Finishers' Think Tank

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Phosphate Coatings: Spearheading Metal Finishing Progress, Part 2

Last month we acknowledged that mankind's endless fight against corrosion began very long ago. One weapon in this struggle has been the use of phosphate coatings. Some ingenious metal finishers, referred to as the "A.D. 300 gang," introduced the world to phosphate coatings. After languishing as a crude surface treatment for more than 1,350 years, a new generation of chemists and finishers took up the phosphate cause. Their timing, as we noted, awoke a sleeping giant that hasn't blinked since!

The phosphate dynamo kept pace with and helped fuel the advancing Industrial Revolution. Its legacy is with us in every facet of our daily lives. Anywhere you look or anyplace you can think of, there is most likely a phosphate coating. Some general "it's there to find" places include: on the earth's surface (cars, tools, road signs, bookshelves, etc.), below the earth's surface (submarines, communication cables), in the sky and beyond our solar system (the Explorer satellites launched almost 30 years ago).

Last month's coverage of phosphate coatings included types, basic anatomy (what makes them tick and makes them unique) and application benefits. Since these last ports of call, the good ship *Fezinphos* has plotted a swift journey through heavy seas of information, casting her nets to retrieve schools of useful knowledge for your factory ship to process. Ahoy mates, as we gather a bountiful plenty of facts.

Phosphates

Typical Process Cycles

Cycles predominantly follow this progression:

1. Clean (immersion or spray). Removes oils, grease and shop dirt.
2. Rinse
3. Phosphate (immersion or spray)
4. Rinse
5. Seal (optional)

Variables based on parts, handling limitations, economics, throughput and ultimate targeted finish allow for cycle flexibility. Some of these are:

- Soak or spray
- Rack, barrel or basket
- Combination clean and phosphate in one step

Two popular soak application cycles can be used to iron phosphate parts.

Immersion #1

1. Soak Clean: Typically an alkaline cleaner. It should provide for complete removal of soils and be free rinsing.
2. Rinse
3. Phosphate: Includes a simple wetter or surfactant system for residual light cleaning demands and lower solution surface tension to enhance penetration and reaction with the surface to form the iron phosphate coating.
4. Rinse
5. Seal: Application of a chromic acid/phosphoric acid or non chromated surface treatment. The effect is to passivate or "seal" those minuscule surfaces between actual iron phosphate deposit sites. Think of it as sealing a driveway, filling the tiny voids between the tamped asphalt-stone mixture.
6. Rinse: This is an optional step added on, or in place of, the seal.

Immersion #2

1. Clean & Phosphate: One step does both tasks. This is a critical decision, because quality cleaning must be accomplished in a mildly acid solution, along with temperature limitation.
2. Rinse
3. Rinse or Seal

Iron phosphates are commercially available in the form of powder and liquid concentrate products. Combo cleaner/phosphates may also provide a detergent additive to boost cleaning. General operating parameters for the two immersion types are shown in Table 1.

Spray Iron Phosphating

There are two likely candidate cycles for spray iron phosphating.

Three-stage Spray

1. Clean & Iron Phosphate: Low-foaming detergent system, coupled with iron phosphating chemistry.
2. Rinse
3. Seal or Rinse

Five-stage Spray

1. Clean: Low-foaming detergent system incorporated with sequestering agents, alkalies, builders and glycol solvents.
2. Rinse
3. Phosphate: Surfactant level reduces solution surface tension and provides light back-up cleaning. Surface conditioned for effective iron phosphate formation.
4. Rinse
5. Rinse or Seal

Table 1
Iron Phosphate Immersion

Method	Clean, min	Rinse, sec	Phos, min	Rinse, sec	Seal, sec
Immersion #1	3-5	30-60	3-6	20-40	45-60
Immersion #2	0	0	3-6*	30-60	45-60

**combo clean/phosphate*

Table 2
Iron Phosphate Spray

Method	Clean, min	Rinse, sec	Clean/ Phos, min	Rinse, sec	Phos, min	Rinse, sec
Three-stage	0	0	1-2	30-60	0	20-40
Five-stage	1-2	30-60	0	30-60	1-2	20-40

Optional Sealer: 45-60 sec

Optimum Temperatures—Iron Phosphating

Process	°F	°C
Cleaning	120 - 165	49 - 74
Clean/Phos	110 - 145	43 - 63
Rinses	80 - 90	27 - 32
Seals	80 - 110	27 - 43

Table 3
Zinc Phosphate Immersion & Spray

Method	Clean, min	Rinse, sec	Rinse, sec	Phos, min	Rinse, sec	Seal, sec
Spray	2 - 4	20 - 40	20 - 40	3 - 5	15 - 30	20 - 40
Immersion	3 - 7	30 - 60	30 - 60	8 - 20	20 - 40	20 - 40

Spray cleaners should contain an effective range of surfactants to remove a wide variety of soils. The levels of these cleaning agents are typically lower compared to immersion soak cleaners. Spray nozzles deliver solution from 15 psi and up, providing mechanical action, facilitating removal of oils and grease. Many types of chlorinated, cutting, lube, paraffins, stamping and rust-proofing oils are encountered. Yes, sometimes people apply silicone oils during the manufacturing process. These must be efficiently removed, preferably by displacement, in a short cycle. Streamlined spray cleaners are fortified with a balance of alkalies, water-hardness conditioners (say no to plugged spray nozzles), grease cutting solvents and derusters (see Table 2).

Zinc phosphates require precleaning to condition the base metal first. This means complete removal of organic soils (oils & grease), scales and rust. A typical process cycle is:

Zinc Phosphate Immersion & Spray

1. Clean
2. Rinse
3. Rinse
4. Phosphate
5. Rinse
6. Seal or Rinse

Application of heavy zinc phosphates may require 6-15 min reaction time to develop the required coating weight.

The following tables describe some of the recommended spray and immersion applications over certain base metals, to achieve optimum organic coating types.

Spray Applications

Steel Types & Coatings

Steel	Coating	Preference
Cold-rolled	Lite zinc	Paint bond
Hot-rolled	Lite zinc	Paint bond
Steel	Medium zinc	Cold deform
Galvanized	Medium zinc	Paint bond

Immersion Applications

Standard Steel & Coatings

Coating	Preference
Heavy zinc	Rustproof
Heavy manganese	Wear resistance
Lite/medium zinc	Paint bond
Lite iron phos	Paint bond

Sealing and rinsing are very important steps in the process cycle. The effect and benefits of each may sometimes be overlooked or under appreciated. In either bath, it doesn't take much chemical or mechanical input to inject value-added features into the final finish.

Sealers

- Remove unreacted phosphate compound and hard water residues.
- Passivate the minute distances between phosphate coating sites.
- Improve corrosion resistance.
- Chromated and/or non-chromated versions (used dilute, approx. 1-2 pints/100 gal)

Rinsing

- Very important and critical to success of each process step.
- Poor rinsing reduces adhesion quality of final top coats.
- Removes collective films and phosphate solutions.
- Water quality (deionized) and agitation are important keys to success.

Process Bath Analysis & Control

The bath chemistry, dynamics of the process, and concentrations of active components continually change with solution use. Specifically, as pH rises, the ratio of chemical reactants, wetters, accelerators and buffers are consumed in the phosphating reaction. Drag in of dilute alkaline solutions from the cleaner, drag out of the phosphate process solution, and dilution of the bath with volume adjustment water also reduce concentration of the proprietary solution. Maintenance additions are usually made on a scheduled basis, predetermined by monitoring actual concentration, pH and other related actives during bath operation. Or, selected analysis is routinely conducted.

Iron Phosphate

- pH measurement
- Titrate acidity to determine active concentration
- Determine coating weight on test panels (mg/ft^2)
- Process standard panels with finished top coat. Measure corrosion by accepted method (*e.g.*, neutral spray of scribed panels)

Zinc Phosphate

- Multiple titration procedures to determine total and free acid concentrations, with corresponding ratios.
- Analysis of accelerator by titration.
- Determine coating weight on test panels (mg/ft^2)
- Process standard panels with finished top coat. Measure corrosion by accepted method (*e.g.*, neutral spray of scribed panels)

Analysis of Sealers

- Analysis by titration based on process type chrome concentration or free and total acid.
- Process standard panels with finished top coat. Measure corrosion by accepted method (e.g., neutral spray of scribed panels)

Standard Test Procedures

These tests (see Table 4) represent some of the more popular and widely used methods for evaluating phosphate/organic topcoats.

Iron and zinc phosphates exhibit process benefits that permit the selection of either one for specific applications. By comparison, iron phosphates are easier to run, control and analyze. Lower heating requirements, reduced chemical consumption and less time to process work also reflect an economic benefit in associated cost savings. Iron phosphates are generally not corrosive. This allows the use of less expensive equipment (tanks, process line ancillary equipment). Iron phosphates provide an excellent underlayer for application of organic top coats. Our review did highlight these benefits related to zinc phosphates:

- Crystalline and microcrystalline structure for superior anchoring and bonding to organic top coats.
- A wider range of coating weights to support industrial applications, such as drawing tube and wire, service life (harsh and weather-related), automotive, aircraft and military specifications.

For exceptional corrosion protection and severe wear applications, zinc phosphates may be preferred.

The A.D. 300 gang would be quite proud of their ability to initially develop the phosphating process.

Table 4
Standard Test Procedures

ASTM	Description
D-714-56	Evaluate blistering on parts
D-870-54	Water dip, organic coats on steel
B-117-64	Salt spray fog test
B-287-62	Acetic acid salt spray fog test

Spec	Description	Class	Phosphate
C-46487	Clean/prep org coat	Gr I, II	Iron
P16232	not to be painted	M, Z (all)	Zn or mn phos
TT-C-490	Clean/prep org coat	Type I,II	Iron & Zn phos

Spec designations: MIL, DOD, TT

How little they probably thought they knew about it. In retrospect, we see how much they taught us, and illuminated the path of R&D, which continually improves phosphating of metals. The *Fezinphos* has docked. Its holds offer a rich cache of valued information for the finisher's benefit. The seas of challenge offer more rewards to harvest as we strive to continually improve metal finishing in the 21st century. As an industry giant, Rod Leeds, used to say, "Smooth sailing!" P&SF