzed by titration, the results are of questionable significance. In the liquid phases, considerably more phosphate ion is present than manganous ion, but considerably higher concentration of manganous ion would be present in the solid phases.

Joulin (14) studied the kinetics of the double decomposition of manganous sulfate and sodium carbonate, and reported that the velocity of the reaction was dependent upon the concentration of the solutions and the relative concentrations of the metal and carbonate ions. When an excess of manganous ion was present, the reaction was greatly retarded, and a matter of hours was required to complete it. Although Joulin was primarily interested in the reaction involving carbonates, he stated that the action of phosphates was substantially identical. Thus in the work reported by Grube and Staesche (11) if the analyses of the moist solids were carried out alkalimetrically the results are questionable.

The compound ditrimanganous phosphate was first described and named by Erlenmeyer and Heinrich (15) who assigned it the formula $Mn_3H_2(PO_4)_4 \cdot 4H_2O$. The mineral hureaulite, the natural form of this material, has been studied by several investigators including Haushofer (16) and de Schulten (17). The later synthesized crystals of artificial hureaulite, which analysis showed to have the formula $Mn_3H_2(PO_4)_4 \cdot 4H_2O$. Viard (18) and Prjanisch-nikow (19) also prepared this compound. Amadori (10) assigned the formula $Mn_5H_2(PO_4)_4 \cdot 5H_2O$ to a similar compound while Durer and Schmid (3,4) reported that the manganese phosphate coatings are $Mn_5H_2(PO_4)_4 \cdot 5\frac{1}{2}H_2O$. The compound studied at this Laboratory appeared to be the tetrahydrate and the composition of the manganese phosphate coatings was shown

TABLE 2
Phase Analyses of the System $\text{MnO}:\text{P}_2\text{O}_5:\text{H}_2\text{O}$

| Solution | | Moist Solids | | Solid Phase |
|---|------------------------|--------------|------------------------|--|
| MnO | P_2O_5 | MnO | P_2O_5 | |
| .816 | 2.435 | - | - | } $\text{Mn}_3(\text{PO}_4)_2$ |
| 2.23 | 5.28 | 18.29 | 15.12 | |
| 3.22 | 7.66 | 13.02 | 13.78 | |
| | | 33.6 | 25.39 | |
| 3.53 | 8.56 | 23.99 | 26.69 | } Mn-H PO_4 |
| 6.22 | 14.30 | - | - | |
| 8.24 | 19.98 | 25.9 | 32.38 | |
| 8.75 | 21.09 | - | - | |
| 10.41 | 25.29 | 17.21 | 29.52 | } |
| | | 36.8 | 41.06 | |
| 11.75 | 28.11 | - | - | } $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ |
| 10.34 | 28.58 | 15.36 | 35.05 | |
| 6.65 | 35.42 | 15.56 | 41.28 | |
| 5.06 | 39.48 | - | - | |
| 3.64 | 43.23 | 13.20 | 44.87 | |
| | | 15.01 | 45.12 | |
| 2.38 | 48.29 | 15.69 | 47.26 | } |
| 1.48 | 55.04 | - | - | |
| 1.43 | 60.45 | - | - | |
| B. Values (weight percent) reported by Amadori (10) | | | | |
| 1.97 | 5.88 | 30.52 | 30.90 | } $\text{Mn H PO}_4 \cdot 3\text{H}_2\text{O}$ |
| 5.04 | 12.22 | 29.92 | 31.25 | |
| 6.55 | 15.46 | 30.12 | 31.40 | |
| 9.74 | 23.16 | 29.15 | 31.54 | |
| 11.57 | 27.45 | - | - | } $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ |
| 9.21 | 30.42 | 21.71 | 45.62 | |
| 6.02 | 36.00 | 21.16 | 47.16 | |
| 3.78 | 43.10 | 19.75 | 48.28 | |
| 2.76 | 45.76 | - | - | |
| 2.29 | 47.40 | - | - | |
| 1.81 | 50.75 | 19.18 | 50.06 | } |
| 1.40 | 53.45 | 20.13 | 50.60 | |
| 1.08 | 59.45 | 18.98 | 51.90 | |
| 0.62 | 62.25 | 8.46 | 61.68 | } $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_3\text{PO}_4$ |
| 0.39 | 65.57 | 7.96 | 64.66 | |

to correspond to this material. The possibility exists that this compound is capable of enclosing zeolitic water, and that all the hydrates mentioned above are the same tetrahydrate compound containing various amounts of loosely held zeolitic water. This would appear in the chemical analysis, but would have relatively little effect on the X-ray diffraction pattern.

A water solution of monomanganous phosphate, $Mn(H_2PO_4)_2 \cdot 2 H_2O$, was digested at room temperature for several days, and a white crystalline material deposited from the solution. The crystals were collected on a filter, washed with water, alcohol, and ether; and the X-ray diffraction pattern recorded. A similar solution was heated to boiling, the solid phase filtered off, washed, dried, and the X-ray diffraction pattern recorded. The patterns obtained from these materials were compared with those established by the studies described above, and with standard patterns from the ASTM Card File (5).

In Table 3 are shown the "d" values for the X-ray diffraction patterns of the crystals obtained from water solutions of monomanganous phosphate, and the patterns for $MnHPO_4 \cdot 3H_2O$ and $Mn_5H_2(PO_4)_4 \cdot 4H_2O$. Column 1 shows the pattern obtained from the crystals deposited from the solution when allowed to stand at room temperature, and column 2 shows the pattern obtained from crystals deposited by boiling the solution.

Phosphate Coatings

A coating deposited from the manganese phosphating bath gave an X-ray diffraction pattern having the "d" values shown in Table 4, column 1. Column 2 of this table shows the "d" values observed for the material $Mn_5H_2(PO_4)_4 \cdot 4H_2O$.

The X-ray diffraction pattern of a coating deposited by a zinc phosphate bath is shown in Figure 5(a). Table 5, columns 1 and 2, shows the observed interplanar spacings of the patterns of the phosphate coating and the compound $Zn_3(PO_4)_2 \cdot 4H_2O$ taken from the ASTM Card File (5).

A photomicrograph of a zinc phosphate coating deposited from a hot solution is shown in Figure 6(a).

The coating deposited from gel medium on the steel surface was made up of small adherent crystals that covered the surface very uniformly. A photomicrograph of such a panel is shown in Figure 6(b). The X-ray diffraction pattern obtained from the panel is shown in Figure 5, (b), and the observed "d" values for this pattern are shown in Table 5, column 3. The similarity of the coatings deposited from a hot solution and a gel medium is quite apparent from the photographs shown in Figure 6. The X-ray patterns shown in Figure 5 suggest that both coatings are oriented, although along different crystal planes. Further investigation, however, would be required to determine the true significance of the observed variations.

CONCLUSIONS

The X-ray diffraction patterns of the following metal phosphates have been established by this study:

| <u>Formula</u> | <u>Name</u> |
|-----------------------------|--------------------------------------|
| $ZnHPO_4 \cdot 3H_2O$ | Secondary zinc phosphate trihydrate |
| $ZnHPO_4 \cdot H_2O$ | Secondary zinc phosphate monohydrate |
| $Zn(H_2PO_4)_2 \cdot 2H_2O$ | Primary zinc phosphate dihydrate |

TABLE 3
Hydrolysis of $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$
X-Ray Diffraction Patterns of the Hydrolysis Products

| Hydrolysis at Room Temp | | Hydrolysis at Boiling Temp | | $\text{Mn HPO}_4^* \cdot 3\text{H}_2\text{O}$ | | $\text{Mn}_2\text{H}_5(\text{PO}_4)_4^\dagger \cdot 4\text{H}_2\text{O}$ | |
|-------------------------|------------------|----------------------------|------------------|---|------------------|--|------------------|
| d | I/I ₀ | d | I/I ₀ | d | I/I ₀ | d | I/I ₀ |
| | | 9.0 | .08 | | | 9.1 | .20 |
| | | 8.3 | 1.00 | | | 8.27 | 1.00 |
| | | 6.7 | .04 | | | 7.30 | .11 |
| | | 6.24 | .06 | | | 6.85 | .13 |
| 5.4 | .54 | 5.50 | .04 | 5.49 | .70 | 5.85 | .11 |
| 4.7 | .39 | 4.68 | .08 | 4.81 | .60 | 5.24 | .07 |
| 4.57 | 1.00 | 4.49 | .06 | 4.61 | 1.00 | 4.60 | .13 |
| 3.73 | .24 | 4.38 | .06 b | 3.74 | .30 | 4.49 | .06 |
| 3.49 | .57 | 4.20 | .02 | 3.49 | 1.00 | 4.42 | .06 |
| 3.11 | .63 | 4.13 | .10 | 3.11 | .40 | 4.32 | .04 |
| 3.07 | .36 | 4.10 | .36 | | | 4.10 | .32 |
| 2.84 | .36 | 3.90 | .10 | 2.84 | .34 | 4.05 | .07 |
| 2.75 | .66 | 3.80 | .04 | 2.75 | .60 | 3.80 | .06 |
| 2.61 | .21 | 3.73 | .02 | 2.61 | .20 | 3.74 | .06 |
| 2.54 | .12 | 3.69 | .06 | 2.54 | .02 | 3.69 | .09 |
| 2.42 | .12 | 3.41 | .04 | 2.41 | .20 | 3.63 | .06 |
| 2.39 | .12 | 3.30 | .10 | | | 3.30 | .06 |
| 2.33 | .12 | 3.21 | .10 | 2.33 | .06 | 3.21 | .13 |
| 2.24 | .15 | 3.18 | .36 | 2.24 | .20 | 3.20 | .40 |
| 2.20 | .09 | 3.12 | .04 | 2.16 | .04 | 3.12 | .06 |
| 2.11 | .24 | 3.07 | .06 | 2.11 | .18 | 3.08 | .07 |
| 2.09 | .24 | 3.03 | .22 | | | 3.03 | .22 |
| 2.06 | .21 | 2.90 | .08 b | | | 2.92 | .07 |
| 2.00 | .21 | 2.71 | .08 | 2.01 | .16 | 2.89 | .07 |
| 1.96 | .12 | 2.67 | .04 | 1.962 | .16 | 2.74 | .06 |
| 1.95 | .12 | 2.65 | .14 | | | 2.71 | .11 |
| 1.91 | .09 | 2.57 | .10 | 1.910 | .12 | 2.65 | .11 |
| 1.89 | .12 | 2.44 | .08 | | | 2.57 | .07 |
| 1.82 | .15 | 2.28 | .08 b | 1.824 | .16 | 2.44 | .09 |
| 1.78 | .21 | 2.21 | .08 | 1.788 | .16 | 2.40 | .07 |
| 1.74 | .12 | 2.02 | .08 | 1.746 | .02 | 2.33 | .07 |
| 1.70 | .24 | 1.97 | .06 | 1.707 | .26 | 2.30 | .09 |
| 1.66 | .15 | 1.94 | .04 | 1.666 | .04 | 2.28 | .09 |
| 1.62 | .18 | 1.76 | .06 | 1.619 | .20 | 2.20 | .09 |
| | | 1.74 | .06 | | | 2.15 | .06 b |
| | | 1.72 | .06 | | | 2.02 | .09 |
| | | 1.69 | .04 | | | 1.75 | .09 |
| | | 1.66 | .04 | | | 1.64 | .04 |
| | | 1.65 | .10 | | | 1.59 | .03 |
| | | 1.58 | .06 | | | 1.58 | .02 |
| | | 1.51 | .04 | | | 1.52 | .02 |
| | | | | | | 1.477 | .03 |

b Denotes a broad or fuzzy line.

* ASTM Card # 680 (5)

† Pattern established in the present study.

TABLE 4
X-Ray Diffraction Data of
Manganese Phosphated Steel

| 1 Phosphated Steel | | 2* | |
|-----------------------|------------------|---|------|
| d | I/I ₀ | Mn ₅ H ₂ (PO ₄) ₄ ·4H ₂ O | |
| 8.2 | 1.00 | 9.1 | .20 |
| 7.30 | .50 | 8.27 | 1.00 |
| 6.93 | .25 | 7.30 | .11 |
| 4.84 | .25 | 6.85 | .13 |
| | | 5.85 | .11 |
| 4.76 | .30 | 5.24 | .07 |
| 4.60 | .25 | 4.60 | .13 |
| 4.49 | .25 | 4.49 | .06 |
| | | 4.42 | .06 |
| 4.32 | .25 | 4.32 | .04 |
| 4.10 | .25b | 4.10 | .32 |
| | | 4.05 | .07 |
| | | 3.80 | .06 |
| | | 3.74 | .06 |
| 3.66 | .12 | 3.69 | .09 |
| | | 3.63 | .06 |
| 3.30 | .25 | 3.30 | .06 |
| | | 3.21 | .13 |
| 3.20 | .75 | 3.20 | .40 |
| | | 3.12 | .06 |
| 3.08 | .25 | 3.08 | .07 |
| 3.00 | .30b | 3.03 | .22 |
| 2.90 | .30b | 2.92 | .07 |
| 2.89 | .12 | 2.89 | .07 |
| | | 2.74 | .06 |
| 2.71 | .12 | 2.71 | .11 |
| 2.65 | .12 | | |
| 2.60 | .12 | 2.65 | .11 |
| 2.56 | .12 | 2.57 | .07 |
| 2.45 | .12 | 2.44 | .09 |
| 2.40 | .12 | 2.40 | .07 |
| 2.33 | .12 | 2.33 | .07 |
| 2.30 | .12 | 2.30 | .09 |
| | | 2.28 | .09 |
| 2.18 | .12 | 2.20 | .09 |
| 2.14 | .12 | 2.15 | .06b |
| 2.08 | .25 | 2.02 | .09 |
| 1.85 | .12 | | |
| 1.68 | .12 | 1.75 | .09 |
| 1.64 | .12 | 1.64 | .04 |
| 1.59 | .12 | 1.59 | .03 |
| 1.58 | .12 | 1.58 | .05 |
| 1.51 | .12 | 1.52 | .02 |
| | | 1.477 | .03 |

* Pattern established in the present study.
b Denotes a broad or fuzzy line.

Formula

Name

| | |
|---|---|
| Fe ₃ (PO ₄) ₂ ·8H ₂ O | Tertiary ferrous phosphate octahydrate |
| FeHPO ₄ ·2H ₂ O | Secondary ferrous phosphate dihydrate |
| FeHPO ₄ ·H ₂ O | Secondary ferrous phosphate monohydrate |
| Fe(H ₂ PO ₄) ₂ ·2H ₂ O | Primary ferrous phosphate dihydrate |
| Mn ₅ H ₂ (PO ₄) ₄ ·4H ₂ O | Ditrimanganous phosphate tetrahydrate |
| Mn(H ₂ PO ₄) ₂ ·2H ₂ O | Primary manganous phosphate dihydrate |
| Mn(H ₂ PO ₄) ₂ ·H ₃ PO ₄ | Primary manganous phosphate monophosphoric acid |

The observed "d" values for the X-ray diffraction patterns for these compounds were recorded in Table 1. This table also showed the intensities of the diffraction lines relative to the strongest line of each pattern.

The X-ray diffraction patterns of the crystals deposited from water solutions of Mn(H₂PO₄)₂·2H₂O have shown that at room temperature MnHPO₄·2H₂O is formed, but at boiling temperature crystals of Mn₅H₂(PO₄)₄·4H₂O are produced. These observations were made in comparing the X-ray patterns of the crystals with X-ray patterns established by the present study and those in the ASTM Card File (5). These conclusions substantiate the work of Erlenmeyer and Heinrich (15) and Viard (18), but again refute the work reported by Grube and Staesche (11), who reported that the compound Mn₃(PO₄)₂·2H₂O is deposited from a solution of the monomanganous phosphate.

It is unlikely that manganous phosphate coatings of normal composition may be readily obtained at room temperature since the composition of the material deposited from monomanganous phosphate solutions differs with temperature as shown above.

This study has indicated that it may be possible to obtain zinc phosphate coatings of normal composition and appearance at room temperature from gelatinous medium.

TABLE 5
X-Ray Diffraction Data of Zinc Phosphated Steel†

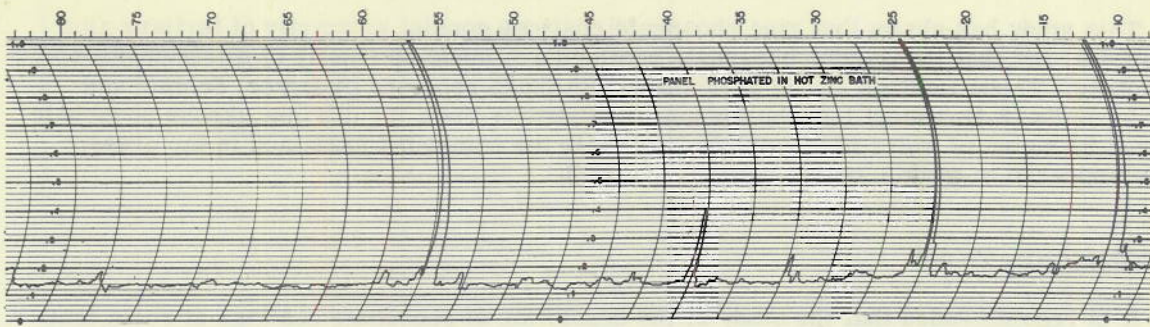
| 1 Phosphated in Hot Bath | | 2 $Zn_3(PO_4)_2 \cdot 4H_2O^*$ $Zn_3(PO_4)_2 \cdot 4H_2O^\ddagger$ | | | | 3 Phosphated in Gel Medium | |
|--------------------------------|------------------|---|------------------|-------|------------------|----------------------------------|------------------|
| d | I/I ₀ | d | I/I ₀ | d | I/I ₀ | d | I/I ₀ |
| 9.1 | 1.00 | 9.1 | .40 | | | 9.1 | .82 |
| | | 5.3 | .08 | 5.38 | .05 | | |
| | | 5.1 | .06 | 5.18 | .05 | 5.1 | .04 |
| 4.86 | .06 | 4.86 | .12 | 4.86 | .05 | 4.86 | .04 |
| 4.59 | 1.00 | 4.59 | .25 | 4.58 | .75 | 4.59 | .11 |
| 4.40 | .10 | 4.40 | .25 | 4.41 | .05 | 4.42 | 1.00 |
| | | 4.01 | .20 | 4.00 | .08 | | |
| | | 3.65 | .08 | 3.87 | .05 | | |
| 3.47 | .06 | 3.47 | .40 | 3.66 | .025 | 3.66 | .04b |
| 3.39 | .12 | 3.13 | .08 | 3.46 | .38 | 3.46 | .07 |
| 2.85 | .30 | 2.85 | 1.00 | 3.37 | .38 | 3.39 | .07 |
| | | 2.75 | .04 | 2.84 | 1.00 | 3.36 | .18 |
| 2.63 | .04 | 2.63 | .40 | 2.63 | .25 | 2.83 | .08b |
| 2.61 | .08 | 2.52 | .40 | 2.60 | .25 | 2.75 | .02 |
| 2.52 | .04 | 2.42 | .20 | 2.52 | .25 | 2.64 | .02 |
| 2.42 | .02 | 2.33 | .10 | 2.41 | .15 | 2.54 | .20 |
| 2.33 | .06 | 2.27 | .20 | 2.32 | .15 | 2.43 | .11 |
| 2.27 | .08 | 2.20 | .08 | 2.26 | .25 | 2.27 | .02 |
| | | 2.15 | .10 | 2.20 | .025 | 2.21 | .11 |
| 2.09 | .08 | 2.09 | .14 | 2.15 | .05 | 2.16 | .02 |
| | | 2.03 | .04 | 2.09 | .05 | 2.11 | .02 |
| | | 2.00 | .20 | 1.994 | .25 | | |
| 1.94 | .08 | 1.94 | .35 | 1.933 | .50 | 1.93 | .08 |
| 1.82 | .02 | 1.82 | .30 | 1.860 | .025 | | |
| 1.77 | .02 | 1.78 | .04 | 1.819 | .50 | | |
| 1.73 | .02 | 1.73 | .08 | 1.774 | .025 | 1.77 | .07 |
| 1.69 | .02 | 1.70 | .10 | 1.728 | .05 | | |
| 1.66 | .02 | 1.67 | .04 | 1.692 | .05 | 1.67 | .04 |
| 1.63 | .02 | 1.63 | .04 | 1.662 | .05 | | |
| | | 1.59 | .06 | 1.631 | .025 | 1.63 | .02 |
| 1.52 | .08 | 1.56 | .12 | 1.594 | .025 | 1.59 | .02b |
| | | 1.52 | .14 | 1.561 | .05 | | |
| 1.50 | .02 | 1.51 | .14 | 1.521 | .05 | | |
| 1.48 | .02 | 1.48 | .02 | 1.505 | .05 | 1.48 | .07 |
| | | 1.440 | .08 | 1.350 | .05 | | |
| | | 1.410 | .08 | 1.322 | .025 | | |
| | | 1.385 | .04 | 1.233 | .025 | | |
| | | 1.353 | .08 | | | | |

† The strong lines from the steel base itself.

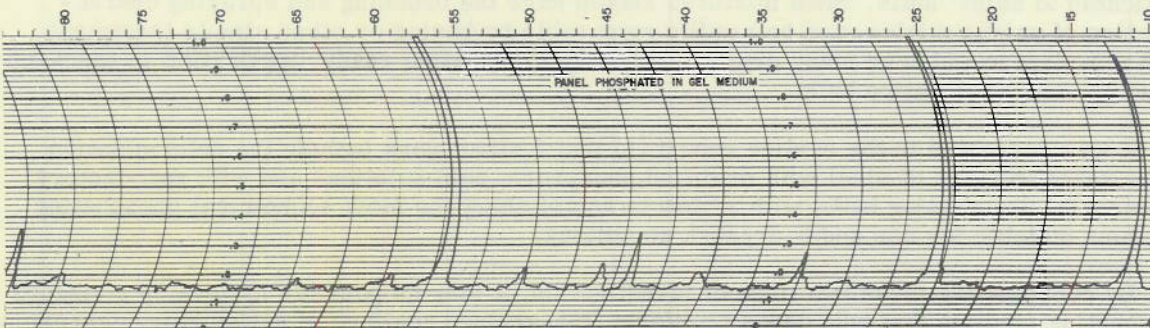
* ASTM (5) Card #2346

‡ ASTM (5) Card #2373

b Denotes a broad or fuzzy line.



(a) Panel phosphated in hot zinc bath

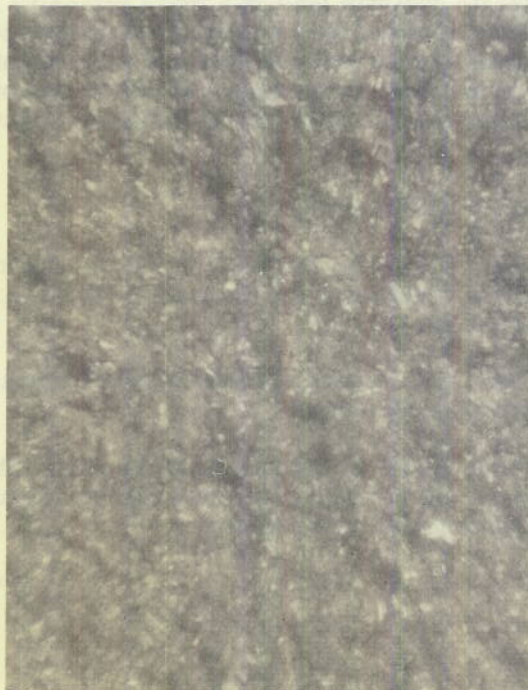


(b) Panel phosphated in gel medium

Figure 5 - X-ray diffraction patterns of zinc phosphate coatings on steel



(a) Panel phosphated in hot bath



(b) Panel phosphated in gel medium

Figure 6 - Zinc phosphate coatings on steel

This study has shown that zinc phosphate coatings consist primarily of tertiary zinc phosphate, and that manganous phosphate coatings are made up chiefly of ditrimanganous phosphate. These findings are in agreement with those reported by Durer, Schmid and v. Schweinitz (3,4), except that the formula reported by them for ditrimanganous phosphate showed $5\frac{1}{2}$ moles of water of crystallization while the compound examined in the present study appeared to contain only 4 moles.

RECOMMENDATIONS

It is recommended that the study of the deposition of phosphate coatings at room temperature from viscous medium be continued and extended to include mixtures that would be applicable to ships' hulls. Such mixtures should have the brushing and spraying characteristics of paint vehicles, and be readily removable by hosing or other simple treatment. Such a system would have many distinct advantages, including ready application to touch-up areas as well as to entire hulls.

It was suggested in the earlier report (1) that further work include the determination of the reaction rates of steel with modified phosphoric acid solutions and with satisfactory commercial phosphating baths with a view to establishing the most economical phosphating solutions suitable for use under drydock conditions.

By coordinating these two lines of investigation, it may be possible to develop a viscous phosphating medium that will deposit uniform fine-grained coatings of satisfactory corrosion-resistance on steel at ordinary temperatures.

It is recommended that continuation of the investigation of the problem concerning phosphate coatings include a more extensive X-ray diffraction study of phosphated steel panels correlated with a corrosion-resistance evaluation of the same panels. Such studies would determine whether coatings rated unsatisfactory show a structure different from that of satisfactory coatings. Identification of the materials in such coatings may be possible through use of the X-ray diffraction patterns established by the present study.

ACKNOWLEDGMENTS

Dr. T. P. May, Engineer of the International Nickel Company and former Head of the Corrosion Section of the Chemistry Division, this Laboratory, has acted as consultant on this problem.

Mr. A. C. Simon, chemist of this Branch of the Laboratory, took the photomicrographs presented in this report.

Mrs. Hazel G. Mortenson of the NRL Library has been very helpful in obtaining rare journals and in tracing the often inaccurate and incomplete references to the early literature pertinent to this problem.

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APPENDIX I
Preparation of the Pure Metal Phosphates

Zinc Phosphates

Materials—The materials used in the synthesis of the several zinc phosphates were Baker's C.P. zinc oxide, phosphoric acid (85 percent solution), and distilled water.

Methods—A slurry of zinc oxide and distilled water was made up in a tared beaker, and the phosphoric acid solution was gradually added to this mixture with stirring. After cooling to room temperature, water was added to bring the mixture to the desired concentration. Usually three duplicate 200-g mixes were made, although several preparations were made in larger amounts. Table 6 shows the amount of materials mixed in preparing the several zinc salts, taken from values lying within the phase boundaries for each salt, as shown in the phase diagram developed by Eberly, Gross, and Crowell (6), Figure 1(a).

TABLE 6
Mixtures Used in Preparing the Zinc Phosphates

| No. | Salt | ZnO (%) [*] | P ₂ O ₅ (%) [*] |
|-----|---|----------------------|--|
| 1 | Zn ₃ (PO ₄) ₂ ·4H ₂ O | 20 | 15 |
| 2 | ZnHPO ₄ ·3H ₂ O | 20 | 30 |
| 3 | ZnHPO ₄ ·H ₂ O | 20 | 40 |
| 4 | Zn(H ₂ PO ₄) ₂ ·2H ₂ O | 10 | 50 |

^{*}Weight percent—sufficient water was present to make 100 percent in each case.

Mixtures 2, 3, and 4 were heated to dissolve all the solid phase, and allowed to digest for several weeks. Mixtures 2 and 4 were allowed to stand at room temperature, but 3 was maintained at 40°C on a hot plate because the desired phase appears above 37°C as indicated by the phase diagram, Figure 1(a). Mixture 1 was cooled in a salt and ice bath in order to dissolve the solid phase, then allowed to digest at room temperature for several weeks. All mixtures were stirred occasionally.

The solids appearing in the various mixtures were filtered on a sintered glass crucible with suction from an aspirator to remove as much of the mother liquor as possible. The tertiary salt was washed with water, alcohol, and ether, and dried by suction; the other salts were washed free of the mother liquor with ether.

The crystals were immediately mounted for X-ray diffraction examination, in order that the patterns could be recorded from the freshly prepared materials.

Ferrous Phosphates

Materials — The chemicals used in the syntheses of the ferrous phosphates were all C.P. grade and were:

| <u>Material</u> | <u>Manufacturer</u> | <u>Remarks</u> |
|---------------------------------------|-------------------------|---------------------------------------|
| Iron Powder | Baker | Reduced by H ₂ |
| Na ₂ HPO ₄ | " | { 85% Solution, Meta and pyro free |
| H ₃ PO ₄ | " | |
| FeSO ₄ · 7H ₂ O | " | |
| NH ₄ OH | " | |
| Acetic acid | " | |
| KH ₂ PO ₄ | Mallinckrodt | Meta and pyro free |
| Sodium silicate | Philadelphia Quartz Co. | |
| Hydrazine hydrochloride | Eastman Kodak | |
| Agar agar | — | |

Solutions of the required concentrations were made up with distilled water.

Methods - Acid Phosphates (Aqueous Medium) — The acid ferrous phosphates were prepared by selecting points lying within the phase areas shown in the diagram Figure 1(b) developed by Carter and Hartshorne (7), and mixing the corresponding amounts of iron powder and phosphoric acid. Table 7 shows the mixtures used.

TABLE 7
Mixtures Used in Preparing the Ferrous Phosphates

| No. | Salt | Fe (%)* | P ₂ O ₅ (%)* |
|-----|--|------------|---------------------------------------|
| 1 | FeHPO ₄ · 2H ₂ O | 15 | 20 |
| 2 | FeHPO ₄ · H ₂ O | 15 | 30 |
| 3 | Fe(H ₂ PO ₄) ₂ · 2H ₂ O | 15 | 50 |

* Weight percent - sufficient water was present to make 100 percent in each case.

Hydrazine solution, made by neutralizing hydrazine hydrochloride with ammonium hydroxide, was added to the phosphoric acid solution to give a 1 percent concentration by weight. After this mixture was heated to boiling the iron metal powder was added slowly with constant stirring, and any water that evaporated during the reaction was replaced with the 1 percent hydrazine solution. The solution was maintained at 80° - 90° C during the reaction.

The crystals that developed in these reaction mixes were filtered off on a sintered glass crucible, and as much as possible of the mother liquor was removed by suction. FeHPO₄ · 2H₂O was washed free of the mother liquor with water, alcohol, and ether. Since the crystals formed in mixtures 2 and 3 are subject to hydrolysis, the mother liquor was

removed by prolonged rinsing with ether. After the crystals were sucked dry on the filter, the X-ray patterns were recorded immediately.

Methods - Neutral Ferrous Phosphate (Gel Medium) - Neutral ferrous phosphate, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ was synthesized by reaction in silica and agar gels. The silica gel was prepared by treating sodium silicate solution (d 1.06) with an equal volume of 1 N acetic acid solution containing sufficient $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to give a final concentration of 0.2 M. After the mixture had set to a gel, a solution of 0.2 M Na_2HPO_4 was poured over the gel, and the mixture was set aside to allow reaction to take place. The agar gel mixture was made by dissolving 15 g agar in 1000 cc hot distilled water, and after cooling $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to give a final concentration of 0.2 M. After setting to a gel, the mixture was covered with a solution of KH_2PO_4 (10g/500 cc), and the mixture set aside to allow crystallization to take place.

After standing about two weeks, the crystals which had developed in the gels were removed by boiling the gel mass in large volumes of distilled water; the supernatant liquid was removed by decantation. After repeating this process three times, the crystals, which were then relatively free of gel chemicals, were collected on filters, dried with alcohol and ether, and the X-ray diffraction patterns recorded. These materials were analyzed chemically for iron and phosphate content.

Manganous Phosphates

Materials - The materials used in the synthesis of the several manganous phosphates were Baker's C.P. manganous carbonate, phosphoric acid, phosphorus pentoxide, and USP hydrogen peroxide.

Methods - Manganous carbonate was weighed out into a tared beaker, and phosphoric acid solution was added; the contents of the beaker were then heated to boiling to dissolve the carbonate and expell the CO_2 . Any deep coloration due to permanganate ion was discharged by dropwise additions of 3 percent H_2O_2 solution. After the CO_2 was completely expelled, the beaker was allowed to cool to room temperature and the proper weight of water added to bring the solution to the desired concentration. In preparing the salt $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_3\text{PO}_4$ solid P_2O_5 was added in order to obtain the desired concentration. Table 8 shows the relative amounts of materials used in preparing the manganous phosphates.

TABLE 8
Mixtures Used in Preparing the Manganese Phosphates

| No. | Salt | MnO (%)* | P_2O_5 (%)* |
|-----|--|-------------|--------------------------------|
| 1 | $\text{Mn}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ | 12.5 | 10 |
| 2 | $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ | 15 | 40 |
| 3 | $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_3\text{PO}_4$ | 5 | 65 |

* Weight percent - sufficient water was present to make 100 percent in each case.

At least three mixtures of each concentration were made up, usually in 200-g quantities, although occasionally larger quantities were used. The mixtures were allowed to digest at room temperature for at least two weeks with occasional stirring, but the time was not critical and some of the mixtures were more than a month old when the solid phase was

removed for examination. Mixtures 2 and 3 represent points lying within the solid phase areas shown in Figure 1(c) developed by Amadori (10).

The solids were filtered on a sintered glass crucible using suction to remove as much of the mother liquor as possible. The ditrimanganous phosphate, $Mn_5H_2(PO_4)_4 \cdot 4H_2O$ was washed with water, alcohol, and ether; and sucked dry on the filter. The two acid salts are water soluble and the mother liquor was removed by prolonged rinsing with ether. In each case the X-ray pattern was recorded as quickly as possible after drying.

* * *

TABLE I
Mixture Used in Preparing the Manganous Phosphates

| Mn | P ₂ O ₅ | Weight % | Formula |
|----|-------------------------------|----------|-------------------------------|
| 1 | 15.5 | 100 | $Mn_5H_2(PO_4)_4 \cdot 4H_2O$ |
| 2 | 16 | 100 | $Mn_5H_2(PO_4)_4 \cdot 4H_2O$ |
| 3 | 7 | 100 | $Mn_5H_2(PO_4)_4 \cdot 4H_2O$ |

* Weight percent - calculated on the basis of 100 percent in each case.

At least three mixtures of each composition were made up exactly to 0.5-g quantities. Although occasionally larger quantities were used, the mixtures were allowed to dry in open air. The solids were washed with water, alcohol, and ether, but the time was not spent in washing with ether. The solids were dried in a vacuum oven at 100°C for 24 hours.

APPENDIX II

The X-Ray Apparatus and Technique

The apparatus used to obtain the X-ray diffraction patterns reported in this study was a modified North American Phillips Geiger Counter X-ray Spectrometer having a highly divergent beam. The Geiger-Muller tube output was fed through scaling and amplifying circuits developed by the Physical Optics Section of this Laboratory and into a recording milliammeter. The X-ray patterns were obtained with K_{α} radiation from copper and iron target tubes run at 35 kv and about 6.8 ma.

Samples of the dry powdered salts were pressed into discs 1" in diameter and about 1/8" thick, at a pressure of about 3000 lb/sq in. The discs were mounted on glass slides in the specimen holder, and the X-ray patterns recorded. The diffraction patterns from the phosphated panels were made directly on the coated samples.

A discussion of the focusing principles embodied in the X-ray spectrometer and the use of flat specimens appears in NRL Report No. H-2517 (20).

The "d" values of the X-ray diffraction patterns shown in this report were calculated by use of the Bragg equation, $n\lambda = 2d \sin\theta$. They appear to be characteristic of each compound since the patterns obtained from different preparations of the same material could be superimposed line for line. In the tabulations of the X-ray patterns, a broad or fuzzy line has been indicated by the symbol "b" following the intensity value.

X-ray diffraction patterns obtained with the instrument described above have been used satisfactorily in ordinary analytical work. Across the 2θ scale shown on the patterns there is a constant correction which is dependent upon the adjustment of the instrument, and usually amounts to 0.1° for the copper-target tube, and 0.6° for the iron-target tube. These corrections must be subtracted from the observed values to obtain the true values of 2θ . The calibration of the instrument was determined by recording the pattern of a sodium chloride specimen, and remained constant as long as the slit adjustment and sample position were unchanged. The method of using an external calibration was adopted because many of the compounds studied were hygroscopic, and once dried, it was imperative that the X-ray patterns be recorded without delay. In addition the number of lines in each pattern is large; and finally, the absolute intensity of the lines in patterns from phosphates is generally quite low and would be considerably reduced if the specimens were diluted with an internal standard.

The intensities of the lines appearing in the X-ray patterns shown in this report were estimated on the basis of the number of scale divisions included by the arcs representing the lines. The intensity of the strongest line in each pattern was arbitrarily taken as unity, and the remaining lines were assigned fractional values corresponding to the relative number of scale divisions described by the arc representing each line in the pattern. These relative intensities are designated by the symbol I/I_0 .

The intensities assigned to the lines of the diffraction patterns are subject to verification since the method of specimen preparation and mounting may produce orientation effects; it is believed, however, that the patterns presented in this report may be used satisfactorily for identification work.

APPENDIX III
Analytical Methods and Results

Analyses for phosphates were made by using the standard molybdate separation followed by precipitation as magnesium ammonium phosphate and weighing as the hexahydrate or, after ignition, as the pyrophosphate.

Analyses for iron were carried out by titration with dichromate ion using diphenyl ammine as an internal indicator. Ferrous iron determinations were run directly, and total iron was determined by reducing ferric iron with stannous chloride, adding mercuric chloride in the usual manner, followed by titration with a standardized dichromate solution. This procedure was checked with phosphoric acid solutions of standard iron wire.

Manganese determinations were carried out by the method of Gibb's (21) which is particularly suitable for these materials. The manganese was precipitated as manganese ammonium phosphate and weighed as such.

TABLE 9
Analyses of the Ferrous Phosphates Prepared in this Study

| Compound | Analysis | | | | |
|--|--------------------------|--------------------------|---------------------------------------|--------------------------|---------------------------------------|
| | Found | | | Theoretical | |
| | Fe ⁺² (%)* | Fe ⁺³ (%)* | PO ₄ ⁻³ (%)* | Fe ⁺² (%)* | PO ₄ ⁻² (%)* |
| Fe ₃ (PO ₄) ₂ · 8H ₂ O | 27.76 | 4.19 | 40.41 | 33.4 | 37.9 |
| FeHPO ₄ · H ₂ O | 32.96 | 0 | 56.28 | 32.9 | 55.9 |
| FeHPO ₄ · 2H ₂ O | 27.99 | 0 | 51.0 | 29.8 | 50.6 |
| Fe(H ₂ PO ₄) ₂ · 2H ₂ O | 19.04 | 0 | 66.0 | 19.5 | 66.6 |

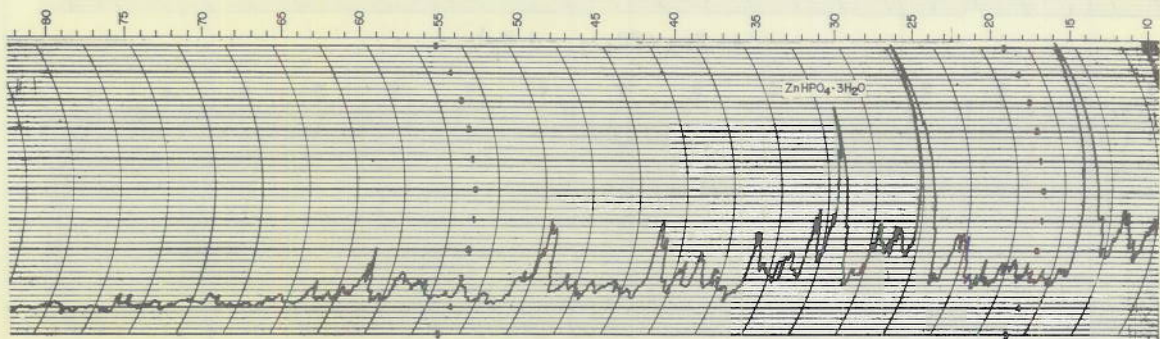
*Weight percent

TABLE 10
Analyses of the Manganous Phosphates Prepared in this Study

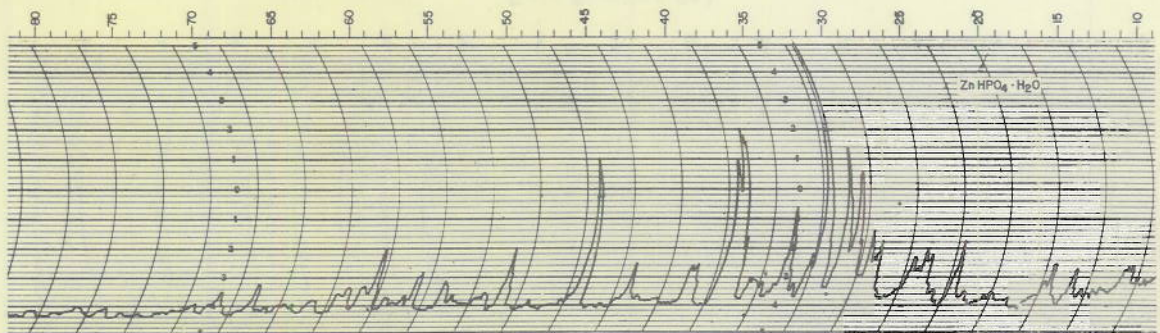
| Compound | Analysis | | | |
|--|--------------------------|---------------------------------------|--------------------------|---------------------------------------|
| | Found | | Theoretical | |
| | Mn ⁺² (%)* | PO ₄ ⁻³ (%)* | Mn ⁺² (%)* | PO ₄ ⁻³ (%)* |
| Mn ₅ H ₂ (PO ₄) ₄ · 4H ₂ O | 37.5 | 53.2 | 37.5 | 52.1 |
| Mn(H ₂ PO ₄) ₂ · 2H ₂ O | 18.13 | 68.4 | 19.3 | 66.4 |
| Mn(H ₂ PO ₄) ₂ · H ₃ PO ₄ | 14.2 | 84.1 | 15.8 | 82.2 |

*Weight percent

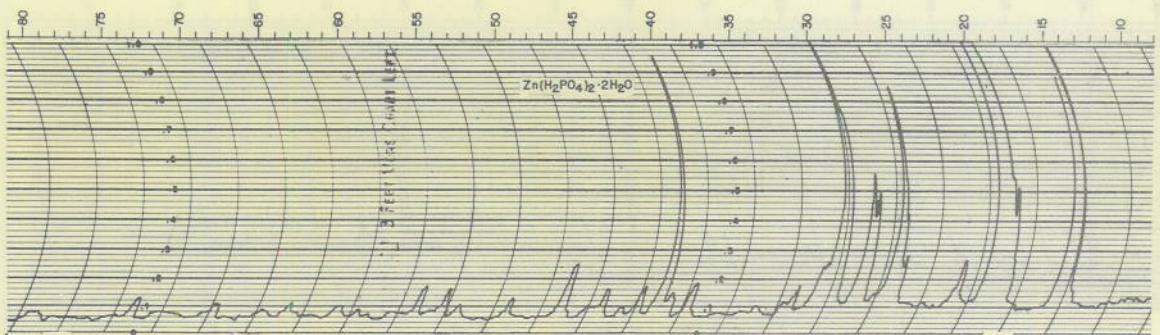
APPENDIX IV
X-Ray Diffraction Patterns of the Pure Metal Phosphates



(a) $\text{Zn HPO}_4 \cdot 3 \text{H}_2\text{O}$



(b) $\text{Zn H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$



(c) $\text{Zn} (\text{H}_2\text{PO}_4)_2 \cdot 2 \text{H}_2\text{O}$

Figure 7 - X-ray diffraction patterns of the zinc phosphates

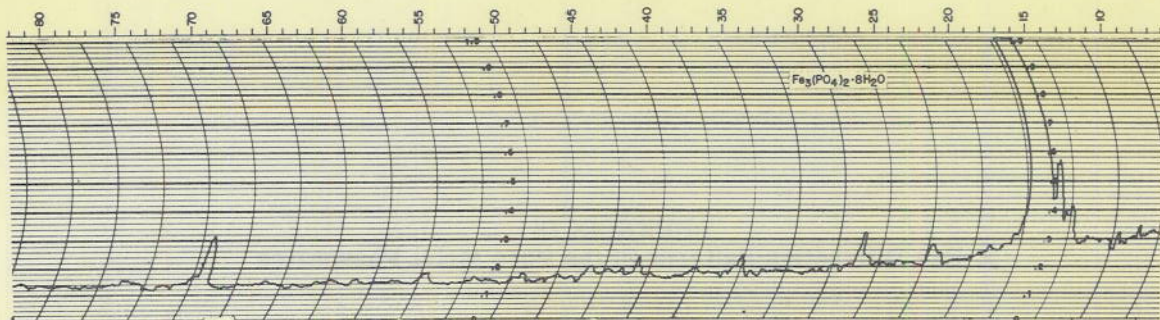
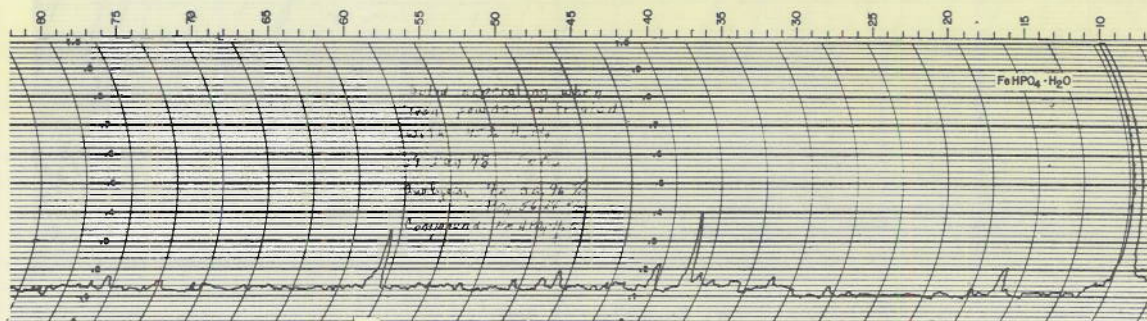
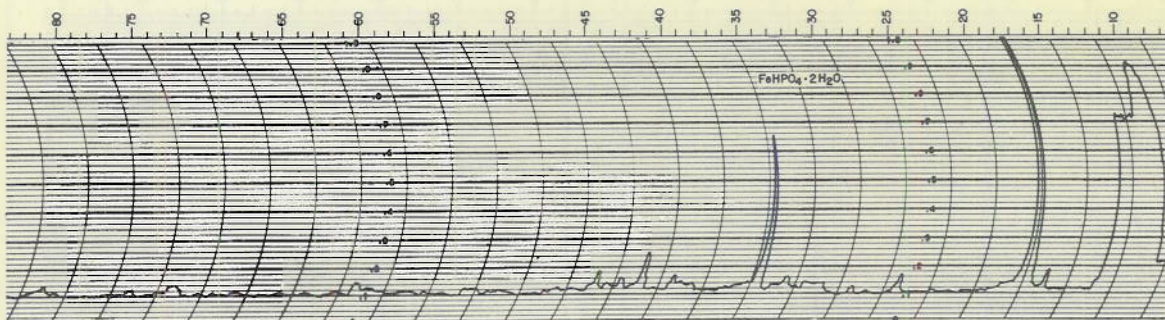
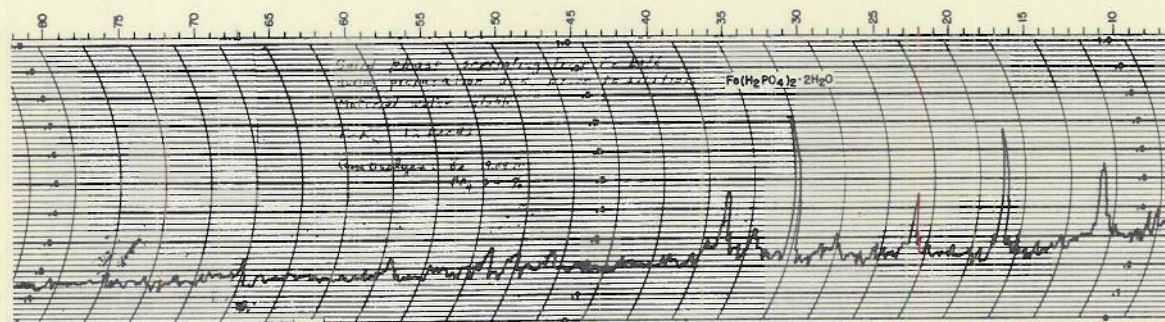
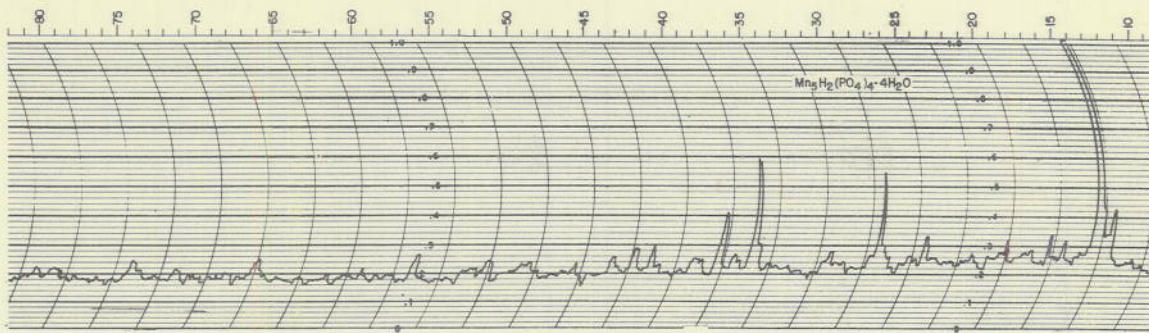
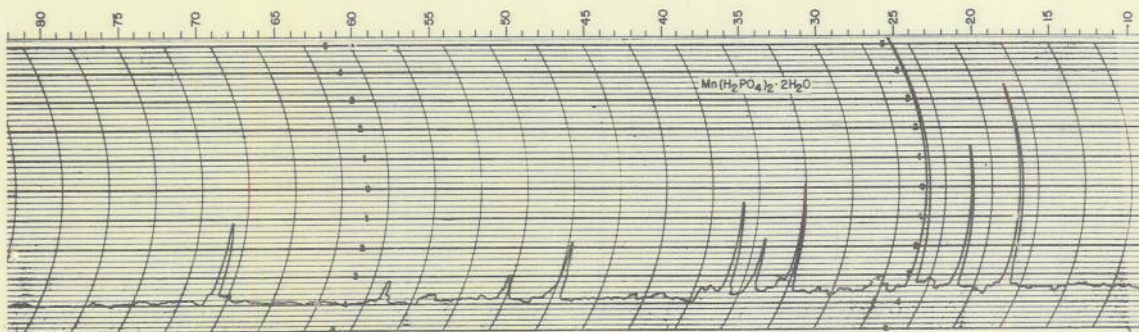
(a) $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (b) $\text{FeHPO}_4 \cdot \text{H}_2\text{O}$ (c) $\text{FeHPO}_4 \cdot 2\text{H}_2\text{O}$ (d) $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

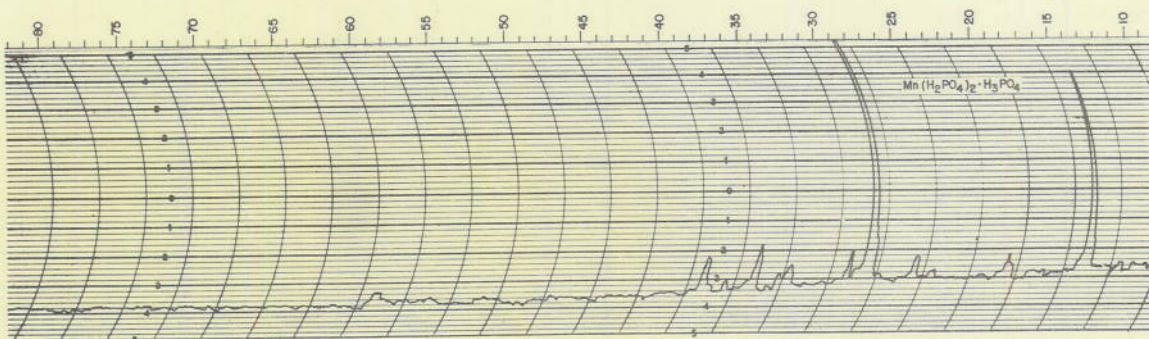
Figure 8 - X-ray diffraction patterns of the ferrous phosphates



(a) $Mn_5 H_2(PO_4)_4 \cdot 4H_2O$



(b) $Mn (H_2PO_4)_2 \cdot 2 H_2O$



(c) $Mn (H_2PO_4)_2 \cdot H_3PO_4$

Figure 9 - X-ray diffraction patterns of the manganous phosphates
