

SURFACE PREPARATION

EMERGING TECHNOLOGY

Innovations in one-step organic passivation processes for metals

Mary Carpenter and Carlo Guidetti *Carpenter Chemicals*

This article describes one-step organic phosphating, a process for pretreatment of metal surfaces in one stage, in a minute of treatment time, using no heat and no water, and generating no solid or liquid wastes. The article provides a general description of how the pretreatment process works and indicates some drawbacks with the more traditional types of liquid-based industrial pretreatments. It then describes improvements and modifications to the one-step organic phosphating technology that have led to a new one-step organic passivation process. Test results provided indicate recent data collected on the effectiveness of the new technology.

Proper pretreatment (cleaning, degreasing, and metal passivation) of metals before applying powder coatings is fundamental to guaranteeing good performance of those coatings and, of course, of the metal products themselves as they're put to use in the market. Many water-based industrial pretreatment processes are available, and many of them are capable of meeting a wide variety of market demands. However, some of them have drawbacks as well that must be taken into account. These include

- Economic and environmental
 - create solid sludge and liquid and oily wastes that must be treated before disposal
 - use high volumes of water, and require regular bath dumping and replenishment
 - produce large amounts of carbon dioxide (CO₂), or greenhouse gas, from the combustion of the fuel to heat the treatment water
 - require proper disposal of the sludge, oils, and wastewater; waste treatment is often expensive

- are multi-step, each part of the chemistry being in a different bath with rinses in between

- High energy consumption
 - use natural gas to heat the water in one or more tanks and to maintain it at temperature
 - use electric energy to circulate and apply the large volumes of liquid in all process stages
- High maintenance
 - require labor-intensive daily operations and bath checks
 - require periodic equipment maintenance, sludge removal and dumping, and dumping tanks to renew the spent chemistry
- Process limitations
 - can lead to chipping and adhesion loss because of inflexibility of inorganic phosphates (particularly zinc, for example)
 - often have limitations on the metals that can be treated by a particular chemistry, requiring changes in chemistry when the metals to be treated are changed

Since the 1970s, a completely different technology has been available to clean, degrease, and organically phosphate metals. This one-step organic phosphating

- Requires only very low energy
- Works in a single step
- Requires no fuel use as it works at room temperature
- Creates no liquid or solid wastes

FIGURE 1

This European company uses the organic passivating process in its powder coating operation.

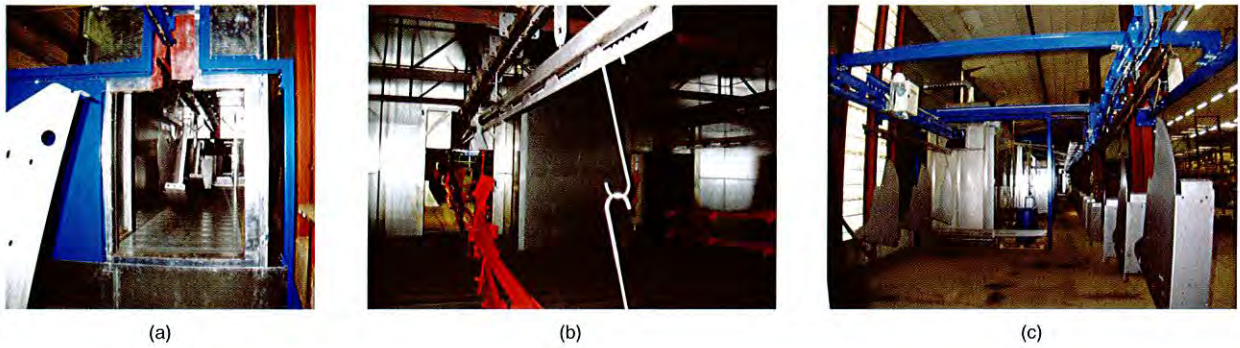
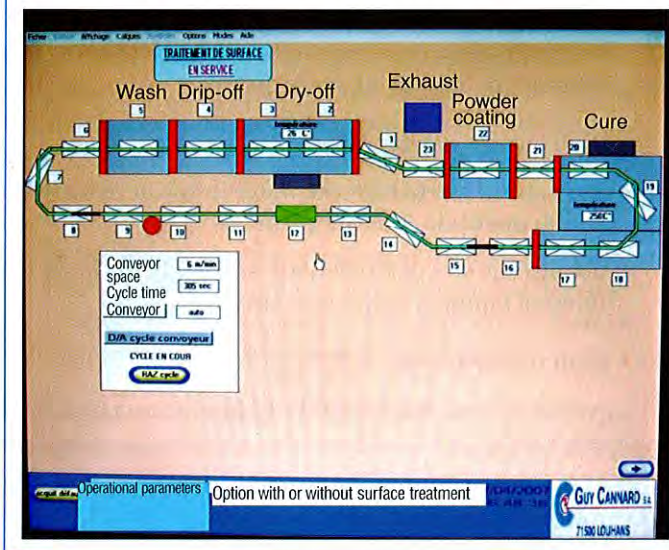


FIGURE 2

Schematic of the powder coating operation at a European plant (translated from French)



- Uses no water, which means no rinsing
- Emits extremely low amounts of CO₂
- Requires no daily or hourly bath checks and virtually no equipment maintenance
- Can treat multi-metals, even simultaneously
- Meets quite a wide range of market demands

After more than 35 years of modifications and improvements of this original technology, a new technology has just been developed—one-step organic passivating. It is based on a completely different metal passivating mechanism accomplished by the seal coat, and a different and stronger bonding mechanism between the metal and the seal and between the seal and the topcoat. One plant using this technology is now in operation in Europe (see figures 1 and 2) and two more are under construction and scheduled for start-up in the near term.

This new technology continues the advantages of the existing organic cleaning process but provides, in addition, a significant increase in corrosion, adhesion, and impact resistance, discussed in the results section of the article. Given the performance of the new technology, the range of potential users is greatly increased, with the result that now a larger segment of the metalworking industry will be able to use it to reduce energy consumption, water use, waste creation, and CO₂ emissions.

How the pretreatment process works

When a metal part, either steel or other metal, is formed by stamping or extruding for example, contaminants are left on the surface, and they must be removed before application of powder coatings. These contaminants normally belong to two basic categories:

- Organic contaminants (natural, animal, mineral, or synthetic oils)
- Inorganic contaminants (metal powder or dust coming from prior manufacturing stages, or dust and dirt from the environment)

If these contaminants aren't removed, the metal clearly can't be properly coated. But beyond this simple cleaning of oil and dirt, it's also often necessary to provide a passivating layer on the metal surface. This passivation improves adhesion, flexibility, and corrosion resistance of the final powder coating, and therefore the performance of the final treated and coated metal product in the field.

Conventional water-based pretreatment processes. The great majority of industrial processes for metal preparation before powder coating are performed in multi-stage systems that have a minimum of three stages and up to 10 or even more; these systems work by using chemical products dissolved in water, with rinse steps between the active chemical stages. Most of these industrial processes to prepare metal before painting are effective and are capable of meeting the full range of market demands. However, it must be borne in mind that these water-based pretreatment processes have some drawbacks as noted previously.

Moreover, the constantly increasing world population and a global desire to improve the quality of life to the level of western societies impose on industry the need to reduce CO₂ emissions, minimize energy consumption, greatly moderate water use, and improve wastewater treatment and purification.

How one-step organic pretreatment works

One-step organic phosphating, an Italian technology, has been available to clean, degrease, and organically phosphate without the detriments of the water-based processes. It works in a single step at room temperature, without water and without creating any waste or sludge. It's capable of pretreating various kinds of metals, including for example steel, galvanized steel, aluminum, and stainless steel (to clean and promote adhesion). It can even treat multi-metals simultaneously in the bath. And it works not only with powder coatings, but also with solvent-based and water-based liquid paints.

From the time of the Montreal Protocol regarding protection of the ozone layer (Jan. 1, 1989) to the present time, the use of many solvent degreasing processes has been on the wane because permissible industrial emissions of chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), halogenated solvents, and finally volatile organic compound (VOC) emissions have gradually been reduced. But for the past 35 years, one-step organic phosphating has been constantly innovated and improved to meet both these new environmental regulations and workplace safety laws, as well as changing customer needs and demands.

The products in the latest generation are formulated based on very particular organic fluids, not toxic or harmful, not even classified as VOCs under European law (1999/13/CE). Currently, about 500 industrial one-step organic phosphating plants are in operation in more than 25 countries in Europe, North America, and Asia.

To date, probably the main technical limitation on the one-step technology has been that it provides a mid-range level of corrosion resistance, better than iron phosphate but, in laboratory testing, less than zinc phosphate.

Because of this mid-range performance, along with the fact that better-performing triglycidyl isocyanurate-based (TGIC-based) polyester powders are not available in the European market for regulatory reasons, many customers in Europe treating and powder coating steel, for example, use the one-step process for indoor applications. In the North American Free Trade Act (NAFTA) market, where TGIC-based polyester powders are in use, the market is broader and includes outdoor applications. But the pretreatment process still has some corrosion resistance limitations.

The innovations—one-step organic passivation. The Italian company's research and development (R&D) laboratory has recently completed development of one-step organic passivation (as distinguished from

existing "organic phosphating"), which is based on some quite different chemical principles. Phosphoric acid has been eliminated, so the product is pH-neutral. The resin that becomes the seal is different from the one used in the one-step organic phosphating, and it passivates and seals in a different manner than the resin in the one-step organic phosphating technology.

The new technology, like the one-step organic phosphating technology, is free of metals, which is an advantage because metals are subject to restrictive laws dealing with worker safety and metal by-product disposal. But unlike the phosphating technology, the new technology is also free of phosphating ions, which are responsible for eutrophication of superficial waters.

The new technology has all the advantages of the previous technology (one step, no water, no waste, no heat). In addition, it provides a very significant increase in corrosion resistance, as shown in salt-spray tests. It also shows improved topcoat adhesion, demonstrated under difficult test conditions and on more difficult metals such as aluminum and galvanized steel.

Process basics. The new one-step organic pretreatment contains a particular blend of organic fluids with a very low vapor pressure (lower than 0.01 kilopascal [kPa] at 25°C [77°F], or 0.075 millimeter [mm] of mercury at 25°C [77°F]). It contains no water and in fact, like the existing line of products, must not be diluted with water. A special set of organic substances is dissolved in the fluid mixture, and these substances act on the metal surface. They also form a seal on the metal surface. The resin consists of several components to accomplish the passivation, seal, and adhesion promotion. Binding is now made directly to the metal rather than by way of a phosphate "bridge" and is much stronger both physically and chemically than its predecessor.

This mixture is used at room temperature so that no fossil fuel combustion is required to heat up the chemicals. It can be applied by dip or in a very low pressure flow-coating operation (maximum flow-coat pressure shouldn't exceed 5 pounds per square inch [PSI]), so the energy required to circulate and apply the product is very low. Because of the low application pressure and the specialized chemistry, the size of the tank is much smaller than that of a conventional pretreatment tank.

One-step organic passivation process. During product application, both organic and inorganic contaminants are removed; the inorganic ones are displaced by mechanical action, while the organic ones are dissolved in the fluid mixture. The dilution mechanism for the process oils depends on the solubility parameters and hydrogen bonding values of the system.

Following the cleaning and drip-off phases, fluids are flashed off in the oven at 140°C-150°C (284°F-302°F). At that point, the reactive groups in the organic substances that form part of the mixture react directly with the

metals, creating a uniform organic passivating coating with a thickness estimated at lower than 1.0 micron.

Part of the curing stage may take place along with powder-coat curing and cross-linking. During the curing stage, the cross-linking of the passivating coating takes place, linking the coating film through a strong chemical bond to both the metal below (such as steel, aluminum, galvanized steel, or stainless steel) and the powder coating above. This results in cleaning, degreasing, organic passivation, and sealing of the metal surfaces treated.

Why are no muds, sludge, or by-products created? The technology is a true one-stage process, and no preliminary degreasing or rinsing is required. In conventional systems, sludge is created by the combination of particulates and process oils. In the one-step organic pretreatment system, no sludge is created, and oils and particulates don't accumulate in the bath.

The inorganic particulates such as dirt and metal fines aren't soluble in the process and are continuously filtered out of the bath. As to the process oils, they're actually absorbed and chemically captured in the resin that becomes the organic passivating coating that is created during curing. Like the fluid mixture, this special resin is also designed to be compatible with the hydrogen bonding and solubility parameters of the process oils. In this case, the oily and fatty contaminants physically combine with the organic polymer by mixing with it, roughly as a plasticizer mixes with a linear polymer. Because the oils are absorbed and trapped in the resin's three-dimensional structure, they don't accumulate in the bath. As a result, no oils need to be removed, treated, and dumped.

How much oil can the bath tolerate? The stability limits of the process can be demonstrated by using a mathematical model of the reactions involved. The formula demonstrating the percentage of oil present in the chemical by the time [P(t)] after the treatment of metal surfaces is as follows:

$$P(t) = \frac{(-\alpha \times 100)}{W} \frac{(W-25)}{25} \frac{(W-25)^t}{W} + \frac{(\alpha \times 100)}{W} \frac{(W-25)}{25} \quad (1)$$

where:

α = quantity of oil in grams introduced into the phosphating solution per 1 square meter (m²) of metal surface

W = total weight in grams of the passivating solution

25 = assuming that 25 grams of product coats 1 m² of metal

It's clear from Figure 3 that when time is very high, the curves show a horizontal asymptote. Moreover, it can be demonstrated that the P(t) at the asymptote point is $P(t) = 4\alpha$, considering α in this case to be a dimensional value. The straight line indicates the P(t) that the chemical solution is capable of absorbing without giving rise to poor film adhesion (organic

coating film alone or in combination with topcoats). This percentage has been determined experimentally and it corresponds to 6 percent by weight of the ready-to-use organic coating solution. Consequently, it can be stated that the process is capable of treating without time limitation, components contaminated with a quantity of oil not exceeding 1.4-1.5 grams/m².

Moreover, inasmuch as the oil contamination normally present on 1 m² of cold rolled steel (CRS) is generally in the range of 0.3-0.4 gram, the process is capable of treating components with an average contamination level four times higher than that on CRS irrespective of time.

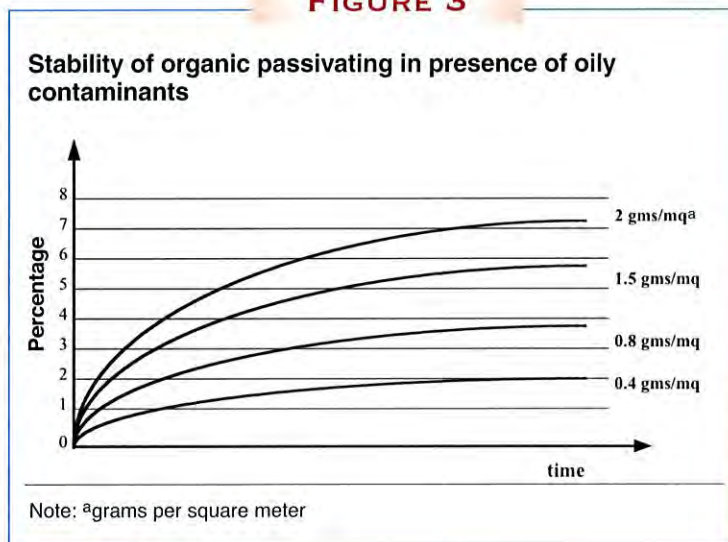
Test results from one-step organic passivating

The organic passivating coating, despite its approximate 1.0-micron thickness, provides excellent temporary protection against flash rust on uncoated parts for weeks to months if they are stored indoors. Moreover, the organic film coats the treated metal surface uniformly and is connected by a covalent chemical bond with the powder coating applied in the subsequent finishing step. (This is also true for solvent- and waterborne coatings.) The result is a strong and continuous interaction between the organic coating and the topcoat over the entire treated surface. Because the organic passivating coating is organic, and plasticized by the oily contaminants, it has higher flexibility than the typical inorganic crystal of iron or zinc phosphate created by conventional processes.

Obviously, one of the key characteristics of the new one-step organic passivation system is the nature of the organic passivating coating, which must

- Guarantee proper lipid-philic behavior, to absorb the process oils correctly
- Crosslink into a three-dimensional structure to prevent oil migration to the top
- Keep flexibility unchanged with changes in the percentage of oil trapped by the resin

FIGURE 3



Sets of panels in CRS, in aluminum, and in electro-galvanized steel for normal industrial use were each treated with either the existing one-step organic phosphating or the new one-step organic passivating chemicals. One bath of each consisted of virgin material and two others of each were contaminated by 2 percent and 4 percent (only on CRS) of mineral oil. The panels were subsequently painted with three different kinds of European powder coatings.

Crosshatch adhesion tests (ISO 2409) were performed, with positive results (GT = 0) on each panel. Subsequently, the panels were subjected to salt-spray testing under ASTM B-117. Results can be seen in Table 1.

With respect to the European non-TGIC-based powders, it should be noted that total salt-spray hours achieved are lower than would be the case with TGIC-based powders. Nevertheless, the comparison between the existing organic phosphating and the new organic passivat-

ing systems demonstrates the degree of improvement between the one and the other. On steel, with oil in the 0 percent to 2 percent range in the bath, the new system gives results, at the limit of those powders, of 2mm-4mm of corrosion creep at the scribe; and at high oil levels, from 4mm-8mm of corrosion creep. The organic phosphating process showed extensive corrosion. On aluminum, the results were very good even at 1,000 hours with both systems, but better with the new one. And on galvanized steel, the results were significantly better with the new system.

Epoxy polyester coatings are more corrosion-resistant in themselves, and therefore the type of pretreatment has a smaller effect on salt spray test results. But here also, it's evident that the organic passivating system provides a better result than the organic phosphating system.

Another test by the Italian company's own R&D laboratory consisted of soaking samples (prepared as described above) in demineralized water 1) at room temperature for 24, 48, and 72 hours or 2) in 90°C (194°F) hot water for 1 hour. Crosshatch adhesion tests were then performed under the ISO 2409 standard. Results of those tests can be seen in Table 2.

These two sets of test results demonstrate that the new pretreatment system provides an important improvement in corrosion resistance (especially over steel and galvanized steel) and in adhesion under difficult test conditions (most particularly on aluminum) in comparison with the one-step organic phosphating system.

Environmental impact of new one-step process

To properly evaluate the environmental impact of an industrial process, it's necessary to take a global approach, focusing attention on all areas of potential pollution—water, soil, and air—rather than looking to make improvements in one area at the expense of another. The one-step process does that:

- **Water:** Because the process is basically anhydrous, water isn't used. As a result, no wastewater and water pollution are created.
- **Soil:** No solid sludge or muds are created to be treated or disposed of.
- **Air:** The organic fluids used in the process have a very low vapor pressure (even lower than 0.01 kPa at 25°C [77°F]), and thus the loss of the organic fluids during application is minimized. These fluids,

TABLE 1

Comparing salt-spray (ASTM B-117) results between one-step organic passivation and one-step organic phosphating

One-step pretreatment	Substrate	Salt spray ASTM B-117 (hours)	Polyester powder coating without TGIC 1	Polyester powder coating without TGIC 2	Epoxy-polyester powder coating
Organic passivation	CRS	640	4a	3 ^a	2 ^a
Organic passivation + 2% oil	CRS	640	4	2	3
Organic passivation + 4% oil	CRS	640	8	4	4
Organic phosphating	CRS	640	> 10	> 10	4
Organic phosphating + 2% oil	CRS	640	> 10	> 10	3
Organic phosphating + 4% oil	CRS	640	> 10	> 10	4
Organic passivation	Al	1,000	0	0	0
Organic passivation + 2% oil	Al	1,000	1	0	0
Organic phosphating	Al	1,000	1	1	0
Organic phosphating + 2% oil	Al	1,000	2	1	1
Organic passivation	EG	640	1	3	2
Organic passivation + 2% oil	EG	640	2	4	2
Organic phosphating	EG	640	3	10	4
Organic phosphating + 2% oil	EG	640	4	6	3

Notes: ^aValues are total average scribe creep in millimeters. CRS is cold rolled steel; Al is aluminum; EG is electrogalvanized.

TABLE 2

Comparing adhesion of one-step organic pretreatment under extreme conditions

Pretreatment	Substrate	Adhesion after 1 hr at 90°C (194°F)	Adhesion after 24 hrs at 20°C (68°F)	Adhesion after 48 hrs at 20°C (68°F)	Adhesion after 72 hrs at 20°C (68°F)
Organic passivation	CRS	GT = 0	GT = 0	GT = 0	GT = 0
Organic phosphating	CRS	GT = 5	GT = 0	GT = 5	N/D
Organic passivation	Al	GT = 0	GT = 0	GT = 0	GT = 0
Organic phosphating	Al	GT = 5	GT = 5	N/D	N/D
Organic passivation	EG	GT = 0	GT = 0	GT = 0	GT = 0
Organic phosphating	EG	GT = 5	GT = 0	GT = 0	N/D

Note: CRS is cold rolled steel; Al is aluminum; EG is electrogalvanized. GT crosshatch adhesion: 0 = very good, 5 = poor.

once evaporated into the atmosphere, are biodegraded quickly to CO₂ and water only.

Moreover, in terms of greenhouse gas generation, it has been calculated that the total amount of CO₂ created as decomposition of these fluids used in the process is roughly 10 times lower than the amount created by the natural gas combustion necessary to heat up the chemicals in one stage of a conventional washer treating the same quantity of metal surface (Table 3).

In the case of an industrial plant of medium to large size (more than 25,000 square feet a day of treated metal), a special scrubber developed and patented by the chemical manufacturer is available, along with specific chemistry adapted to this system. Using this equipment and chemistry, up to 70 percent-75 percent of the fluids used in the process can be recovered and recycled back into the process.

For small- to medium-size plants, because of the constant thermodynamic losses from the scrubber, the efficiency of the recovery is too low, and so the very minimal vapors are simply exhausted from the oven and emitted into the atmosphere where they're quickly photo-chemically degraded to CO₂ and water. Table 3 compares CO₂ creation between the organic passivation system and a heated three-stage degreasing and phosphating system.

Conclusions

One of the most important challenges for manufacturers of chemicals for metal pre-treatment before powder coating is to reduce process energy consumption, CO₂ emissions, water use, and wastes and by-products.

New one-step technology cleans, degreases, and creates an organic passivating and uniform coating with a thickness of less than 1.0 micron without any use of water, without the creation of solid or liquid waste, and with less

energy consumption than conventional processes. The technology provides results that can meet the demands of a larger market segment, serving customers with traditional as well as higher performance demands. **PC**

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Editor's note

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Mary Carpenter is a graduate of Stanford University and Georgetown University Law Center. She is president of Carpenter Chemicals, LC, Alexandria, VA, NAFTA distributor of the single-stage organic pretreatment technology. She can be reached at 703/683-1570 or e-mail [mary@cc-lc.com]. For more information about the technology, visit [www.cc-lc.com].

TABLE 3

Comparing carbon dioxide creation between the one-step organic passivation system and a heated three-stage degreasing and phosphating system

One-step organic passivation potential customer: 12,000 square meters metal treated a month

Coverage of one-step organic passivation system: 25 square meters per liter	Estimated consumption: 480 liters a month
Specific gravity	0.915 grams per cubic meter
480 liters a month	440 kilograms
Carbon percentage	53.95
Carbon kilograms (pounds)	238 (525)

Same customer's heated conventional three-stage installation

Burner rating	1,500,000 BTUs
Assume operating at 75% of capacity 8 hours a day, monthly BTU use	187,500,000 BTUs a month
Volume of fuel (methane)	187,500 cubic feet
Mass of fuel (methane) 16 pounds = 357 cubic feet	3,812 kilograms (8,403 pounds)
Carbon percentage (methane)	75
Carbon kilograms (pounds)	2,859 (6,303)

Note: The first calculation is to estimate the consumption per month of organic passivating system chemicals for this hypothetical customer and the resulting carbon emissions. The second calculation takes the burner rating of the customer's existing conventional washer and determines the amount of carbon emitted from the combustion of heating fuel.

Carlo Guidetti earned his degree in pure chemistry from Milan University. Guidetti, a member of the fourth generation of the Guidetti family involved in the business at Pai-Kor srl, has managed the Italian manufacturer's international business development since he joined the company 5 years ago. He keeps at least 1 foot in the lab to guarantee the technical evolution and continuity of organic pretreatment know-how to meet the challenges of new global markets. Dr. Guidetti can be reached at 39-02-988-0411 or e-mail [carlo.guidetti@paikor.it]. The company Web site is [www.paikor.com].