Improved Iron Phosphate Corrosion Resistance by Modification with Metal Ions

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Iron phosphate coatings have found a wide range of use in the metal-finishing industry as a convenient method for achieving reasonably high levels of corrosion resistance. Flexibility of processing parameters and ease of use are probably the biggest reasons that iron phosphating enjoys its continued popularity.

The corrosion resistance of iron phosphate coatings can be dramatically improved by the selective addition of combinations of certain divalent metals. Excellent results have been attained by adding mixtures of zinc, nickel, and calcium at concentrations below 200 ppm to conventional iron phosphating baths. Changes in the iron phosphate coating brought on by these metal additions have promoted increases in corrosion resistance from 10 to 75%.

EXPERIMENTAL

Standard cold-rolled steel test panels were used throughout this study. They were subjected to a six-stage pretreatment process, summarized as follows: alkaline cleaner, water rinse, iron phosphate, water rinse, chromated final rinse, and deionized water rinse. The phosphated panels were then dried at 150°C (300°F) for 15 min.

Two different types of iron phosphate baths were used as standards of comparison. These are commercially available products and are typical of those employed in contemporary metal-finishing operations. The baths were accelerated either by sodium chlorate ($NaClO_3$) or by sodium m-nitrobenzenesulfonate (SNBS). These baths were modified by introducing combinations of metal ions, nickel/calcium (Ni/Ca) or zinc/calcium (Zn/Ca). The metal ions were added to the baths as ZnO, $Ca(NO_3)_2 \cdot H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$. The parameters for all of the phosphating baths are listed in Table I.

Table I. Iron Phosphate Bath Parameters

Accelerator	*Total Acid (pts)*	*pH*	*Contact Time (min)*	*Temperature (°C)*	*Zinc (ppm)*	*Nickel (ppm)*	*Calcium (ppm)*
$NaClO_3$	6.7	4.83	3	60	0	0	0
$NaClO_3$	6.5	4.84	3	60	0	100	33
$NaClO_3$	6.2	4.88	3	60	200	0	67
SNBS	9.3	4.64	3	60	0	0	0
SNBS	9.2	4.59	3	60	0	225	75
SNBS	8.6	4.52	3	60	400	0	50

SNBS, sodium m-nitrobenzenesulfonate.

The phosphated panels were coated (drawdown bar application) in the laboratory with eight different paint systems. The panels were cured according to manufacturer's specifications. The panels remained under ambient conditions for another 72 hr, ensuring completeness of cure. The descriptions of the resin systems and the appropriate codes for each paint are listed in Table II.

Accelerated corrosion testing was performed using a method based on ASTM B 117-90.[1] The painted panels were masked around the edges and received a single diagonal scribe down to bare metal. All of the panels that were coated with a particular paint remained in the salt spray chamber as a set. When a measurable amount of corrosion creepage away from the scribe was evident, the panels were removed and evaluated. Loose paint and corrosion products were removed by means of scraping along the direction of the scribe with the flat end of a spatula or by applying adhesive tape to the scribe area. In some instances, both methods were employed to ensure complete removal of nonadhering paint. Eight individual measurements of total creepage about the scribe were made on each panel. The eight measurements were averaged for each panel, and the averages from three replicate panels were averaged, to provide a final creepage value for each phosphating system.

Coating weights were determined for all of the phosphating baths studied using a gravimetric method. The phosphated panels were weighed before and after immersion in a 6 M hydrochloric acid solution, inhibited by the addition of 2% by weight Sb_2O_3. Complete removal of the conversion coating was effected after a 1-min, ambient-temperature immersion.

RESULTS AND DISCUSSION

$NaClO_3$-Accelerated Baths

Coating weight determinations were performed on panels phosphated in the three chlorate-accelerated baths. The addition of metal ions did not substantially change the amount of coating deposited. The standard bath provided 0.66 g/m^2, the bath modified by Ni/Ca, 0.72 g/m^2, and the bath modified by Zn/Ca, 0.59 g/m^2.

Results from accelerated corrosion testing are displayed in the column charts in Figures 1 and 2. The vertical axis on each chart describes the average total creepage of the various systems, expressed in millimeters. The appropriate paint code is listed below

Table II. Descriptions of Paint Systems

Paint Code	*Description*
MEL 1	Melamine-polyester
HS POL 1	High-solid polyester
POL	Red oxide primer, polyester topcoat
BK ENM	Bake enamel
MEL 2	Melamine-polyester
EPX	Epoxy primer
ALK EPX	Alkyd epoxy melamine
HS POL 2	High-solid polyester

Table III. Coating Weight Results

Phosphating Bath	*Coating Weights, g/m² (mg/ft²)*	*Percent Improvement*
Chlorate standard	0.66 (61.32)	—
Chlorate modified by Ni/Ca	0.72 (68.89)	52
Chlorate modified by Zn/Ca	0.59 (54.81)	10
SNBS standard	0.45 (41.81)	—
SNBS modified by Ni/Ca	0.28 (26.0)	75
SNBS modified by Zn/Ca	0.33 (30.66)	53

each group of columns. The number in parentheses is the exposure interval for each paint system.

The results decisively demonstrate the effectiveness of metal ion additions. Examination of Figures 1 and 2 shows that modifying the standard bath with Ni/Ca produced a conversion coating that furnished superior corrosion resistance in all eight cases. The average level of improvement over the chlorate standard was 52%.

Excellent performance was also exhibited by the Zn/Ca modification. The phosphate coating produced by this bath provided corrosion protection that was equal to or better than that provided by the coating from the standard bath for six of the eight paints. The modified coating was only slightly worse than the standard in two instances (HS POL #1 and EPX). In the six cases where the Zn/Ca-modified coating displayed superior performance, the level of improvement over the standard was 24%.

The Ni/Ca modification appeared to be a slightly more effective alternative for the chlorate-accelerated system than the Zn/Ca modification. Comparing results of the modified baths shows that corrosion resistance of the Ni/Ca-modified panels was superior to that from the Zn/Ca panels in four cases, whereas the latter panels were superior in three instances.

SNBS-Accelerated Baths

The phosphate coating weights produced by the three SNBS-accelerated baths showed a much wider range of variation than was observed with the chlorate-accelerated baths. In general, the coating weights from the SNBS-accelerated baths were lower than those produced by baths accelerated by chlorate. All of the coating weights in these studies are listed in Table III. The standard SNBS bath produced a coating weight of 0.45 g/m², the SNBS bath modified by Ni/Ca a coating weight of 0.28 g/m², and the bath modified by Zn/Ca a coating weight of 0.33 g/m².

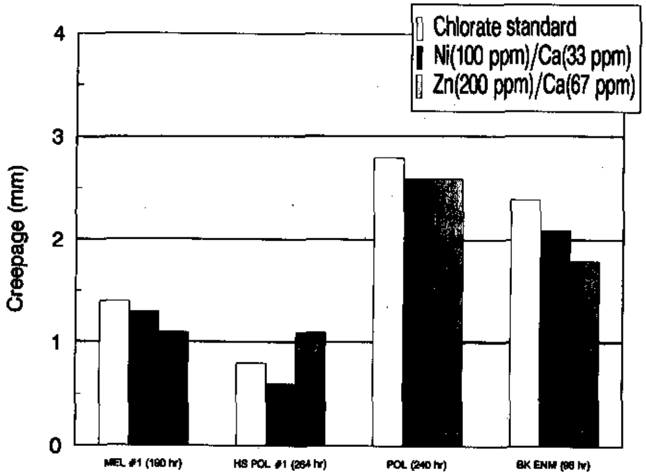

Figure 1. Adding nickel/calcium and zinc/calcium to a chlorate-accelerated iron phosphate bath.

Examination of salt spray results shows that modifying the standard SNBS-accelerated bath with metal ions proved to be even more effective than modifying the chlorate-accelerated bath. Creepage comparisons for the SNBS baths are shown in Figures 3 and 4.

Adding Ni/Ca to the conventional SNBS bath improved corrosion resistance for all eight paint systems. The average level of improvement was a substantial 75%.

A similar level of improvement was attained for panels treated with the SNBS bath modified by Zn/Ca. The experimental panels provided corrosion protection that was superior or equal to that of the standard in seven of eight cases. The magnitude of the improvement was significant for this altered bath also, at 53%.

Coatings from SNBS baths modified by Ni/Ca narrowly outperformed those from Zn/Ca-modified baths. The former coatings provided better corrosion resistance in seven cases, but the magnitude of this improvement is small. This is in contrast to the results observed with metal-modified chlorate baths, where neither altered coating appeared to provide a discernible advantage over the other. The composite levels of improvement (listed as per-

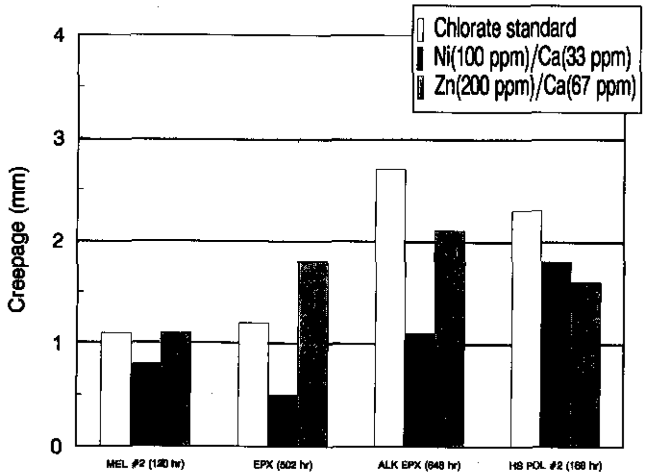

Figure 2. Adding nickel/calcium and zinc/calcium to a chlorate-accelerated iron phosphate bath.

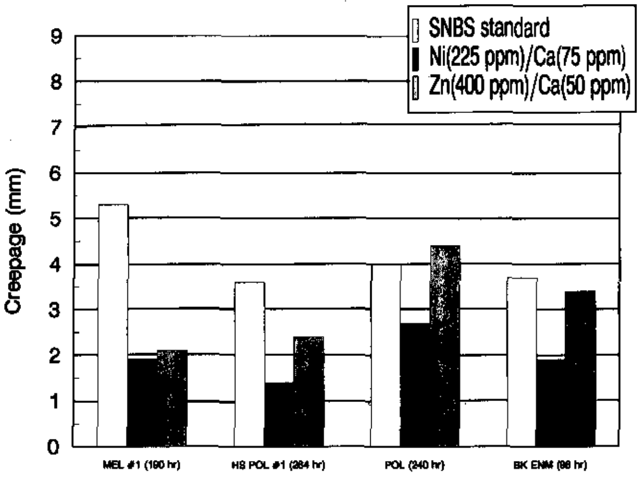

Figure 3. Adding nickel/calcium and zinc/calcium to a sodium m-nitrobenzenesulfonate-accelerated iron phosphate bath.

cent difference) for the coatings produced by the modified baths are listed in Table III.

Clearly, the addition of metal ion combinations to conventional iron phosphating baths yields conversion coatings that significantly improve corrosion resistance. These improvements likely derive from changes in the composition of the phosphate coating brought on by variations to the phosphating bath.

There has been a great deal of discussion in the literature concerning the composition of iron and zinc phosphate coatings. Various metal phosphate and oxide compounds have been characterized and suggested as being possible constituents of phosphate coatings. Reviews by Lorin[2] and Freeman[3] describe the results of various workers regarding coating compositions. A composite list shows that a wide range of possibilities exists: $Zn_2Fe(PO_4)_2{\cdot}4H_2O$ (phosphophyllite), $Zn_3(PO_4)_2{\cdot}4H_2O$ (hopeite), Fe_3O_4 (magnetite), $FeHPO_4{\cdot}H_2O$, $Fe_3(PO_4)_2{\cdot}8H_2O$ (vivianite), $CaHPO_4{\cdot}2H_2O$ (brushite), and $Zn_2Ca(PO_4)_2{\cdot}2H_2O$ (scholzite). Additionally, Cheever[4] reported finding nickel present in phosphate coatings produced by a conventional zinc phosphate bath. These findings demonstrate that modification of phosphate coatings (especially zinc phosphate coatings) by the addition of metal ions is readily accommodated by the phosphating mechanism.

Zinc phosphate coatings have long been known to provide the highest levels of corrosion resistance on steel. This technology has always been the first choice where long-term corrosion resistance has been required. Zinc phosphate coatings provide better protection against corrosion because zinc-containing salts (such as phosphophyllite and hopeite) are inherently less soluble in a corrosive environment than those containing iron as the only metal.

Varying zinc phosphate coating composition by the addition of nickel and calcium to the bath is a well-established practice. It has been shown that the coatings produced by such baths induce a reduction in crystal size, as compared with a simple bath, which uses only zinc oxide and phosphoric acid. Smaller crystals result in a coating that is more compact, which permits more crystals per unit area. This compaction ensures a better coverage of the metal surface, thereby reducing the number of pores and occlusions in the conversion coating. Minimizing coating porosity delays the onset of corrosive attack of the base metal. A highly compact coating results in improved paint adhesion as well.

Changes in the composition of the experimental iron phosphate coatings examined in the present work may have been the reason for the significant increases in corrosion resistance. Inclusion of salts containing zinc, nickel, or calcium may have sufficiently decreased the solubilities of the conversion coatings so as to improve salt spray performance.

In previous work,[5] the compositions of iron phosphate coatings formed from baths accelerated by chlorate and SNBS were established. The coatings were comprised of about 70% Fe_3O_4 and about 30% $FeHPO_4{\cdot}H_2O$. It is conceivable that the experimental coatings have somehow been modified due to the presence of zinc and nickel in the phosphating baths. The nature and mechanism of these modifications have not been examined, but such a determination will be necessary in order to gain a full understanding of the improvements in corrosion resistance.

There are several factors that probably limit the effectiveness of metal-modified iron phosphate coatings. The improvements in corrosion protection provided by the experimental iron

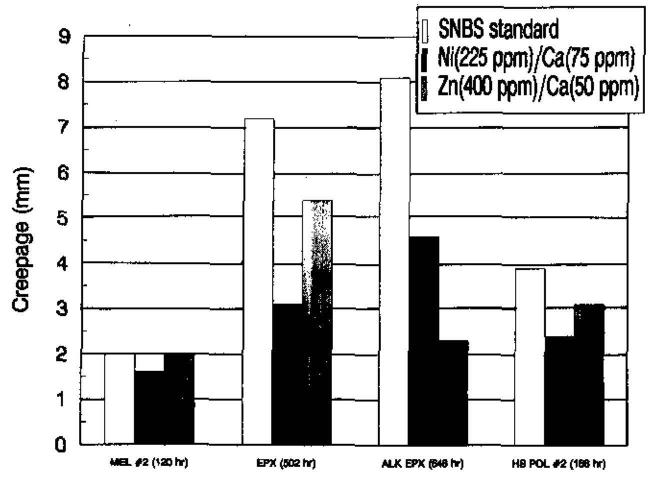

Figure 4. Adding nickel/calcium and zinc/calcium to a sodium m-nitrobenzenesulfonate-accelerated iron phosphate bath.

phosphate coatings are substantial, but these levels of corrosion resistance are far short of what can be expected of a conventional zinc phosphate coating, for example. Thus, the amount of modification to the iron phosphate coatings is probably small. If nickel and calcium make an iron phosphate coating more compact (as they do in zinc phosphating technology), then the decrease in porosity probably occurs only to a small (though observable) degree. The concentrations of the metal ions in the experimental phosphating baths are relatively low, approximately one-tenth what is normally found in a conventional zinc phosphate bath. It is for this reason that the degree of iron phosphate coating modification is thought to be small.

The kinetics of iron phosphating are also different in many ways from that of zinc phosphating. As a result, it is probably more difficult to form phosphophyllite and hopeite in an iron phosphating scenario, even with, for example, zinc in the bath. These salts may be present in the experimental conversion coatings, but their amounts are likely to be very small. A typical zinc phosphate bath is operated at a much higher acid level than is an iron phosphate bath. The efficiency of coating formation is governed by the point of incipient precipitation (PIP), the pH at which phosphate salts come out of solution to be deposited on the metal substrate.[6] Zinc phosphate coatings tend to be deposited at relatively low pH values. It is unlikely that a large amount of phosphophyllite is formed at iron phosphating pH values, i.e., values greater than 4.5. Iron phosphating's higher PIP permits the formation of iron-containing salts.

Despite these mechanistic obstacles, the improvement in corrosion resistance provided by metal-modified iron phosphate coatings is unmistakable. The degree of improvement might even be further increased by making changes in the operation of the phosphating bath. In this work, the experimental iron phosphating baths were run using the same parameters normally employed by the standard baths. Altering these parameters (e.g., running the bath at lower pH in order to promote the formation of zinc-containing phosphates) may promote further beneficial changes to the composition of the iron phosphate coating.

It is clear that more work is necessary to characterize the nature of the altered conversion coating. Discovering the identities and amounts of new components in the experimental iron phosphate coatings and determining their morphologies will go a long way in deciding how to operate metal-modified iron phosphate baths in order to maximize corrosion resistance.

CONCLUSION

Conventional iron phosphate baths accelerated by $NaClO_3$ or SNBS were altered by the addition of small concentrations of metal ions. The metal ions were added as pairs, Ni/Ca and Zn/Ca. The conversion coatings produced by the modified baths provided substantial increases in salt spray resistance over coatings obtained from conventional phosphating baths. Both types of modified coatings furnished outstanding corrosion protection, but the data indicate that the Ni/Ca approach is superior, especially in the case of SNBS-accelerated phosphating baths.

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Calcium as a Phosphating Additive: An Overview

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The development of modified phosphate pretreatments to suit the ever-changing needs of the finishing industry has always proved to be a challenge to phosphators. The modified processes attempt to satisfy one or more of several criteria—such as simplicity of bath operation and control, tolerance to variable operating conditions and varying metal substrates, and low maintenance and operation costs—without making a compromise on coating quality and performance. The additive used to modify conventional processes is chosen so that it serves a distinct purpose without increasing material or handling costs that would offset the advantages associated with the additive's use. Additives that can perform more than one role in the bath are preferred.

CALCIUM-MODIFIED PHOSPHATING FORMULATIONS

One of the most versatile of the inorganic additives that has hitherto found widespread use in phosphating is calcium. The use of calcium as a phosphating additive stems from the fact that calcium is an acknowledged corrosion inhibitor. Calcium is rarely used as the sole metallic component in phosphating baths, although the use of calcium phosphating for electrical insulation and paint-base applications has been reported.[1,2] It is most commonly and effectively utilized as a component in zinc phosphating baths containing nitrate or nitrite accelerators. The addition of calcium in zinc phosphating baths results in a decrease in coating weight and calcium-zinc baths usually yield lightweight coatings, which find widespread applications as paint bases. Further, the fact that the deposition of coatings from calcium-zinc baths is associated with slow kinetics[3,4] contributes to their use in low coating-weight applications, which require good grain quality and compactness.

Among the earliest applications of calcium in phosphating was its use as an in-built grain refiner in the phosphating bath, which obviated the need for a separate activation or a titanium prerinse step.[5,6] Thus, the introduction of calcium not only resulted in the formation of coatings of good quality, but also contributed to the economy of the process through the elimination of the prerinse process stage.

The ability of calcium to substantially reduce grain size often resulted in the formation of microcrystalline or near-amorphous phosphate coatings when used as an additive in conventional zinc phosphating baths.[7,8] These coatings prove to be particularly useful in applications where thin, smooth, compact, dense, uniform coatings of low porosity are required. This also resulted in the improvement of corrosion resistance,[8] reduction of porosity, and enhancement of adhesion, especially in one-coat finishes.[3,9]

CALCIUM AS AN INGREDIENT IN COLD PHOSPHATING

To overcome the problem of slow kinetics associated with calcium-modified baths, high temperatures in the range of 80–90°C are often used.[4] At these temperatures, good quality coatings are obtained at practical operating times. The high-temperature processes are not popular, however, since they involve the use of expensive electrical energy and contribute to scaling and bath control problems. A survey of the literature shows that the recent trend has been to use calcium as a useful ingredient in cold phosphating formulations.[±°↑±×] Despite the drawback of slow deposition kinetics of calcium-modified baths, their use in cold phosphating is related to the fact that bath kinetics can be accelerated in these baths through the use of "initiators" such as nickel,[12,15] fluoride,[11,13] manganese,[16] borohydride,[17] etc. Several multication baths containing calcium have also been used for cold phosphating applications.[10,12,13,16,18] Judicious combinations of calcium, along with surface-active agents, have been used to obtain superior quality coatings from phosphating baths operating at low temperatures. Such combinations integrate the grain-refining and corrosion-inhibition properties of calcium with the cleaning, pore-sealing, and water-repellant properties of surfactants in the coatings obtained from these baths.[10,19,20]

CRYSTAL TYPE AND PHASE CONSTITUENTS

Calcium-zinc baths produce coatings of similar hues as do the zinc phosphating baths; however, they differ from each other in their phase constituents. The phosphate coatings obtained from calcium-zinc phosphating baths essentially consist of the characteristic phosphate coating constituents, including $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ (phosphophyllite) and $Zn_3(PO_4)_2 \cdot 4H_2O$ (hopeite), along with a distinct crystalline phase of $Ca_2Zn(PO_4)_2 \cdot 2H_2O$ (scholzite). Other phases, such as $CaHPO_4 \cdot 2H_2O$ (brushite) and $CaHPO_4$ (monetite), may also be found.[1] The relative proportion of calcium in the phosphate coatings is related to its concentration in the formulated composition. It is also known that calcium phosphate precipitates later than zinc phosphate from calcium-zinc compositions.[3,9] Like the hopeite crystals, scholzite also forms orthorhombic crystals[1] and grows epitaxially on ferrous substrates.[9] The dihydrate nature of scholzite crystals (as compared with the tetrahydrate crystals of hopeite and phosphophyllite) reportedly contributes to improved corrosion resistance as well as improved paint adhesion and high-