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The use of phosphoric acid as a pickling reagent for enamels

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THE USE OF PHOSPHORIC ACID AS A PICKLING REAGENT FOR ENAMELS

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INTRODUCTION

A review of the available literature reveals that no one has used phosphoric acid for pickling sheet steel for enameling purposes. Articles have been published indicating the corrosive action of phosphoric acid,[1, 2] but these investigations were carried out in an attempt to find an alloy that would resist the corrosive action of this acid.

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1 Rohrman, F. A., "Corrosion of Metals by Phosphoric Acid", Chemical and Metallurgical Engineering, Vol. 42, No. 7, July 1935, pages 368 - 369.

2 Kosting, Peter R., and Heins, Conrad Jr., "Corrosion of Metals by Phosphoric Acid", Industrial and Engineering Chemistry, Vol. 23, Feb. 1931, pages 140 - 150.

OBJECT OF INVESTIGATION

The object of this study was to determine the possibility of substituting phosphoric acid for sulphuric acid and hydrochloric acid as a pickling reagent for the preparation of sheet-iron for enameling purposes.

Hydrochloric and sulphuric acids, the acids commonly used for industrial pickling, fume if heated above $70^{o}F$ and $150^{o}F$, respectively. Phosphoric acid was selected because it is a non-volatile acid, and on dilution yields ions according to the following equations:

(1) $H_3PO_4 = H^+ + H_2PO_4^-$

(2) $H_2PO_4 = H^+ + HPO_4^=$

(3) $HPO_4 = H^+ + PO_4^{\equiv}$

Equation Number 1 occurs to a greater extent than either of the other two equations.

MATERIALS USED

Three-inch by four-inch 18-gage sheet-iron strips were used as the test pieces. The cleaning solution was prepared by dissolving a commercial cleaner in water.

In preparing the acids of the desired concentrations the following amounts of distilled water were added to the chemically pure acids:

TABLE I

Amount of Acid and Water Added in Preparing Desired Concentrations

Acid	Original conc.	Desired conc.	cc. Acid added	cc. Water added
H_2SO_4	66° Be.	6%	35.05	940
HCl	22° Be.	11%	266.50	890
H_3PO_4	60° Be.	10%	68.75	900
H_3PO_4	60° Be.	20%	117.00	800
H_3PO_4	60° Be.	35%	242.50	650
H_3PO_4	60° Be.	50%	344.00	500

The neutralizing solution was approximately three-tenths per cent sodium-oxide, being composed of soda ash.

The ground coat enamel was prepared from the following commercial formula:

Commercial ground coat	1000.0 gms.
Vallender clay	60.0 gms.
Borax	7.5 gms.
Magnesium carbonate	2.5 gms.
Feldspar	20.0 gms.
Water	400.0 gms.

METHOD OF PROCEDURE

The sheet-iron strips were cleaned, pickled in six per cent sulphuric acid at a temperature of 150°F, and run through a neutralizing bath. Other pieces of sheet-iron were pickled in eleven per cent hydrochloric acid at room temperature, the rest of the procedure being the same. Sheet-iron ground coat was applied and the test pieces fired. The test samples thus prepared were considered as samples for comparison.

Additional pieces of sheet-iron were pickled in phosphoric acid. The concentrations of the phosphoric acid used were ten, twenty, thirty-five, and fifty per cent. Sheets were pickled in each concentration at the following temperatures: $70^{o}F$, $100^{o}F$, $150^{o}F$, and the boiling point of the solutions or approximately $210^{o}F$. These samples were dipped and fired in the same manner as the standards for comparison.

These prepared enameled pieces were then submitted to an adherence test, and a comparison of their adherent properties was made. Comparison of possible defects was also made. The following defects were sought: blistering, which may be caused by defects left on the surface; fishscaling, which is frequently caused by improper pickling of the iron; and copperheading, which may be caused by insufficient pickling time.

LABORATORY PROCEDURE

Six major operations were performed in changing the sheet-iron to pieces of enameled metal. These steps were: cleaning, pickling, neutralizing, drying, preparation and application of the enamel, and firing. These various steps will be thoroughly discussed in the order in which they were preformed.

Monel metal baskets were used in handling the test pieces in the initial operations. Five pieces of sheet-iron were placed in a basket and these were not removed until the neutralization and drying operations had been completed.

CLEANING

The cleaner was dissolved in water and the solution kept at the boiling point at all times. The action of the cleaner is increased as the temperature is raised. Heat is also valuable in expanding the surface of the metal and opening up the pores, so that the cleaning solution may effectively remove the oil and grease which may be present due to the stamping operations employed by the steel mills. Boiling is effective because it promotes agitation of the bath, which is highly essential. The sheets were rinsed in a hot water bath before being placed in the pickling solution.

PICKLING

The purpose of the pickling operation is to remove from the sheet-iron all of the scale, rust, or other iron oxide, by placing the metal in an acid solution, where these latter are not dissolved, but are mechanically removed from the iron. The reactions for the various acids and iron are shown in the following chemical equations:

$$2Fe + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2$$

$$2Fe + 6HCl = 2FeCl_3 + 3H_2$$

$$2Fe + 2H_3PO_4 = 2FePO_4 + 3H_2$$

The various concentrations and temperatures that were used for the pickling solutions are shown in Table II. The sulphuric and hydrochloric acids were run at only one concentration and one temperature, because these conditions are most frequently used by the enameling industry.

TABLE II

Acid Concentrations and Temperatures

Acid	Per cent conc.	Temperatures			
H_2SO_4	6	----	-----	150°F	-------
HCl	11	70°F	-----	-----	-------
H_3PO_4	10	70°F	100°F	150°F	Boiling (210°F)
H_3PO_4	20	70°F	100°F	150°F	Boiling (211°F)
H_3PO_4	35	70°F	100°F	150°F	Boiling (210°F)
H_3PO_4	50	70°F	100°F	150°F	Boiling (208°F)

The test pieces were rinsed again in a hot water bath after the pickling had been completed.

NEUTRALIZING

Following the rinsing the sheet-iron pieces were immersed in an alkali neutralizing solution. The baskets of ware were transferred as rapidly as possible from the water rinse to the neutralizing solution to avoid any rusting of the metal before the final traces of acid in the pores of the metal had been neutralized. The bath was always kept hot, 150°F, because the heat contributes to the rapid interaction of the acid and the alkali.

DRYING

After neutralization, the basket of ware was allowed to drain thoroughly, and then placed in an electrically heated drier; it was dried as rapidly as possible before any rust could form on the pieces.

PREPARATION AND APPLICATION OF THE ENAMEL

Three batches of enamel were prepared for this study. The enamels were ground in ball mills for ten hours, and then mixed before being checked for fineness by the flat-screen test.[3] Five grams of residue were

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3 Hansen, J. E., The Advanced Technique of Porcelain Enameling, Cleveland, Ohio, Enamelist Publishing Company, 1932, page 73.

were found on the 200-mesh screen when this test had been completed.

The ground coat enamel, prepared in this manner, was stored and allowed to age until needed for dipping of the sheet-iron pieces.

The liquid enamel was applied to the sheet-iron test pieces by the dipping process. It was necessary to adjust the enamel by adding a small amount of water before the enamel was brought to the proper consistency for dipping. In the dipping opperation the pieces of metal were immersed in the enamel slip and then withdrawn and allowed to drain before being placed upon the electric hot-plate drier. The test pieces were marked for identification purposes after drying.

FIRING

All of the test pieces were fired in a four-inch by six-inch Hoskins Electric Furnace of the muffle type. The temperature of the furnace was regulated by a rheostat and measured with a chromel-alumel thermocouple. The temperature of the furnace was maintained between 860°C and 890°C. The firing time for each test piece was five minutes. The sample pieces were introduced into the furnace on monel-metal tongs, and were supported in the furnace upon metal points.

TESTS

The fired enameled pieces were examined for any physical defects that might have been present. None of the pieces showed marks of blistering or fishscaling, and copper-heading was apparent on only a few of the pieces. These defective marks were not present in sufficient quantity to indicate that the sheet-iron pieces had not been thoroughly and properly cleaned and pickled.

ADHERENCE TEST

A falling weight metal deformation test was used to give an index of the adherence of the pieces which had been pickled in the various concentrations of acid and at different temperatures.

The apparatus, which is shown in Figure 1, consists of a steel bar, one-inch in diameter with a 3/4-inch radius end. This bar weighs 1280 grams and is used as the falling weight. It is free to fall through a 1-1/8-inch diameter guide tube. A 3/8-inch steel

ADHERENCE TEST APPARATUS

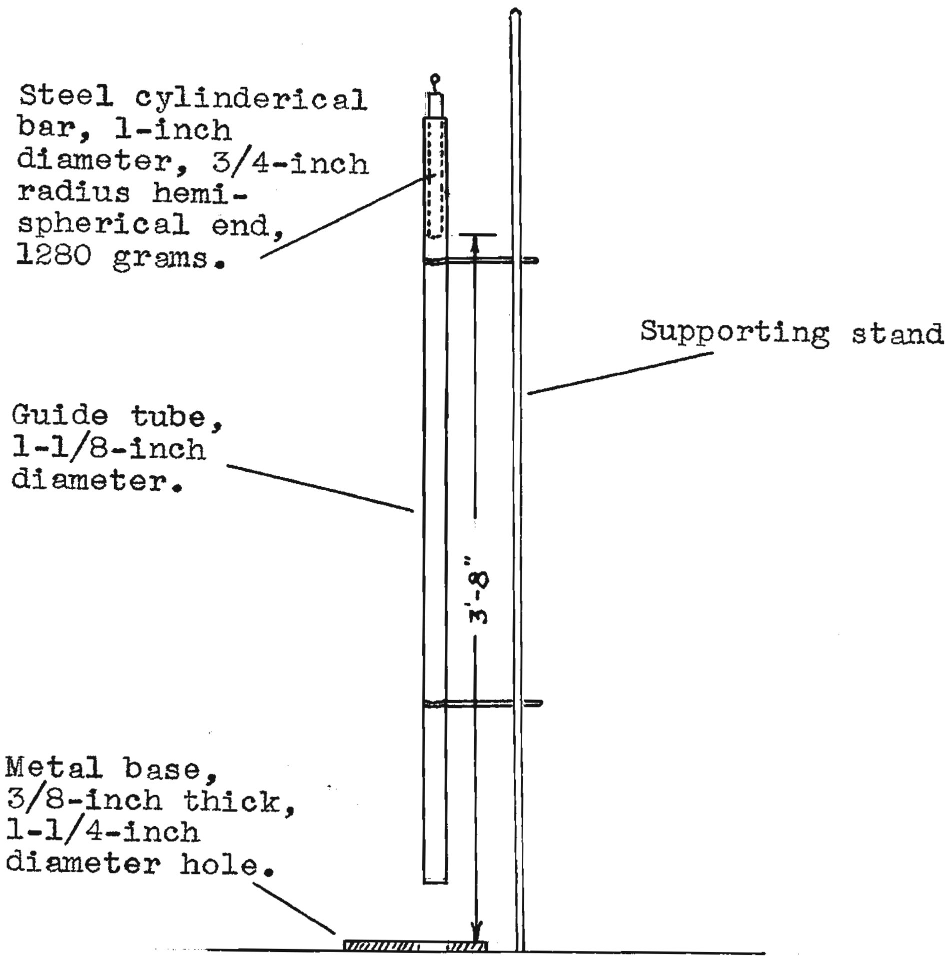

Figure 1

plate, with a 1-1/4-inch diameter hole, is used as a block upon which the bar is allowed to fall. When the weight strikes the enameled sheet it has a force of 144,053 dynes or 10.35 foot-pounds, having fallen through a distance of 111.76 centimeters or 3-feet 8-inches.

The procedure in making the test is as follows: The test specimen is placed over the hole in the metal block and the guids tube is adjusted so that the weight will just clear the space between the specimen and the lower end of the tube. The dropping of the weight is controlled by a line tied to one end of the weight and run through a reverse pulley system.

This test is a modification of the test developed by C. J. Kinzie and described by A. I. Andrews.[4]

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4 Andrews, Andrew I., Enamels, Champaign, Illinois, Twin City Printing Company, 1935, pages 351 - 352.

TABLE III

RESULTS OF ADHERENCE TESTS

Study of Standard Results

H_2SO_4 - 6% 150°F	HCl - 11% 70°F	No pickling	No treatment
Good adherence	Good adherence	Fair adherence	Fair adherence
Good surface	Good surface	Good surface	Good surface

Study of Phosphoric Acid Results

Temperature	Per cent acid 10	20	35	50
70°F	Good adherence Slight copper-heading	Good adherence Good surface	Good adherence Good surface	Fair adherence Good surface
100°F	Good adherence Good surface	Fair adherence Good surface	Good adherence Good surface	Fair adherence Good surface
150°F	Good adherence Good surface	Fair adherence Good surface	Good adherence Good surface	Good adherence Good surface
Boiling (210°F)	Good adherence Good surface	Fair adherence Good surface	Good adherence Good surface	Good adherence Good surface

DISCUSSION OF RESULTS

The results of the adherence tests run in connection with this study show only slight variations when the different acids and acid concentrations are used. This would seem to indicate that the test made are not sufficient to obtain data that can be correlated. Some of the probable reasons for the failure to find variations, as would normally be expected for the various acid concetrations and temperatures, are discussed in the following paragraphs.

One of the major sources of variations in applying the tests is the adherence apparatus that was set up. With the equipment assembled it was practically impossible to obtain exactly the same impact every time the weight was dropped upon an enameled test piece. In order for the adherence data to have a true meaning, it must be possible to repeatedly duplicate the impact of the weight on the enameled sheet.

There is a known variation of 30°C in the temperature of the furnace, from 860°C to 890°C. Although the firing time was controlled as carefully as possible, the rate of comeback should be known so that it may be repeated every time a test piece is fired. Another source of slight error in the firing procedure, is that all of the pieces were not fired at the same time. In fact, the time of firing was extended over a period of several weeks, so that the firing conditions were difficult to duplicate.

The weight of the enamel applied to the sheet-iron was not checked. In all probability there was enough variation in thickness to account for some change from the expected results.

From the results obtained, the sheet-iron was apparantly received from the manufacturer in a very clean state. As further basis for this belief, five samples were dipped in the ground coat without having been cleaned or pickled. These pieces had the same appearance as the other samples when fired, and their ability to withstand the adherence test was almost the same.

SUGGESTIONS FOR FURTHER RESEARCH

In doing further research on this problem, it is suggested that the adherence apparatus be constructed with a concrete base so that the equipment will be exceptionally solid.

It would be advisable to use sheet-iron manufactured by different companies so that the information will be more general and will have a wider application to the enameling industry.

A check should be made on the weight of the enamel applied to a unit surface of the sheet-iron. A more accurate control of firing conditions should also be maintained.

Further investigation should also be made on the possibilities of using phosphoric acid for pickling one-coat enamel pieces.

APPLICATION TO INDUSTRY

Because of the absence of fumes at practically all temperatures and concentrations, phosphoric acid should be useful in the pickling field. At the present time the price is its only prohibitive feature. The prices mentioned below refer to quotations from the New York market. They were obtained from a recent publication of a technical journal.[5]

Muratic acid, 22°Be., tanks, cwt.	\$1.00 - \$1.10
Phosphoric acid, tech., c'bys. lb.,	.09 - .10
Sulphuric acid, 66°Be., tanks, ton,	\$15.50

From these quotations the following prices per pound were calculated:

Hydrochloric acid	---	\$0.01 - .011
Phosphoric acid	---	.09 - .10
Sulphuric acid	---	.0077

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5 "Chemical and Metallurgical Engineering", Vol. 43, No. 4, April 1936, page 221.

CONCLUSIONS

The results indicate that phosphoric acid has possibilities of replacing hydrochloric and sulphuric acids in the pickling field. The non-volatile property of this acid is its main advantage over other acids.

The large number of well enameled test pieces indicates the ability of this acid to act as a pickling reagent.

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