THE APPLICATION OF HEAT AND CORROSION RESISTANT PHOSPHATE COATINGS UNDER STEAM PRESSURE

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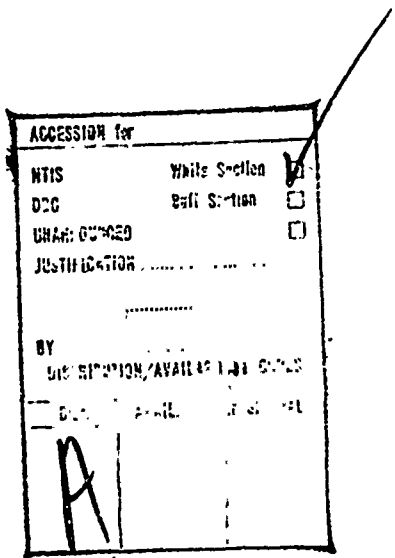

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Processing methods to produce zinc and manganese phosphate coatings with greater heat and corrosion resistance on ferrous items were investigated. Conventional phosphating solutions enriched with salts of the alpha-reactive-carboxylic-acids, such as manganese salts of citric, tartaric, and gluconic acids were processed under steam and atmospheric pressure. Manganese carbonate and manganese dihydrogen phosphate were added to control the free

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and total acids. Evaluations were made of the coating weight, amount of iron etched from the surface, loss of coating weight due to thermal exposure, and resistance of the coatings to heat and corrosion in the salt-spray tests. The results showed that zinc coatings were not greatly improved by increases in steam pressure; whereas, manganese coatings that had been produced under steam pressure exhibited improved heat and corrosion resistance. Manganese tartrate enrichments produced coatings with thermal resistance to 450°F and corrosion resistance for 500 hours in the salt-spray tests. Coatings processed with manganese gluconate additions provided thermal resistance to 350°F and salt-spray resistance of 380 hours; coatings processed with manganese citrate enrichment exhibited only a slight improvement over conventionally processed coatings.

Fax film replicas were made to examine the crystallinity, porosity and continuity of the phosphate coatings. Conductometric titration curves indicated that the additives buffered the solution and raised the pH.

FOREWORD

The project was carried out under the title "Application of Heat and Corrosion Resistant Phosphate Coatings." This work was authorized as part of the Manufacturing Methods and Technology Program of the U. S. Army Materiel Command and was administered by the U. S. Army Production Equipment Agency.

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OBJECTIVE

The objective of this study was to evaluate a method for the application of high temperature, corrosion resistant phosphate coatings on ferrous alloys in a conventional phosphating solution containing metal salts of the alpha-reactive-carboxylic acids under steam pressure in an autoclave.[1,2]

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[1] Hache, A., "The Corrosion Protection of Steel by the Process of Phosphating under Pressure," French Iron and Steel Research Inst., St. Germaine-in-Laye, France. Presented at N.A.C.E. 2nd International Congress on Metallic Corrosion, New York City, March 1963.

[2] Menke, Joseph, "A Study of Manganese Phosphating Reactions," Research Directorate, Weapons Laboratory at Rock Island, Research, Development and Engineering Directorate, U. S. Army Weapons Command, Technical Report RE-TR-71-60, September 1971.

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BACKGROUND

Modern rapid-fire weapons require a phosphate coating that will withstand high temperatures without thermal decomposition. Such a coating is of prime importance to the military services because the resistance of the presently used coating to heat[3,4,5,6] and corrosion[7,8,9] has not been too satisfactory.

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[3] Doss, Jodie and W. D. McHenry, "Study of the Water of Hydration Contained in Phosphate Coatings by Radiometric Techniques," Rock Island Arsenal Laboratory Report 54-900, March 1954.

[4] Doss, Jodie, "Corrosion Resistance of Phosphated Steel after Heating under Oil," Rock Island Arsenal Laboratory Report 55-3256, August 1955.

[5] Bessey, R. E. and W. M. Kisner, "Heat Resistance of Phosphate Protective Coatings," Technical Report SA-MR18-1026, Springfield Armory, Massachusetts, January 1953

[6] Wagner, L. H., "Heat Resistant Conversion Coatings for Steel," Rock Island Arsenal Laboratory Report 63-3345, August 1963.

[7] Doss, Jodie, "Comparative Corrosion Resistance Tests on Phosphate Coatings," Rock Island Arsenal Laboratory Report 58-1842, July 1958.

[8] Doss, Jodie, "Composition of Zinc Phosphate Coatings," Rock Island Arsenal Laboratory Report 57-2612, January 1956.

[9] Gilbert, L. O., "The Effect of Phosphate Solution Analysis on the Decomposition of the Phosphate Coating," Rock Island Arsenal Laboratory Report 47-250, May 1947.

The following information was obtained from literature pertaining to thermal stability of phosphate coating. Conventional zinc and manganese phosphating baths have been operated at atmospheric pressure at a temperature of 205 ± 5°F[10,11,12,13,14] to provide an insoluble protective coating for small arms weapons. The minimum requirements of the current military specification (MIL-P-16232, Phosphate Coatings, Heavy, Manganese or Zinc Base) for ferrous metals prior to the application of any supplementary treatment is that the metal "shall show no signs of corrosion when subjected to the salt spray test for 1-½ hours for manganese and 2 hours for zinc phosphate coatings." However, no thermal requirement is given for either of these coatings. Gilbert[9] found that the phosphate coatings produced in baths with a ferrous iron content below 0.06 percent showed little or no decomposition when heated to 500°F. He also pointed out that coatings formed in a bath of 60 points total acidity and in excess of 0.65 percent

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[10] Knanishu, J., "A Study of Innovations of Salt Spray (Fog) Testing Equipment," U. S. Army Weapons Command, Rock Island Arsenal, Research and Engineering Division, Report 65-1191, May 1965.

[11] Tinsley, E. C., "Phosphating Treatments - Patent Literature Survey," Rock Island Arsenal Laboratory, Report 57-1022, April 1957.

[12] Gilbert, L. O., "Phosphating Materials and Process," Rock Island Arsenal Laboratory, Report 54-2906, May 1954.

[13] Gilbert, L. O., "A Study of Phosphate Treatment of Metals," Rock Island Arsenal Laboratory, Report 56-2995, June 1956.

[14] Jenkins, H. A. H. and J. O. Surrey, "Production of Phosphate Coatings on Metals," U.S. Patent 3,338,755, Hooker Chemical Corp., 1967.

ferrous iron content decomposed when heated in air above 350°F. The generally accepted temperature at which manganese coatings were believed to decompose was 350°F. When Doss and McHenry[3] heated manganese phosphate coatings in air, they found that the coatings did not lose water of hydration until a temperature of 250°F had been reached. The coatings did lose water of hydration fairly linearly with temperature up to 360°F where a retention of about 10 percent occurred. No effort was made to relate loss of water of hydration with deterioration of the coating by thermal decomposition. Doss,[4] on the otherhand, heated phosphate coated panels in the absence of air. Zinc and manganese coatings were heated under oil at 25-degree intervals in the range of 175°F through 450°F. Subsequently, Doss subjected the coatings to the salt-spray test. He found that the zinc phosphate coatings heated in the absence of air lose their corrosion resistance between 300°F and 325°F. Manganese phosphate coatings heated in the absence of air lose their corrosion resistance between 400°F and 425°F. Bessey and Kisner[5] determined the weight loss from zinc and manganese phosphate coated specimens at various temperatures. They also tested zinc and manganese phosphate coatings in the salt-spray tests. These coatings had been heated in air at 212°F, 300°F, and at 100-degree intervals up to 1400°F. Bessey and Kisner reported that the corrosion products initially appeared on phosphate coated specimens at 212°F for zinc and 400°F for manganese. The investigations given above on the thermal stability of the phosphate coatings[15] showed that corrosion tests should be conducted on the coatings after these have been heated in air. The present work was intended to evaluate a method whereby manganese phosphate coatings processed in manganese enriched solutions under low steam pressure[1] would provide improved resistance to heat and salt spray corrosion.

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[15] Wagner, L. H. and P. G. Chamberlain, "Method and Composition for Phosphatizing Steel under Pressure," U. S. Patent 3,767,476, October 1973.

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EXPERIMENTAL PROCEDURE

Construction of Pressure Vessel

A pressure vessel was fabricated from a 12-inch-diameter steam pipe and designed to operate in a vertical position. The bottom was welded shut, and a lid was bolted to the top so that it could be removed manually. Appurtenances included a steam gauge, a purging valve, a bypass steam valve, and a manually operated steam pressure regulating valve.

Preparation of Steel Panels

SAE 1020 steel panels, 2 inches by 3 inches by 1/8 inch, were vapor-degreased in trichloroethylene and abraded with No. 80 steel grit. They were weighed and placed in a desiccator before use.

Preparation of Metal Phosphates

In the preparation of the metal salts, an alpha-reactive carboxylic acid was combined with manganese carbonate in an aqueous solution at room temperature. The insoluble salt was decanted, washed with water, and dried in an oven before use. The metal salts consisted of zinc citrate, manganese citrate, manganese tartrate, and manganese gluconate. Conventional zinc and manganese phosphating stock solutions were prepared. Six liter portions of the zinc stock solution were enriched with zinc citrate. Six liter portions of the manganese stock solution were enriched with manganese citrate, manganese tartrate, and manganese gluconate, respectively.

Processing Procedure

The study was divided into two processing procedures. A new method of processing steel panels under steam pressure with and without enrichment of the bath was investigated. Steel panels were also processed in a conventional bath at atmospheric pressure. Comparative evaluations were made between the two methods. The following processing procedure was used: A stainless steel beaker containing 6 liters of the stock solution at 160°F-170°F was placed in the pressure

vessel. The thermocouple was inserted, and the bath was enriched with a metal organic salt. A potentiometer with a copper-constantan thermocouple was used to measure the temperature of the solution under pressure. A sample of the bath was taken before processing for chemical analysis. Steel panels previously grit-blasted and weighed were put into the solution. The time of immersion was noted, and the lid was clamped in position. The steam was turned on and the air was purged from the vessel. Potentiometric readings were taken about every two minutes. When the temperature of the bath reached 210°F-212°F, the purging and the bypass valves were closed. The following example is given for the processing of panels at the maximum pressure. Similar procedures were used for the coating of panels at lower pressures. When the bath temperature reached 230°F, the initial processing time was noted and the pressure was maintained at 22 pounds per square inch gauge (PSIG) until the temperature reached 260°F. When the processing time was completed, the steam was turned off, the purging and the bypass valves were opened, the pressure was reduced, and the cover lid was removed. The work load was quickly withdrawn and immersed in the rinse water. The time of immersion was noted, and the total time of processing was determined. A sample of the bath was withdrawn after processing for chemical analysis. The coated panels were removed, dried in air, and weighed.

Testing Procedure

The coated panels were evaluated for resistance to thermal decomposition and to salt-spray corrosion. Some coated panels as processed were not heated and were used as control specimens. Other coated panels were weighed and then heated in an air convection oven at test temperatures of 350°F, 400°F, and 450°F for one-hour exposures. They were cooled at room temperature and reweighed to determine the loss in coating weight due to thermal exposure. The thermally treated coatings and the as-processed coatings were exposed in the 5% salt-spray test described in ASTM Method B117. The coated panels were examined visually at periodic intervals. Initiation of rust was noted when three or more dots appeared on the coatings. Failure was noted when about 5% of the surface area was rusted.

The coated panels from each processing bath were divided and tested as follows:

No. of Panels	Tests	Remarks
1	none	for display purposes
2	removal of coating	determine coating weight and iron etched from panel
3	350°F exposure + salt spray	determine resistance to corrosion and loss in coating weight
3	400°F exposure + salt spray	determine resistance to corrosion and loss in coating weight
3	450°F exposure + salt spray	determine resistance to corrosion and loss in coating weight
3	salt spray only	control specimens for comparison purposes

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RESULTS AND DISCUSSION

Zinc Phosphate Coatings

Zinc phosphate coatings were evaluated as follows:

Steel panels were processed in a conventional zinc bath under steam pressures of 1, 5, 16, and 22 PSIG for 10 minutes. In the next series of runs, the procedure given above was repeated except that the bath was enriched with 10 grams per liter of zinc citrate and processed under 1, 10, 16, and 22 PSIG for 10 minutes. Steel panels were also processed in a conventional zinc bath at atmospheric pressure at 205°F-208°F for 30 minutes to serve as controls for comparative purposes.

The chemical composition of the baths is shown in Table 1 under the headings as free acid (FA), total acid (TA), and the ratio of $(\frac{TA}{FA})$, percentage of ferrous iron (Fe) and pH. The FA and TA values are given in points (a point is equivalent to one-milliliter of 0.1N NaOH solution when titrating a 10-milliliter sample of the bath). Analysis of the conventional zinc bath processed at atmospheric pressure for 30 minutes are shown in the first line of figures. Processing tests conducted in the conventional bath under 1, 5, 16, and 22 PSIG are also listed. Results of the processing tests with zinc citrate as the addition agent in the bath are shown under 1, 10, 16, and 22 PSIG. Because of the poor results shown in the salt-spray tests, no analyses were made of the baths. The total processing time is calculated from the time the steel panels were placed in the phosphating bath until they were removed and immersed in the rinse water. The 10-minute processing period was initiated when the steam pressure reached the desired PSIG reading at a given temperature. The initial temperature of the six-liter baths was not identical, so additional time was necessary to bring the bath up to the processing temperature. This is reflected in the total processing time.

Coating Weights

The coating weight of 2590 milligrams per square foot was obtained on the steel specimens processed in the

TABLE I - ZINC PHOSPHATE COATINGS APPLIED IN A CONVENTIONAL BATH WITH AND WITHOUT THE ADDITION OF ZINC CITRATE

Treatment of Bath	FA*	TA**	TA/FA	Iron (%)	pH	Total Process Time (Min)	Coating Wt. (mg/sq ft)	Iron Etched (mg/sq ft)	Loss in Wt due to exposure at (mg/sq ft)			Resistance to Corrosion after Thermal Exposure (Hours to Failure)			
									350°F	400°F	450°F	No Heat	350°F	400°F	450°F
Conventional zinc bath at atmospheric pressure 205°-208°F, for 30 minutes	4.9	26.6	5.5	0.28	2.7	30	2590	235	167	198	226	9	1	1	1
Conventional zinc bath under pressure:															
1 PSIG; 212°F for 10 minutes															
After processing	5.8	29.0	5.0	0.29		39	2490	562	154	109	214	9	1	1	1
5 PSIG; 226°F for 10 minutes															
Before processing	6.0	27.1	4.5	0.26											
After processing	6.1	26.9	4.4	0.27		33	1630	498	109	129	148	5	1	1	1
16 PSIG; 246°F for 10 minutes															
Before processing	4.0	24.6	6.1	0.23											
After processing	4.8	27.2	5.6			34	1480	429	89	104	113	5	1	1	1
22 PSIG; 260°F for 10 minutes															
After processing	5.6	25.5	4.5			30	1500	541	97	124	128	5	1	1	1
Conventional zinc bath with 10 g/l of zinc citrate under pressure:															
1 PSIG; 212°F for 10 minutes						30	2650	388	172	215	226	22	1	1	1
10 PSIG; 220°F for 10 minutes						28	2620	416	172	204	230	62	1	1	1
16 PSIG; 238°F for 10 minutes						39	3260	420	256	285	327	38	1	1	1
22 PSIG; 260°F for 10 minutes															
Before processing	4.8	27.7	5.8	0.24											
After processing	7.8	34.0	4.3	0.26		30	3030	611	249	295	326	14	1	1	1

* Free Acid ** Total Acid

conventional bath at atmospheric pressure. Steel specimens processed in the pressurized conventional baths without enrichment showed a decrease from 2490 to 1500 mg-per-sq-ft as the pressure was increased from 1 PSIG to 22 PSIG. In the pressurized enriched baths, heavier coatings were exhibited in which the values varied from 2620 to 3260 mg-per-sq-ft. A comparison of the coating weights obtained at 22 PSIG with and without enrichment showed that the coatings in the enriched baths with zinc citrate doubled in weight during the total processing time of 30 minutes.

Iron Etched from the Surface

The conventional zinc bath after processing at atmospheric pressure for 30 minutes etched 235 mg-per-sq-ft of iron from the surface of the panels. The amount of iron etched varied from 429 to 562 mg-per-sq-ft during pressurized processing. Therefore, the least amount of iron was etched when the panels were processed at atmospheric pressure. When the conventional bath was enriched with zinc citrate, the amount of iron etched varied from 388 to 611 mg-per-sq-ft during pressurized processing. These values were a little less on the average, than those processed without enrichment under 1, 5, 16, and 22 PSIG.

Resistance of Coating to Heat and Corrosion

The coatings as-processed in the conventional bath at atmospheric pressure and under 1 PSIG provided corrosion protection for 9 hours. However, when the coatings were heated to 350°F, 400°F, or 450°F, the resistance to salt spray corrosion was reduced to only one hour. When the phosphating bath was enriched with 10 grams per liter of zinc citrate, the as-processed coatings showed an increase in salt-spray resistance from 22 to 62 hours. Again, after thermal exposure, the coatings did not provide salt-spray resistance beyond one hour.

Loss in Coating Weight

The loss in coating weight due to heat was determined after one-hour exposure at 350°F, 400°F, and 450°F. At 350°F, the coatings applied in the conventional zinc bath

under pressure showed a decrease in loss of weight from 154 to 89 mg-per-sq-ft. The coatings applied in the zinc enriched baths under pressure showed a greater loss in weight than those applied under pressure in the conventional bath. An explanation can be given for the increased loss from the coatings. Coatings processed under pressure without enrichment of the bath weigh less than those processed under pressure with enrichment of the bath. Generally, the weight loss relates to the as-processed coating weight. Therefore, the weight loss probably is due to the water of hydration in the original coating. Results of this study showed that the conventional zinc bath enriched with zinc citrate and processed under pressure did not improve the corrosion resistance after thermal exposure of the applied coatings. However, the as-processed coatings without thermal exposure did show an improvement in the salt-spray corrosion test. Consequently, this phase of the research work on zinc phosphate coatings was discontinued. The present effort was directed to determine whether superior heat and corrosion resistant manganese phosphate coatings could be applied to steel by processing at lower pressures and temperatures in a bath enriched with metal organic compounds of the alpha-reactive carboxylic acids by which the process is more economical.

Manganese Phosphate Coatings

Steel panels were processed at atmospheric pressure in a conventional bath enriched with 5 and 10 grams per liter of manganese citrate at 202°F to 204°F for periods of 15, 30, and 45 minutes. The results are shown in Table 2. A comparison may be made between values obtained in the conventional bath versus those obtained by enrichment of the bath. The addition of 5 and 10 grams per liter of manganese citrate to the phosphating bath, as the processing time was extended, increased the FA and the TA. The ratio $\frac{TA}{FA}$ showed only a slight change. The coating weight and the iron etched in the conventional bath increased with the processing time. With the 5 gram/liter enrichment, the coating weight decreased with the processing time, and the amount of iron etched decreased slightly. With the 10 gram/liter enrichment, the coating weight showed an increase with the processing

TABLE 2 - MANGANESE PHOSPHATE COATINGS APPLIED IN A CONVENTIONAL BATH WITH AND WITHOUT MANGANESE CITRATE

Treatment of Bath	FA*	TA**	TA/FA	Iron (%)	pH	Process Time (Min)	Total Process Time (Min)	Coating Wt. (mg/sq ft)	Iron Etched (mg/sq ft)	Resistance to Corrosion (Hrs to Failure)
Conventional manganese bath at atmospheric pressure 202°-204°F										
Before processing	2.3	20.7	9.0	0.08						
						15		1648	989	3
						30		1976	1152	5
						45		2140	1250	6
Conventional manganese bath with 5 grams per liter Manganese Citrate										
Before processing	4.5	29.1	6.5	0.08						
						15		1717	880	1
						30		610	717	1
After processing	3.9	30.7	7.9	0.05		45		693	739	2
Conventional manganese bath with 10 grams per liter Manganese Citrate										
						15		628	260	2
						30		1226	891	4
After processing	6.2	37.6	6.0	0.07		45		1595	1413	4
Conventional manganese bath under 1 PSIG (212°F)										
Before processing	1.9	14.6	7.3	0.06	2.7					
						15	34	2085	753	9
						30	45	2841	689	9
After processing	2.0	14.7	7.3	0.05	2.7	45	59	2944	825	9

* Free Acid ** Total Acid

time, and the amount of iron etched also increased. The processing temperature of the bath operated at atmospheric pressure was too low to effect a coating that would provide protection from corrosion beyond 6 hours.

Phosphating Steel under Pressure of 1 PSIG

As shown in Table 2, steel panels were processed consecutively in a conventional bath under 1 PSIG (212°F) for periods of 15, 30, and 45 minutes. The ferrous iron of the bath was very low (0.06 percent). The free acid was 2.0 points and the total acid was 15 points. When the total acid is below 27 to 30 points, the bath is considered a poor phosphating bath. After a processing time of 45 minutes, the coating weight showed an increase, the iron etched varied from 689 to 825 mg-per-sq-ft, and the corrosion resistance of the coatings remained at 9 hours even though the thickness of the coatings changed. The coatings processed for a period of 15 minutes appeared to be as satisfactory in providing the same protection as those processed for 45 minutes.

Manganese Organic Compounds

As shown in Table 2, 15 minutes appeared to be a reasonable length of time for processing steel panels in the pressure vessel at 1 PSIG. Therefore, 15-minute pressure times were used in the following experiments for the steel panels under the following conditions:

1. In a conventional bath,

2. In a conventional bath enriched with 10 grams per liter of the following additives:

    a. manganese citrate
    b. manganese tartrate
    c. manganese gluconate

The following changes were made in the processing procedure: As each 6-liter bath was taken from the stock solution, near the temperature of 160°F, enrichment was added.

The steel panels were then introduced into the vessel. The pressure vessel was closed, the steam was turned on, and the air was purged from the vessel. The initial time and temperature were noted. The 15-minute processing period was initiated when the bath temperature reached 212°F. As shown in Table 3, the total processing time was about 30 minutes. Enrichment additives of the bath appeared to buffer the free acid and to increase the pH. Coatings applied in the baths enriched with manganese tartrate and manganese gluconate provided the best resistance to heat and corrosion. Coatings applied in the bath enriched with manganese citrate at 1 PSIG provided less protection than those of the control coating. Photographs of the coated panels after exposure in the salt-spray test are shown in Figures 1, 2, 3, and 4. Coatings applied in the baths enriched with manganese tartrate and manganese gluconate under steam pressure showed a significant improvement in resistance to heat and corrosion.

Fax Film Replica

A Fax film is an imprint made of the coated surface area and recorded on a photograph. Fax film replicas were made of the phosphate coatings to examine the nature of the surface layer. Examination of the coatings was made as follows:

As shown in Figure 5, the coating as-processed in a conventional bath at atmospheric pressure at 210°F for 45 minutes exhibited a fine, dense, crystalline structure with dark spots of porosity.

The coatings shown in Figures 6, 7, 8, and 9 were applied under steam pressure of 1 PSIG (212°F) for 10 minutes. The coating processed in the conventional bath without an additive had a mass deposition of coarse crystals with dark areas of porosity (Figure 6). The coating processed in the bath with 10 grams per liter of manganese citrate exhibited a conglomerate mass of fine crystals with dark areas of porosity (Figure 7). The coating processed in the bath with 10 grams per liter of manganese tartrate exhibited a fine, dense, crystalline structure,

TABLE 3 - MANGANESE PHOSPHATE COATINGS APPLIED IN A BATH WITH AND WITHOUT ENRICHMENT UNDER STEAM PRESSURE

Treatment of Bath	FA*	TA**	TA/FA	Iron (%)	pH	Process Time (Min)	Total Process Time (Min)	Coating Wt. (mg/sq ft)	Iron Etched (mg/sq ft)	Loss in Wt due to exposure at (mg/sg ft)			Resistance to Corrosion after Thermal Exposure (Hours to Failure)			
										350°F	400°F	450°F	No Heat	350°F	400°F	450°F
Conventional Manganese Bath at 1 PSIG																
Before processing	2.5	13.4	5.4	0.05	2.6											
After processing	1.6	13.1	8.1	0.05	2.6	15	31	2240	645	16	27	59	96	6	6	1
Conventional Manganese Bath with 10 gram/liter of Mn-Citrate at 1 PSIG																
Before processing	1.9	9.8	5.2	0.05	4.3											
After processing	1.5	12.0	8.0	0.05	3.8	15	43	1300	377	37	40	60	1	1	1	1
Conventional Manganese Bath with 10 gram/liter Mn-Tartrate at 1 PSIG																
Before processing	2.9	14.9	5.1	0.05	3.1											
After processing	3.6	14.4	4.0	0.05	3.0	15	30	4990	341	26	39	58	>720	>720	384	384
Conventional Manganese Bath with 10 gram/liter Mn-Gluconate at 1 PSIG																
Before processing	1.6	13.1	8.2	0.05	2.9											
After processing	1.1	6.8	6.2	0.05	3.0	15	33	5010	942	20	33	35	>720	>720	384	384

* Free Acid ** Total Acid

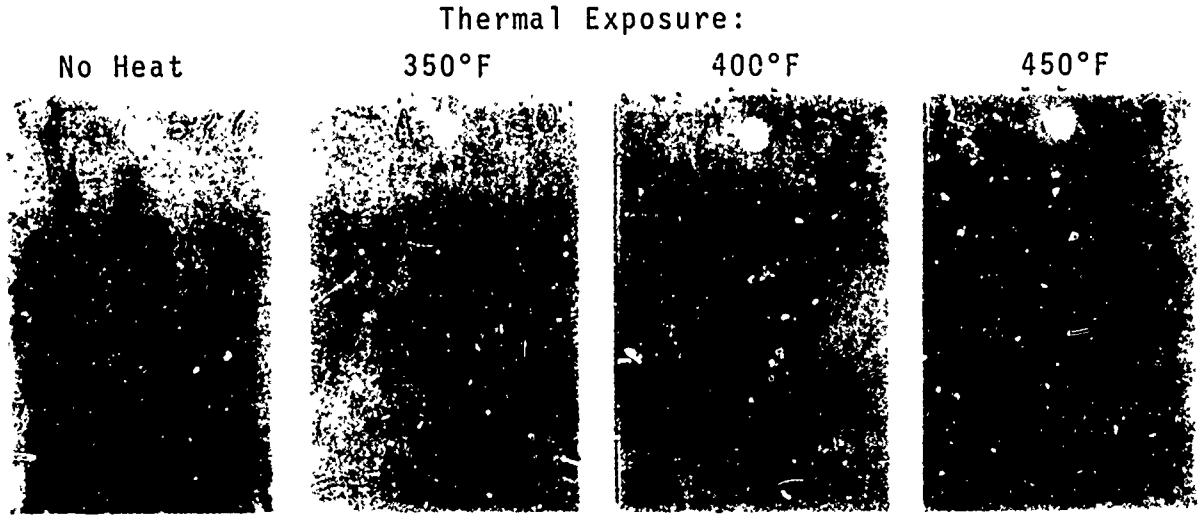

Figure 1 Manganese Phosphate Coated Panels after Salt-Spray Exposure Processed under Steam Pressure

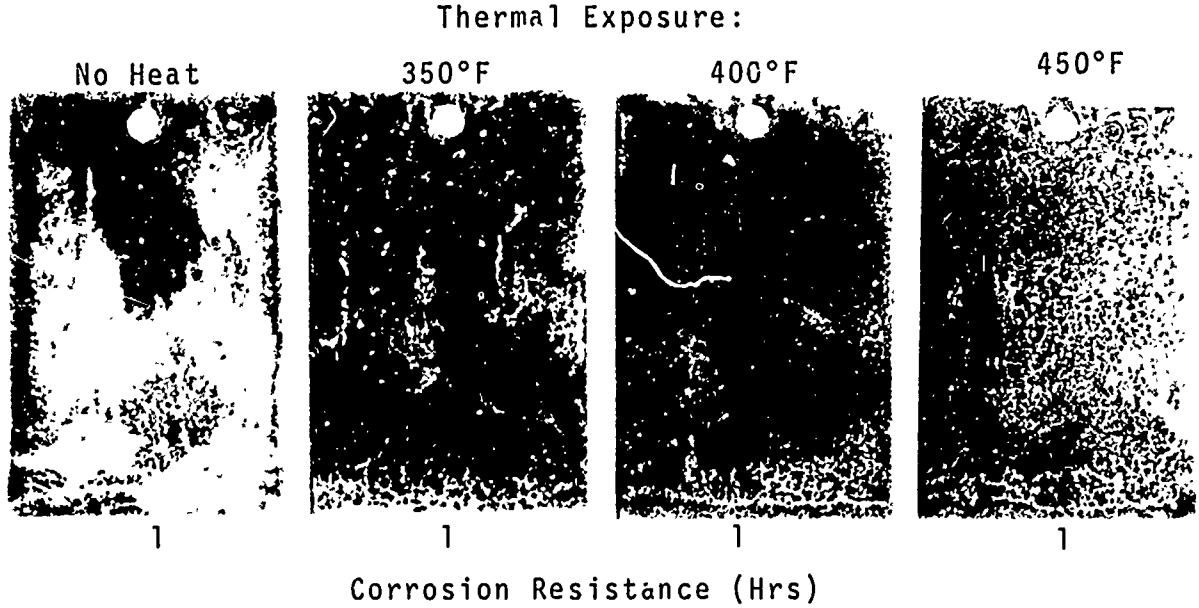

Figure 2 Manganese Phosphate Coated Panels after Salt-Spray Exposure Processed in a Bath Enriched with Manganese Citrate

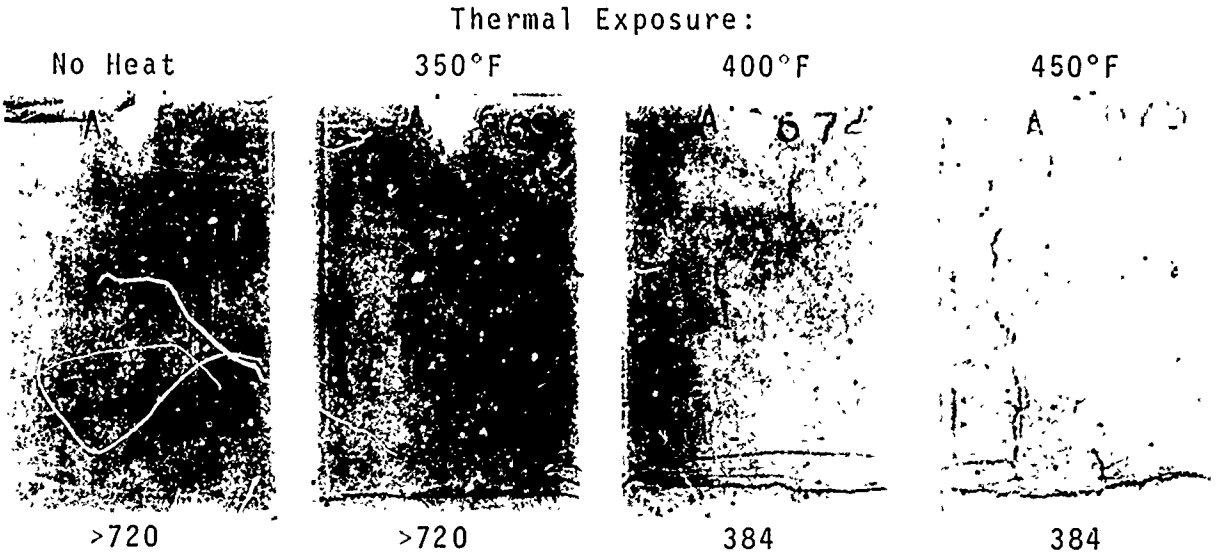

Figure 3 Manganese Phosphate Coated Panels after Salt-Srray Exposure Processed in a Bath Enriched with Manganese Tartrate under Steam Pressure

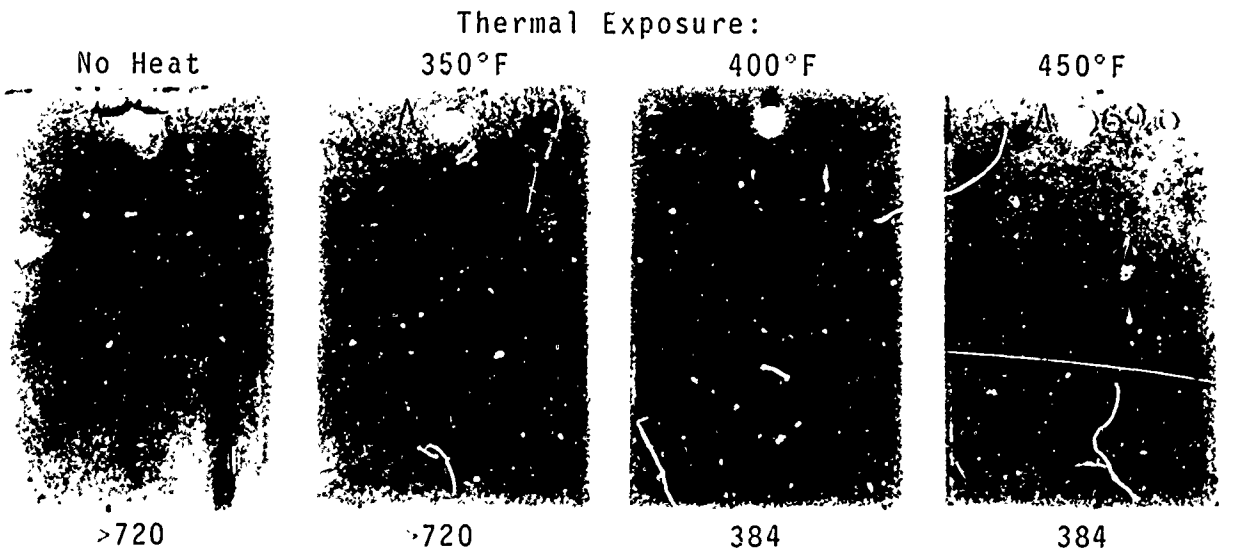

Figure 4 Manganese Phosphate Coated Panels after Salt-Spray Exposure Processed in a Bath Enriched with Manganese Gluconate under Steam Pressure

Figure 5 Fax Film Replica of Manganese Phosphate Coating Processed in a Bath at Atmospheric Pressure (100X)

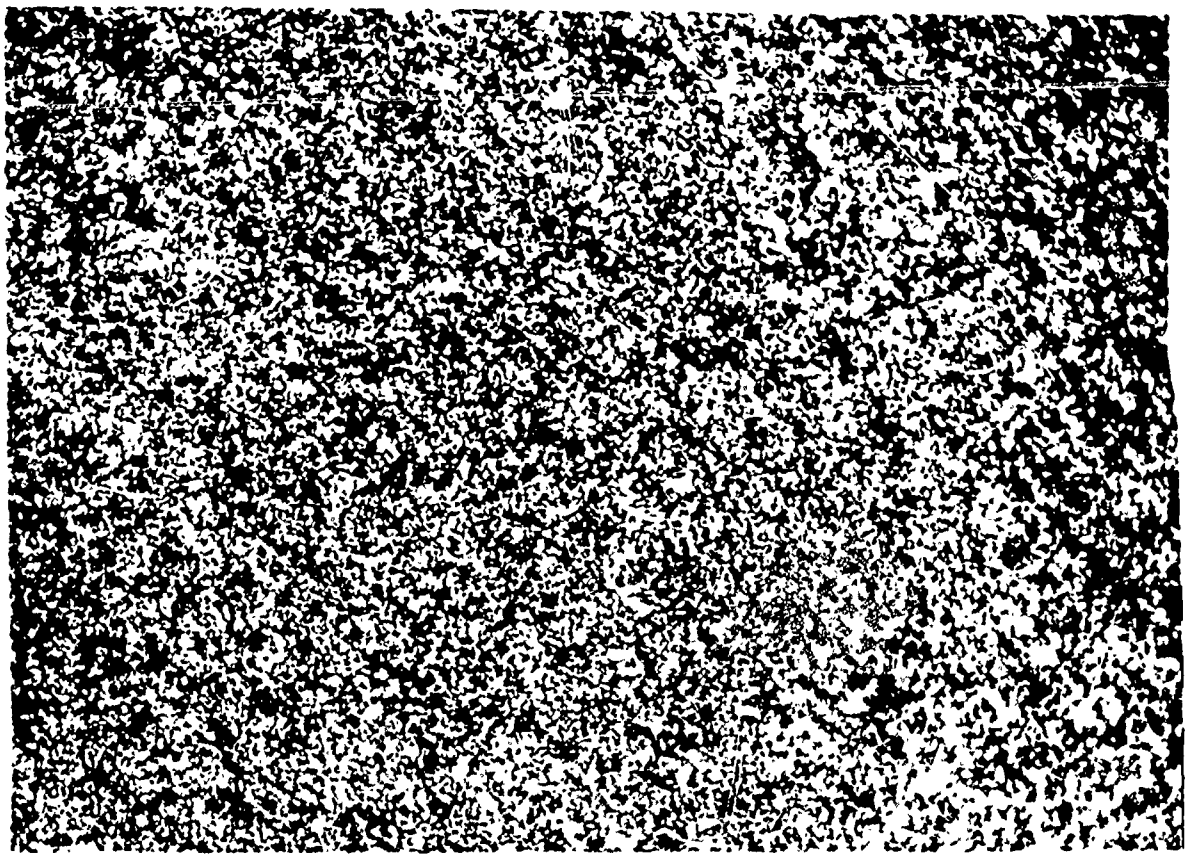

Figure 6 Fax Film Replica of Manganese Phosphate Coating Processed in a Bath under Pressure (100X)

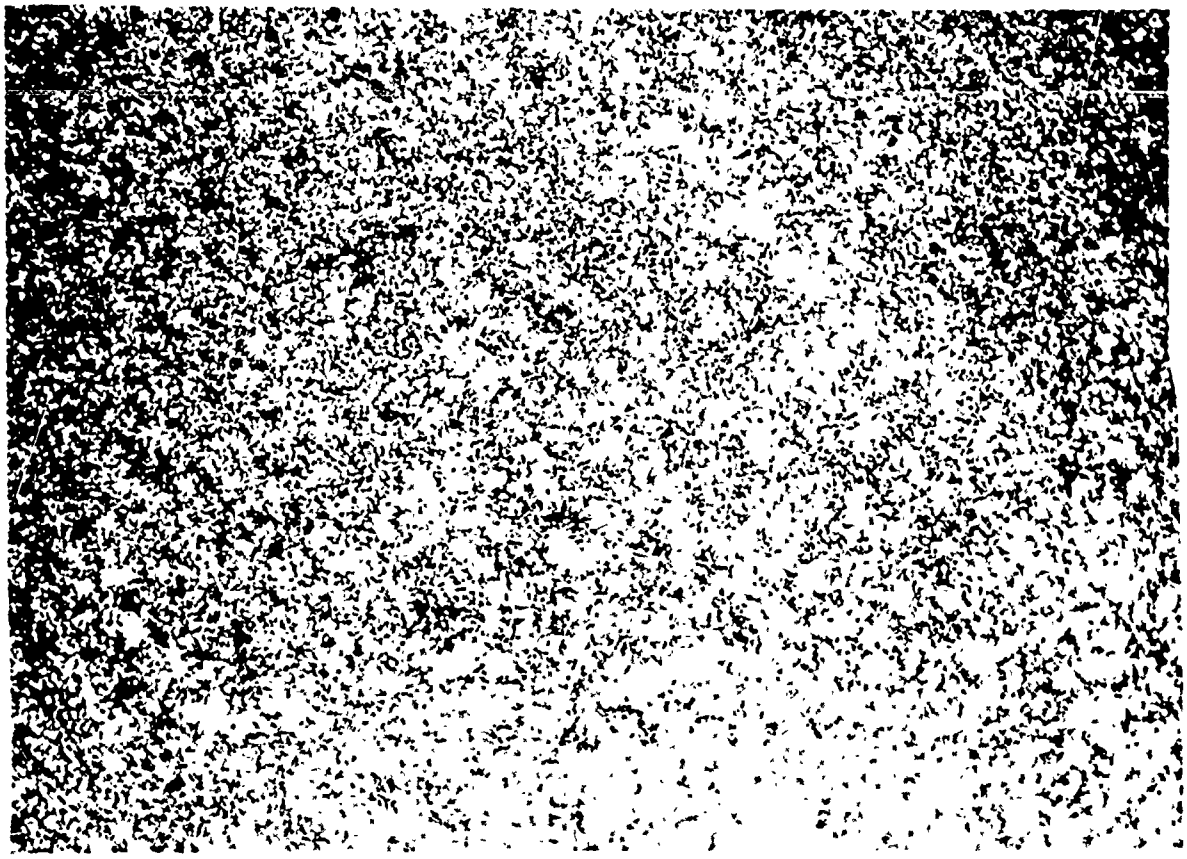

Figure 7 Fax Film Replica of Manganese Phosphate Coating Processed in a Bath Enriched with Manganese Citrate under Pressure (100X)

Figure 8 Fax Film Replica of Manganese Phosphate Coating Processed in a Bath Enriched with Manganese Tartrate under Pressure (100X)

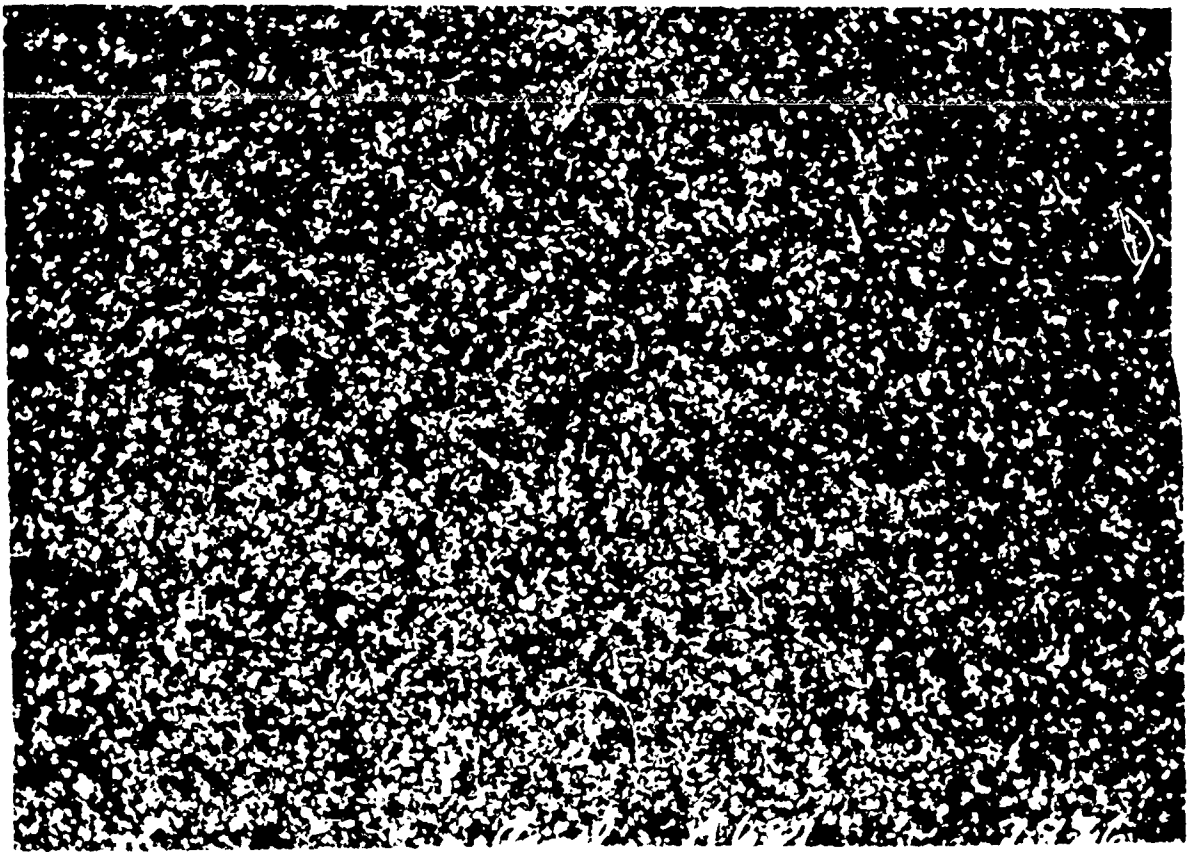

Figure 9 Fax Film Replica of Manganese Phosphate Coating Processed in a Bath Enriched with Manganese Gluconate under Pressure (100X)

minimum porosity, and uniform continuity (Figure 8). The coating processed in the bath with 10 grams per liter of manganese gluconate exhibited a conglomerate mass of medium size crystals, minimum porosity, and continuity (Figure 9). The coating was without rust after 720 hours of salt-spray exposure.

Phosphate Coatings Applied under Atmospheric Pressure

Manganese baths enriched with manganese tartrate and manganese gluconate produced coatings under steam pressure with superior resistance to heat and corrosion. For this reason, data were needed to determine whether these same baths would produce improved coatings when processed at atmospheric pressure after a period of 45 minutes at 203°F and 206°F under the following conditions.

1. In a conventional manganese bath enriched with manganese carbonate.

2. In a conventional manganese bath enriched with 10 grams per liter of the following additives:

   a. manganese citrate

   b. manganese tartrate

   c. manganese gluconate

3. After stabilization overnight, the above-listed baths were processed under steam pressure of 3 PSIG (222°F) for a period of 30 minutes.

A phosphating bath during overnight stabilization, in contact with the sludge becomes changed in that a reversal of the equilibrium condition occurs. Phosphating baths set aside to stabilize over the weekend have been noted by Eisler and Chamberlain[16] to produce coatings possessing increased resistance to salt-spray corrosion. This result was attributed to increased ferric phosphate redissolved from the sludge. The results are shown in Table 4. Initially the free acid of the stock solution was high, so manganese carbonate was added to reduce the acidity. The

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[16] Eisler, S. L. and P. G. Chamberlain, "Determination of the Solubility of Ferric Phosphate in Phosphating Solutions Using Radioiron," Rock Island Arsenal Laboratory, Report 53-638, June 1953.

TABLE 4 - MANGANESE PHOSPHATE COATINGS APPLIED IN A CONVENTIONAL BATH WITH AND WITHOUT ENRICHMENT AT ATMOSPHERIC PRESSURE

Treatment of Bath	FA*	TA**	TA/FA	Iron (%)	Total Process Time (Min)	Coating Wt. (mg/sq ft)	Iron Etched (mg/sq ft)	Loss in Wt due to exposure at (mg/sq ft)			Resistance to Corrosion after Thermal Exposure (Hours to Failure)			
								350°F	400°F	450°F	No Heat	350°F	400°F	450°F
Conventional Manganese Bath														
Stock Solution	4.7	27.0	5.8	0.17										
After processing at 203°-206°F	4.3	29.4	6.8	0.19	45	1217	488	27	35	46	2	2	1	1
With 1 lb. $MnCO_3$ to Stock Solution	3.1	22.5	7.2	0.16										
After processing	4.5	27.5	6.1	0.16	45	1937	444	22	33	55	5	5	5	1
with 10g/liter Mn-Citrate After processing	3.2	25.9	7.8	0.14	45	841	283	63	61	66	2	1	1	1
with 10g/liter Mn-Tartrate After processing	4.0	24.8	6.2	0.13	45	2376	243	45	76	87	16	120	120	48
with 10g/liter Mn-Gluconate After processing	4.2	21.8	5.2	0.14	45	2542	252	9	41	38	96	48	48	48

* Free Acid ** Total Acid

addition of manganese carbonate also enriched the bath in manganese content. The heat and corrosion resistance of the coatings was best, however, when the bath was enriched with manganese tartrate. Manganese gluconate was second best. Manganese-citrate enriched baths produced coatings inferior to those enriched with manganese carbonate. The addition of manganese carbonate improved the coating applied in the conventional bath at atmospheric pressure.

After the previous tests, the baths were allowed to stabilize overnight in contact with the sludge. The control bath consisted of a new portion taken from the stock solution. Each of the enriched baths was placed in the pressure vessel and heated to 200°F. Steel panels were introduced and processed at 3 PSIG (222°F) for 30 minutes. The results are shown in Table 5. The control bath that had been set aside to stabilize overnight showed an improvement in the coating. The coatings processed under steam pressure in the enriched baths did not show an improvement. In the previous test, about 1.4 sq. ft. of steel had been processed in the 6-liter bath at atmospheric pressure. After the bath had stabilized overnight, a similar area of steel was processed in that same bath under steam pressure without replenishment. This, without doubt, accounted for the decrease in the heat and corrosion resistance of the coatings. In processing under steam pressure as the temperature gradient increased the rate of reaction, mainly dissociation of the primary phosphates resulted in the formation of tertiary phosphates of iron and manganese. A rapid coating-buildup took place, and the excess of iron and manganese phosphates was precipitated as sludge. The sludge was low in ferric phosphate because the bath was initially low in ferrous phosphate. Manganese phosphate was in excess, so the sludge consisted largely of manganese phosphate. Upon stabilization, overnight, the sludge was very slow to dissolve, so the content of primary phosphates was greatly reduced. Processing under steam pressure did not improve the phosphate coatings because the baths, which had been previously used at atmospheric pressure, were low in primary phosphates.

Conductometric Titration Curves

Conductometric titration curves were made of the baths to determine the free and total acids before and after each

TABLE 5 - MANGANESE PHOSPHATE COATINGS APPLIED UNDER STEAM PRESSURE IN A BATH PREVIOUSLY USED AT ATMOSPHERIC PRESSURE

Treatment of Bath	FA*	TA**	TA/FA	Iron (%)	pH	Process Time (Min)	Total Process Time (Min)	Coating Wt. (mg/sq ft)	Iron Etched (mg/sq ft)	Loss in Wt due to exposure at (mg/sq ft)			Resistance to corrosion after Thermal Exposure (Hours to Failure)			
										350°F	400°F	450°F	No Heat	350°F	400°F	450°F
Conventional Manganese Bath Stabilization Overnight***	2.7	21.3	7.9	0.17												
After processing @ 3 PSIG	3.9	20.8	5.4	0.14		30	51	3466	312	9.8	30	66	40	88	88	88
With 10g/liter Na-Citrate Stabilization Overnight	3.5	26.3	7.5	0.12	7.5											
After processing @ 3 PSIG	3.2	25.5	7.9	0.12	7.9	30	52	329	485	16	19	22	1	1	1	1
With 10g/liter Na-Tartrate Stabilization Overnight	---	----	---	----												
After processing @ 3 PSIG	4.3	26.4	6.1	0.15		30	48	452	324	13	16	19	1	1	1	1
With 10g/liter Na-Gluconate Stabilization Overnight	4.0	21.8	5.5	0.14												
After processing @ 3 PSIG	4.2	22.5	5.4	0.12		30	50	2364	434	13	58	67	16	16	6	1

* Free Acid ** Total Acid *** All baths were allowed to reach equilibrium overnight.

processing cycle. Analyses were made to determine the effect of additives and to follow the changes in the baths when processing under two pressures. Initially, the free acid of the bath is kept at a low level to control the pickling action of the free acid (H_3PO_4) on the work surface. The total acid is a measure of the free acid and the combined phosphates in the bath. From the analysis of the bath, the ratio of total acid to free acid is calculated. The bath is most effective when the ratio is kept at 6 to 1 or greater. A conductometric titration curve was made of the stock bath at room temperature and after the bath was preheated to 200°F. A work load of 1.4 sq. ft. of mild steel was introduced and processed for 30 minutes at 1 PSIG. The procedure was repeated on a portion of the stock bath for the same length of time at 3 PSIG. Samples of the bath were analyzed after the preheat at 200°F, and before and after the 30-minute-processing periods at 1 and 3 PSIG, respectively. The same procedure was repeated as outlined except that 10 grams per liter of manganese citrate, manganese tartrate, and manganese gluconate were added, respectively, to a portion of the stock bath and processed under 1 PSIG (212°F) and 3 PSIG (222°F). Analyses were made on a recording titrimeter. A 10-milliliter sample was titrated with 0.3N NaOH solution. The analysis of the bath made at a temperature of 70°F and after the bath had been heated to 200°F without processing any work is shown in Figure 10. Changes in the FA, TA, and pH were noted. The analysis of the bath after it had been preheated to 200°F is shown in Figure 11. A second curve shows the change in the bath after 1.4 sq. ft. of steel had been processed at 212°F for 30 minutes. A third curve shows the change in the bath after a similar amount of steel had been processed at 222°F for 30 minutes. The curves show that the free acid increased and the total acid decreased as the bath temperature was increased. The initial free acid and the final total acid range when manganese citrate was added to the bath are shown in Figure 12. The relative closeness of the curves after the processing periods with manganese tartrate is shown in Figure 13. The curves crossed each other as the temperature was increased. The interval between the curves at the initial pH and the final pH is shown in Figure 14. The curves on the tartrate analysis of Figure 13 crossed each other at lower values than those shown on Figure 14 of the gluconate analysis. The buffering action of the free acid is shown on Figure 13 by the closeness of the curves at the initial pH readings.

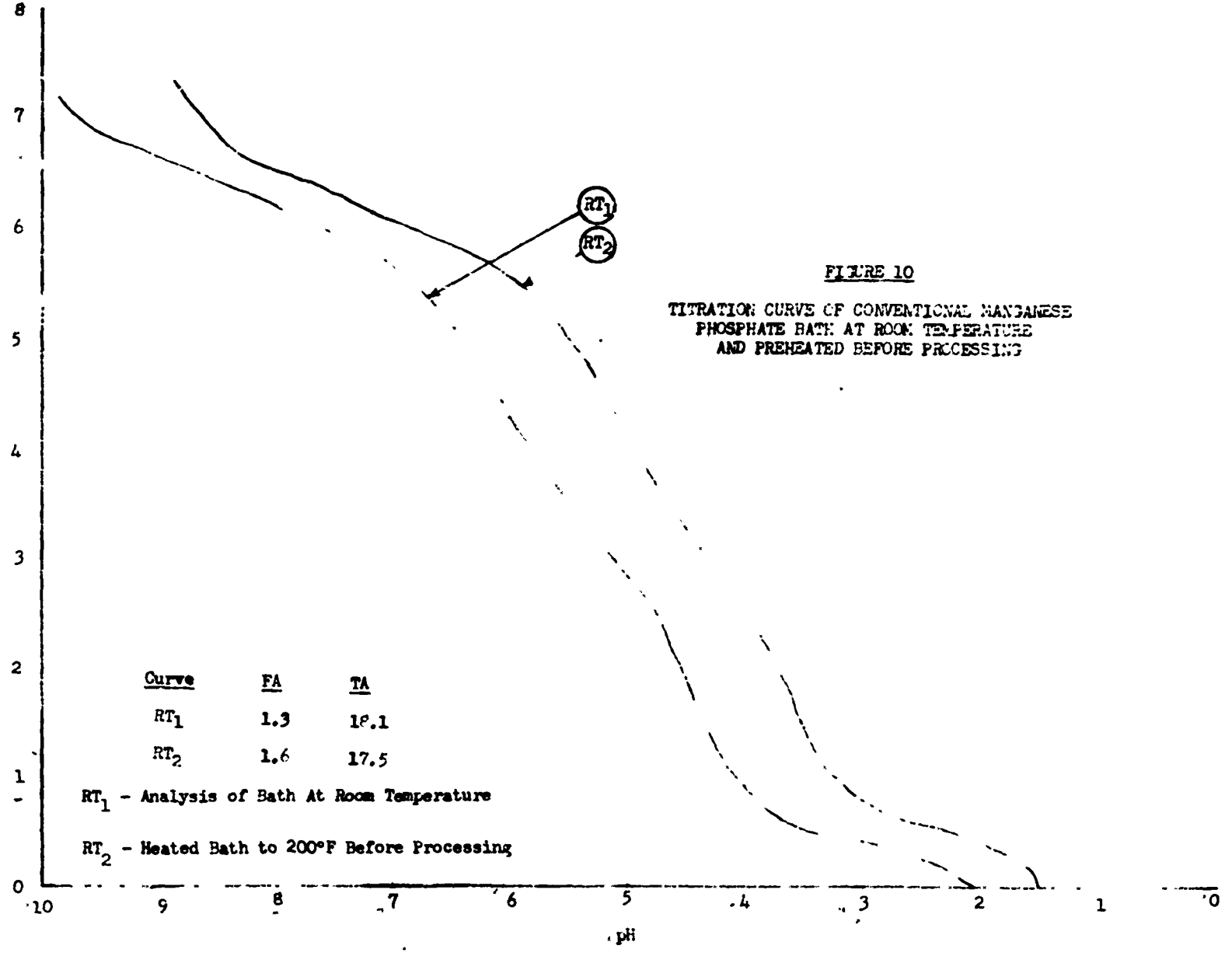


FIGURE 10

TITRATION CURVE OF CONVENTIONAL MANGANESE PHOSPHATE BATH AT ROOM TEMPERATURE AND PREHEATED BEFORE PROCESSING

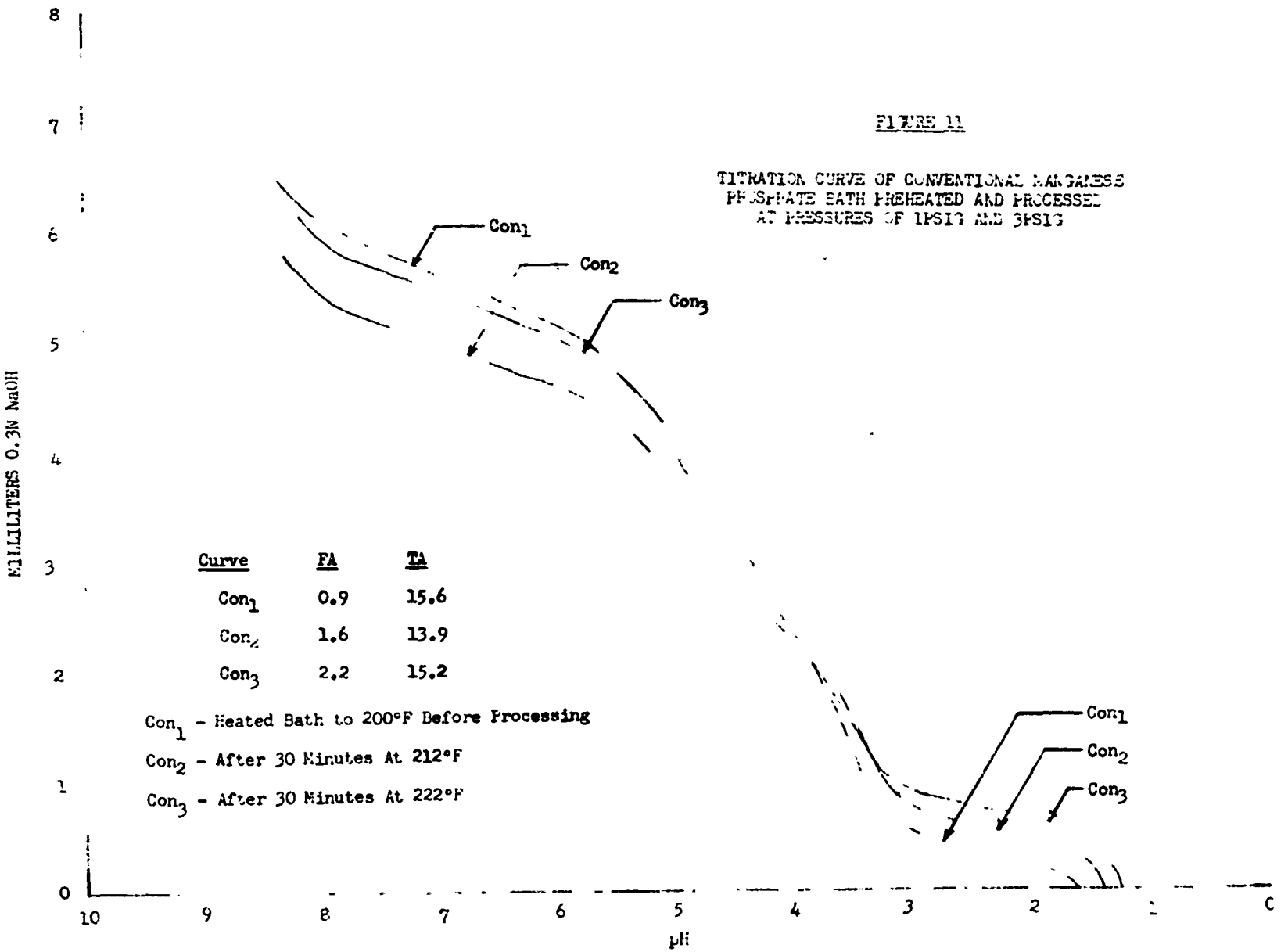
Curve	FA	TA
RT_1	1.3	18.1
RT_2	1.6	17.5

RT_1 - Analysis of Bath At Room Temperature

RT_2 - Heated Bath to 200°F Before Processing

FIGURE 11

TITRATION CURVE OF CONVENTIONAL MANGANESE PHOSPHATE BATH PREHEATED AND PROCESSED AT PRESSURES OF 1PSIG AND 3PSIG



Curve	FA	TA
Con_1	0.9	15.6
Con_2	1.6	13.9
Con_3	2.2	15.2

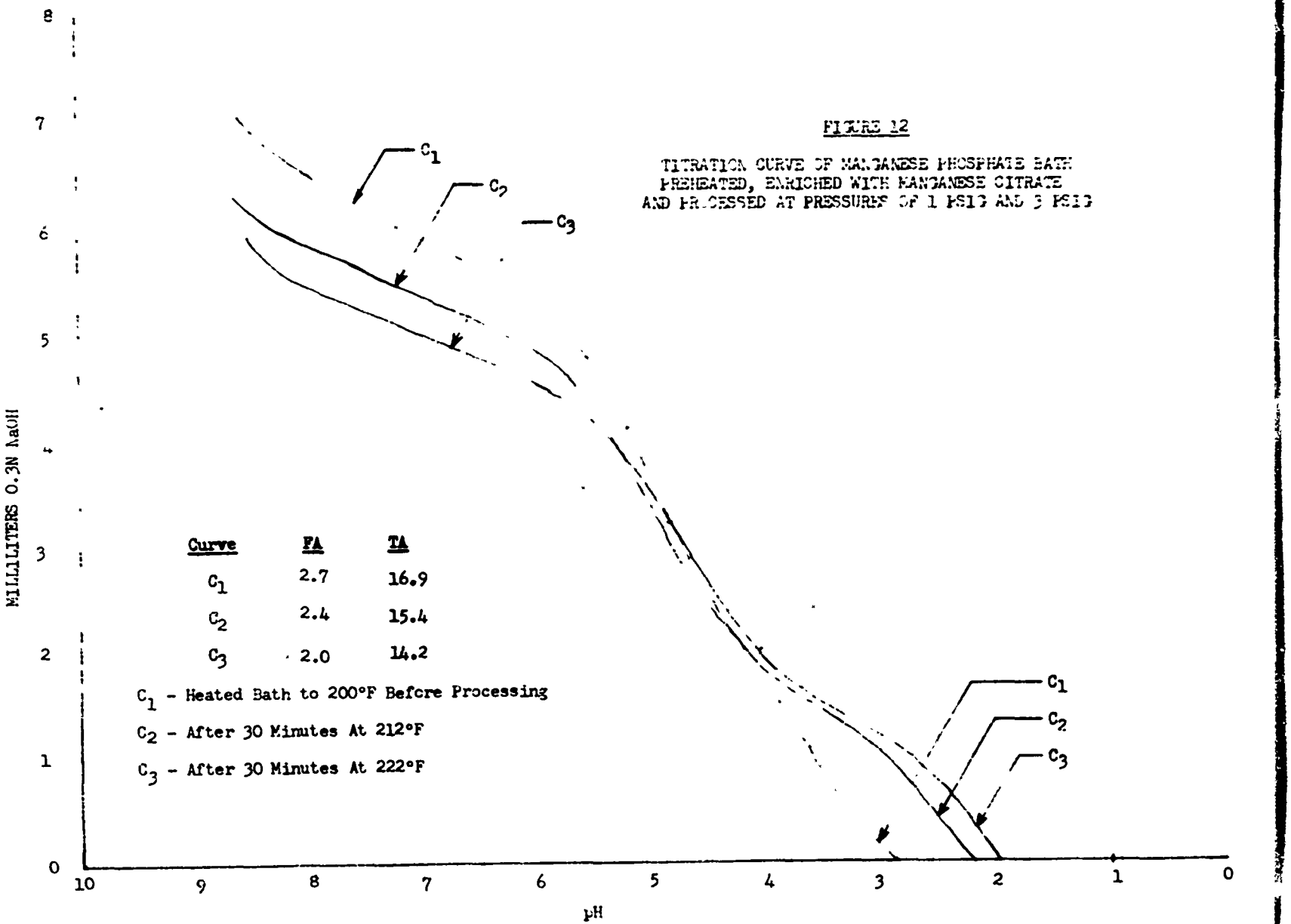
Con_1 - Heated Bath to 200°F Before Processing

Con_2 - After 30 Minutes At 212°F

Con_3 - After 30 Minutes At 222°F

FIGURE 12

TITRATION CURVE OF MANGANESE PHOSPHATE BATH PREHEATED, ENRICHED WITH MANGANESE CITRATE AND PROCESSED AT PRESSURES OF 1 PSIG AND 3 PSIG



Curve	FA	TA
C_1	2.7	16.9
C_2	2.4	15.4
C_3	2.0	14.2

C_1 - Heated Bath to 200°F Before Processing

C_2 - After 30 Minutes At 212°F

C_3 - After 30 Minutes At 222°F

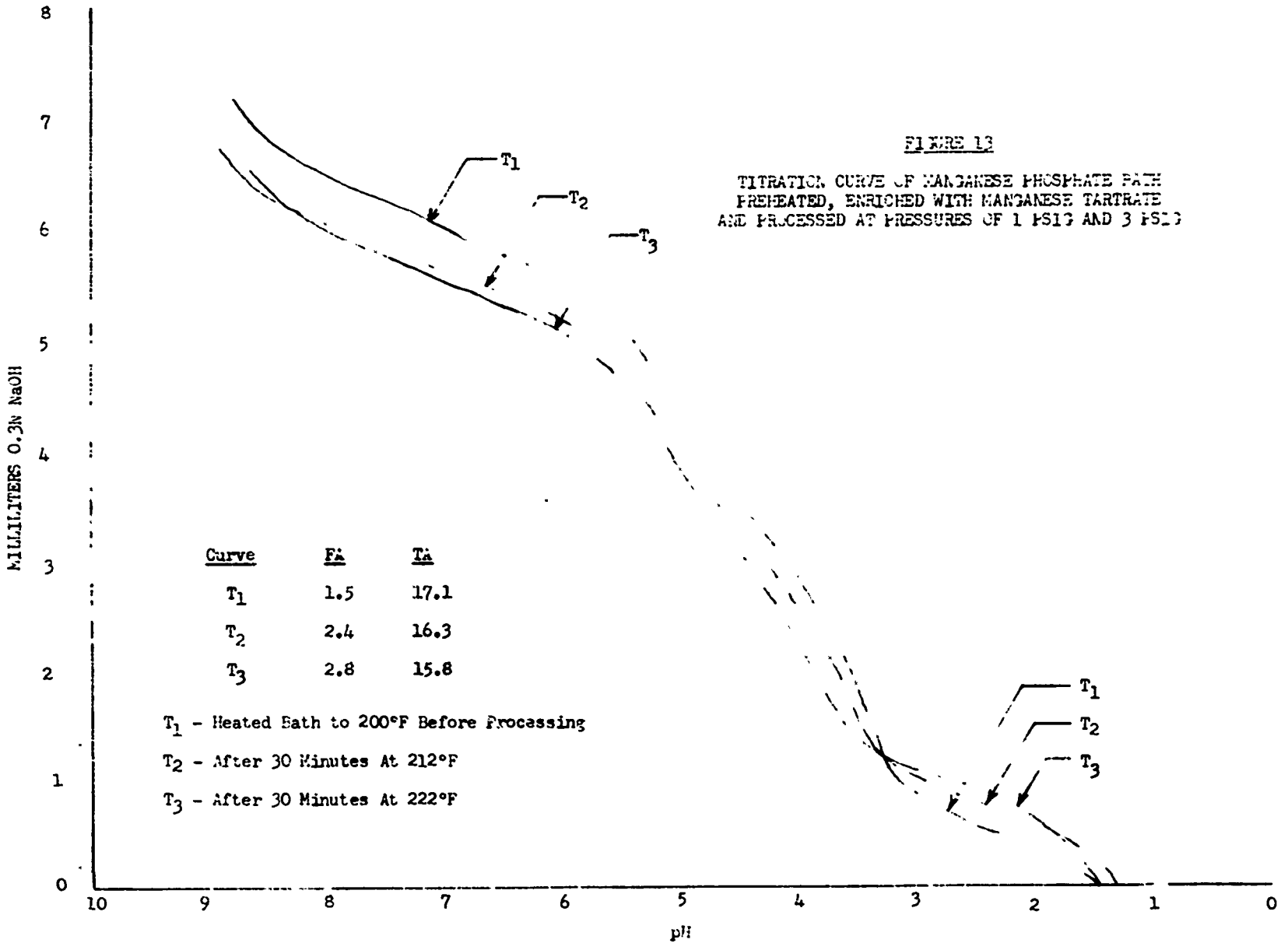


FIGURE 13

TITRATION CURVE OF MANGANESE PHOSPHATE PATH PREHEATED, ENRICHED WITH MANGANESE TARTRATE AND PROCESSED AT PRESSURES OF 1 PSIG AND 3 PSIG

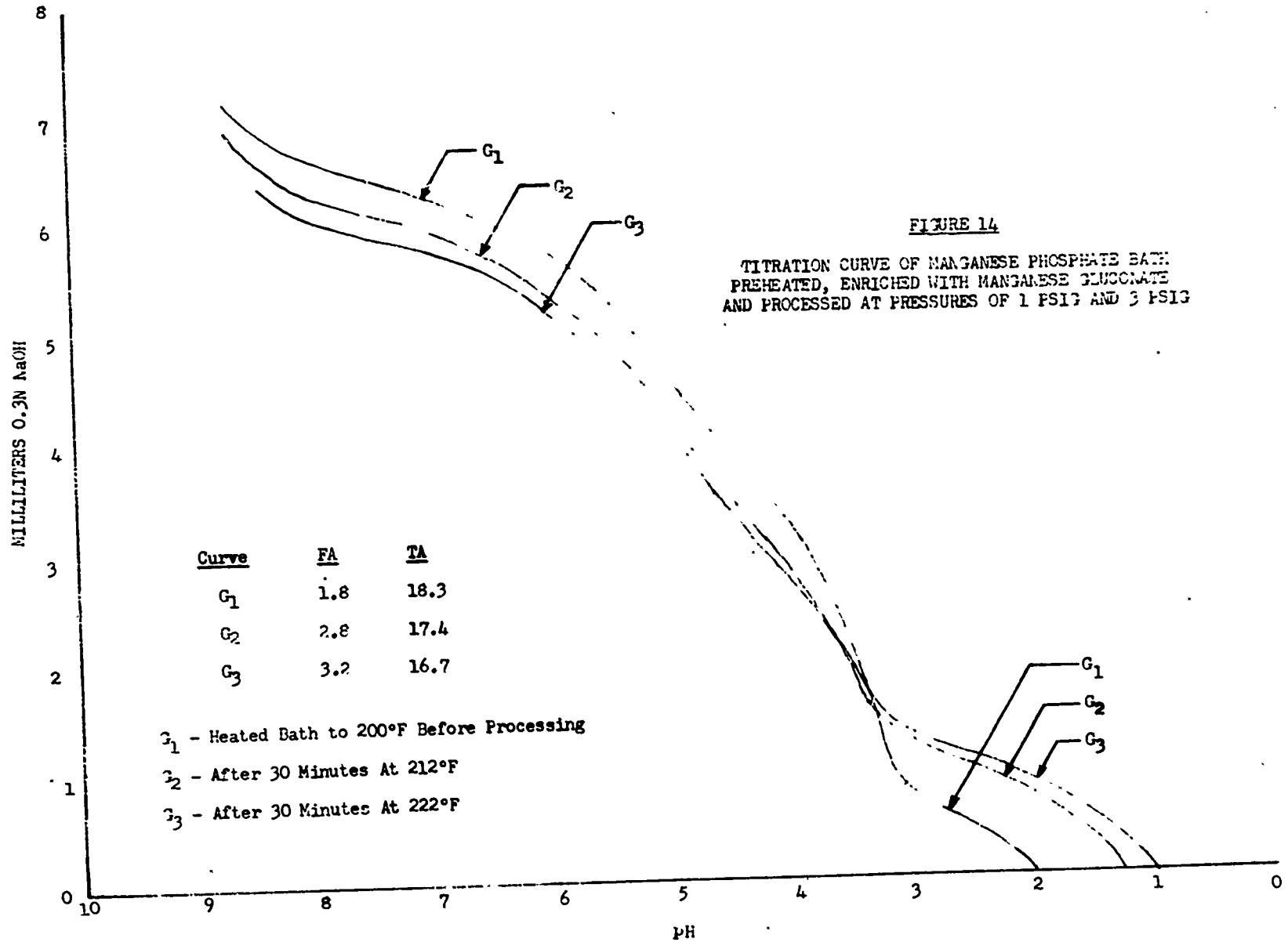


FIGURE 14

TITRATION CURVE OF MANGANESE PHOSPHATE BATH PREHEATED, ENRICHED WITH MANGANESE GLUCONATE AND PROCESSED AT PRESSURES OF 1 PSIG AND 3 PSIG

Processing under Atmospheric Pressure

This process does not lend itself to the production of quickly formed phosphate coatings for heat and corrosion resistance. However, the method has many advantages. The operation can be conducted in a tank open to the atmosphere. The size of the tank can be changed with relative ease to meet the workload. The contents can be heated internally or externally, and the temperature of the bath can be maintained between 205°F and 210°F. Usually 35 to 45 minutes are required under these conditions to effect a coating that will successfully pass a two hour salt spray exposure.

Processing under Steam Pressure

The method of processing under steam pressure has its advantages. The processing is done in an autoclave. The temperature of the bath can be raised under pressure from a minimum of 210°F at atmosphere pressure to 260°F at 22 PSIG. A relatively thick coating with a minimum porosity can be quickly formed in 10 to 20 minutes of processing time. The coating is enriched with manganese from solution, and possesses excellent resistance to heat at 450°F with subsequent resistance to salt spray corrosion. The operational cost is dependent upon the size of the autoclave, the working pressure, and replenishment of the bath with acid salts. The most logical method is to conduct the processing at the lowest pressure that will effect a high quality phosphate coating in the shortest processing time.

Metal Organic Additives

Additives, such as manganese dihydrogen phosphate and phosphoric acid were used to maintain the total acid level, and manganese carbonate to control the free acid. The ferrous iron content of the bath should be less than 0.1 percent. The conventional bath can be enriched with metal salts of manganese citrate, manganese tartrate, and manganese gluconate, respectively. The processing procedures conducted at a minimum pressure of 1 PSIG (212°F) has shown that manganese tartrate and manganese gluconate aid in the formation of the insoluble coatings. These coatings afford superior resistance to heat and corrosion in the salt spray tests.

Improvement in the Rate of Phosphating by Pressurized Processing

In phosphating under steam pressure, line steam is circulated over the bath, and air is removed from the vessel. The temperature of the bath follows a time-temperature gradient as the pressure is increased. The following temperatures and pressures have been approximated:

Temperature (°F)	Pressure (PSIG)
212	1
222	3
232	7
242	11
252	16
262	22

As the temperature of the solution is increased, the rate of dissociation of the phosphating solution increases, the free acid increases, the total acid decreases, the iron in solution decreases, and the pH decreases. These changes affect the solution and the coating as follows: As the rate of reaction increases, some of the phosphate materials are "thrown out of solution" as a flocculent precipitate. Under thermal movement of the solution, the particles grow in size and some of them are codeposited in the coating. The total acid is reduced through the loss of these materials. However, the free acid in solution increases and lowers the pH. This increase in free acid accelerates the etching action on the metal surface and reduces the rate of deposition of the insoluble phosphate coating. When the ratio of total acid to free acid decreases below 6, the coating becomes thinner and porous and may eventually result in only a pickling action with discoloration of the surface. The corrosion protection afforded by the porous coating is unsatisfactory. The addition of manganese citrate, manganese tartrate, and manganese gluconate to the solution buffers the free acid and stabilizes the solution. This is shown in Figures 10 through 14. Phosphating at two temperatures is shown by

a variation in the pH and at the point at which the curves cross each other.

Fax film replicas of the applied coatings show that the use of metal salts in the baths aid in the rapid formation of conglomerate crystals in the insoluble coating. The heat and corrosion resistance of the coatings is directly related to the thickness of the insoluble coating applied as a conglomerate mass of crystals in the shortest processing time. Coatings applied in the shortest time results in continuous and uniform distribution, minimal porosity, limited iron loss at the metal-solution interface, and enrichment of the insoluble coating with metal from solution.

CONCLUSIONS

The following conclusions are made:

1. Steel specimens processed in a manganese solution enriched with manganese tartrate and manganese gluconate, respectively, at 1 PSIG for 30 minutes, did provide a phosphate coating that afforded over 720 hours of protection in the salt spray tests.

2. In comparative tests, the manganese phosphate coatings applied in an autoclave bath with manganese compounds of the alpha-reactive-carboxylic acids afforded significantly superior heat resistance to 450°F and corrosion resistance than conventional coatings processed under atmospheric pressure.

3. Steel specimens processed in a conventional zinc bath enriched with zinc citrate under steam pressure produced coatings which exhibited only slight improvement in salt spray corrosion resistance over conventional zinc phosphate coatings.

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RECOMMENDATIONS

1. The process of phosphating under steam pressure at low temperatures (212°F) with the use of manganese baths enriched with manganese tartrate and manganese gluconate, respectively, should be adopted for use on ferrous metal items requiring a high-temperature, corrosion-resistant, phosphate coating.

2. The use of metallic chelating agents in phosphating solutions should be investigated to determine how they affect the heat and corrosion resistance of the phosphate coatings.

3. Analytical methods should be developed to determine the amount of metal organic compounds in the phosphating solution so that process control can be more effective.

4. The sludge evolved in the bath should be controlled so that it will not be codeposited in the coating.

5. A continuous process should be developed for phosphating steel items under steam pressure.

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