Molybdate-Based Alternatives To Chromating As a Passivation Treatment for Zinc

By Peter T. Tang, Gregers Beth-Nielsen and Per Mailer

Zinc-plated parts are typically passivated with chromate-based solutions to reduce corrosion. Chromates, however, are a cause of environmental concern, for their toxic effects on plants and wildlife, and allergic effects on workers who come in contact with them.

A molybdate-based alternative has been developed that can be used to replace chromates in a wide range of applications. The **process has been tested in a project set up by the Danish Government in 1989, at the Centre of Advanced Electroplating (CAG) in Denmark. Procedures used for the alternative process are similar to those used in chromating. The corrosion protection provided by the process on zinc-plated parts is comparable to chromates. Depending on test conditions, especially pH value, the molybdate/phosphate process was found to be better than chromate at low pH values, equal to chromates in outdoor exposure tests and prohesion tests, but not as good in neutral tests, such as salt spray.**

This edited version of a presentation from the joint AESF/EAST Session at SUR/FIN® ‘94—Indianapolis, discusses the effectiveness, cost, stability,0 chemistry, layer composition, and performance of this alternative process.

Chromated zinc parts are used in the automotive, aerospace, electronics, and many other industries. The passivation treatment used to create the protective film on zinc contains significant amounts of Cr6+-compounds, which are considered undesirable because of environmental and health concerns.

A molybdate/phosphate treatment[a] has been developed as an alternative to replace chromates. In the early stages of development, an extensive optimization of the treatment parameters (temperature, duration, concentrations, etc.) resulted in the formulation of two baths- one with a molar ratio of Me/P equal to 0.33 and a pH value of 2.1, and the other with Me/P equal to 0.66 and a pH value of 4.6. These two baths were both tested, and will be referred to as 0.33[b] solution and 0.66’ solution.

Pre-treatment

There is hardly any gas evolution during a treatment with these alternative processes. The amount of zinc dissolved during surface treatment is modest. It is important that the zinc surface be clean and without oxides, organic surfactants or other films that may hinder the formation of the passivation layer.

Parts should be passivated immediately after the zinc coating has been applied (they should not be allowed to dry). If the zinc plating solution is cyanide-based (cyanide-zinc), and if the zinc solution contains additives, it is necessary to rinse the parts in a very dilute nitric acid (about 0.15 mole/L HNO_3. This pretreatment (called a bright dip) will clean the zinc surface and remove traces of organic additives (especially important for cyanide-zinc).

Passivation Conditions

The passivation process itself is simply a dip for approximately two min in the molybdate-based bath at 60 ‘C. To ensure a uniform concentration of the active components throughout the bath, and to avoid fluctuations in temperature, a good stirring is recommended, using air bubbling, sample movement, or something similar.

The process time is not critical, although baths with high pH values usually require longer dipping intervals for a good layer to develop. Process times of between 80-130 sec for the 0.33 solution, and 100-180 sec for the 0,66 solution, are acceptable. A temperature range of 60 °C ± 5 °C is adequate. Small differences in the temperature will not cause changes in the coating properties. When passivation is completed, the samples are washed in clean (preferably de-ionized) water and dried at room temperature (or in hot air up to 60 “C).

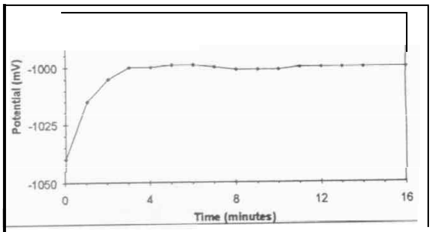

Fig. I—Typical potential versus time chart, measured during the passivation of a cyanide-zinc sample. Potentials **are** *measured versus SCE.*

The potential versus a saturated calomel electrode (SCE) was measured for several of the samples during treatment. Although there were some differences in the results, the basic pattern was the same.

As illustrated in Fig. 1, a process time of more than two min is unnecessary. There is indication that dipping for too ong can be a disadvantage.

Post-treatment

experiments have shown that molybdate-based solution passivated surfaces accept post-treatments, such as paints, sealers and lacquers. Tests have indicated that some organic sealers (also involving a short dip in a warm solution) will improve corrosion resistance of the combined system.

Performance Evaluation

The molybdate/phosphate-based treatment performed well in a number of tests. Figures 2–7 illustrate tests used and results.

Coating Properties

After the first promising results with the molybdate-based treatment, numerous tests became very important. Throughout the development and optimization of he methods,’ corrosion resistance was

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[a] MolyPhos, patent WO 93/10278 pending

[b] MolyPhos 33

[c] MolyPhos 66

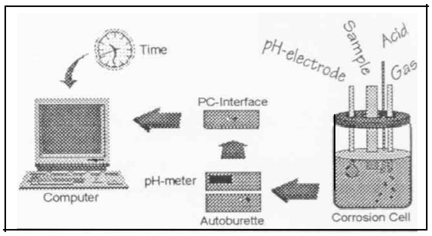

Fig. Z-Corrosion measurement by titration (CMT). A simplified drawing of the corrosion cell and the basic flow of information.

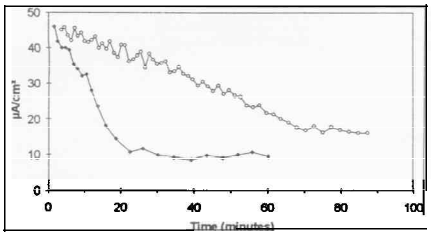

Fig. 3-Typical CMT charts for cyanide-zinc passivated with solutions 0.33 (◆) and 0.66 (0).

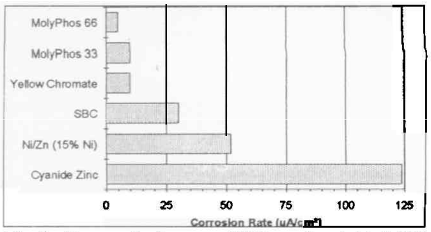

Fig. 4—Frame of reference. CMT results at pH=5.000 for selected passivated and unpassivated zinc coatings.

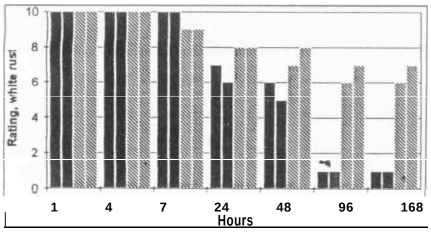

Fig. 5-Neutral salt spray test of Zn/Co (0.8% Co) plafed steel panels, protected by solution 0.66 (solid bars) and yellow chromate (patterned bars). Evaluated according to ISO 4540 at Danfoss A/S; test confines with AESF B117.

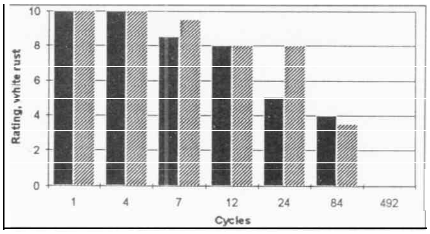

Fig. 6-Prohesion test results. Solid bars represent solution O. 66; pattened bars are yellow chromate on acidic zinc substrate. Each cycle equals two hr.

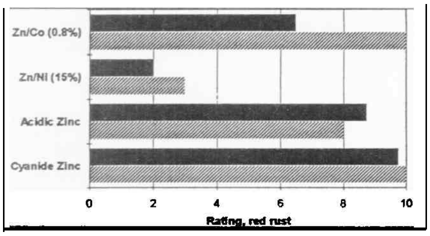

Fig. 7-Outdoor exposure test showing the difference between four popular zinc coatings and the passivation processes molybdate-based (solid bars) and chromate (patterned bars).

the only parameter investigated. New tests, involving properties such as adhesion, paintability, electric conductivity, heat resistance and more, had to be planned and carried out.

Chemical Composition

The passivation coatings, or layers formed by the process on different surfaces and alloys, have been studied in detail. For the studies of the surface and the chemical composition of the coatings, Auger analysis[2] and several other methods, such as EDAX,12 XPS,13 and SEM[1] have been used. This investigation indicates a significant difference between the 0.33 solution and the 0.66 solution. The 0.66 solution exhibits a homogeneous surface with a constant composition within the entire passivation layer. The 0.33 solution coatings are usually much rougher and thinner.

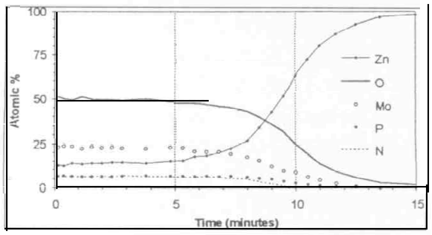

Fig. 8-Auger profile of solution 0.66 on acidic zinc. The sputtering rate is about 180 monolayers/min.

Auger profiles show that the thickness of the molybdate-based passivation layer is within a range from 0.2-0.4 μm, and that the layer formed on acid zinc using the 0.66 solution is significantly thicker than the others, This is not a coincidence, because this combination also had the lowest corrosion rates, using CMT, between 4.0-7.0 μA/cm^2 (twice as good as yellow chromate). The following components are found in the coating layers:

- Large amounts of zinc (16-22 atomic percent) were found in all coatings, indicating that some zinc dissolved during the passivation process, but was precipitated as part of the layer on the surface. The Auger signal for sodium (Na) is at the same position as zinc (Zn), but by using XPS, it was possible to separate the combined signal into some 13-15 percent Zn and 5-7 percent Na.

- Oxygen (0) is found in large amounts (45-50 percent), but is not surprising because molybdate and phosphate hold four oxygen atoms. The amount of oxygen may be higher than the 50 percent indicated in the diagram (Fig. 8), because it is the lightest element in the film.

- The amount of molybdenum (Me) is quite constant in all tests (20 percent). The oxidation state of molybdenum is believed to be Mo^{2+}, except for the first few atomic layers where Mo^{5+} and Mo^{6+} have been identified.

Phosphorus (approximately seven percent) was expected to be higher. The low amounts of active components in the passivation film explain why the bath is used up at a relatively slow rate.

- Nitrogen (less than six percent) originates from the additives used in the zinc baths. The presence of nitrogen was not intended.

- Carbon is only found in the first few monolayer of the surface, and is impossible to avoid. The carbon signal (C) has been removed in Fig. 5.

Adhesion and Paintability

It is important for the passivated surface to accept paint and different printing techniques. It is also important that the coating be firmly attached to the surface, and that it be reasonably resistant to scratches and damage that may occur during handling.

Solution 0.33 does not work with acidic zinc baths and there also have been some problems with cyanide zinc. So, it is not recommended for items exposed to rough handling or rubbing. The adhesion problems do not occur with alloys such as zinc/nickel or zinc/cobalt.

No adhesion problems have been observed with solution 0.66, and it has been found to be better than chromate treatments in general.

The coating accepts ethanol-based paint, powder coatings and different "silk" or "screen" printings. Resistance to organic thinners is good.

Other Properties

The electrical contact resistance of passivation layers formed with molybdate/phosphate-based treatments is less than 1.5 percent of that found in chromate layers.[3] This new treatment, which is

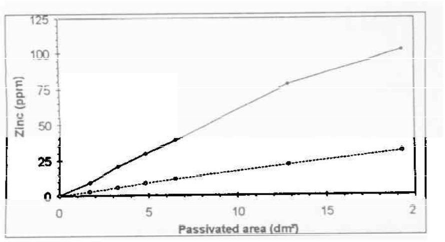

Fig. 9-Accumulation of zinc in 0.66 solution (0) and 0.33 solution (◆), as a function of the total zinc area treated.

Fig. 10-Hägg diagram for the Ortho phosphate system. The initial concentration C is 0.3 mole/L.

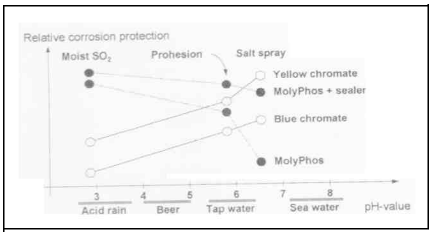

Fig. 11—Relative corrosion resistance of chromate and molybdate-based conversion coatings, with and (without sealer, as a function of the pH value in three different chamber tests. A typical pH range for some well-known liquids is also included. Several commercial sealers have been tested with good results.

based on molybdate/phosphate, is within the same region as some pilot tests have indicated. This difference in contact resistance could make it possible to use this passivation process for applications where chromate results in too much contact resistance.

Friction and adhesion properties have also been tested, and it was generally found that the newly developed molybdate/phosphate solution has about the same frictional properties as yellow chromate. Friction properties are important for assembly and construction tasks using passivated fasteners.

The heat resistance of the molybdate-based passivation film has been tested at 90 and 120 “C without observing any measurable change in corrosion resistance following the test.

Solution Maintenance

A total zinc surface of about 20 dm^2 has been passivated in each of two test baths (1 L total volume each) to measure stability. Using atomic absorption analysis, the concentration of zinc in the baths was measured continuously. There seems to be a constant relationship between zinc concentration and passivated area. The most significant difference in zinc concentration between the two baths (0.33 and 0.66) can be explained by the difference in pH value. The 0.33 solution is more acidic than the 0.66 solution, and will dissolve more zinc. The process time and temperature (2 min at 60 ‘C), were the same in both experiments.

The simplest bath analysis is a pH measurement. Even if this value is within an acceptable range, however, we cannot be sure if other concentrations are out of control. The accumulation of zinc can be especially dangerous, because it will not show directly in a pH measurement.

The pH value of the bath is controlled by the buffer system formed by ortho phosphate and molybdate. The points where the concentration of protolized phosphate ions meet (Fig. 10) are pH stable. The 0.33 and 0.66 solutions are the best, because they have pH values of 2.1 and 4.6. Experiments with baths containing up to 400 ppm of zinc did not indicate any reduction in the quality of the passivation. The molybdate-based solutions (especially 0.66) are believed to last as long as yellow chromate solutions.

Fig. 9 shows that the relationship between zinc accumulation and the passivated zinc area is predictable. By using this chart, it is possible to track the zinc concentration in the solution, and assure that it does not become a problem. With this in mind, frequent analysis of zinc content should be conducted, using atomic absorption spectrophotometry, normal spectrophotometry, or voltametry.

Because the main components in these two solutions are used up very slowly, continuous analysis of molybdate and phosphate is unnecessary. When there is a need, the well-known strong blue color (maximum absorbance at 620 nm) formed by hetero polyacids[d], where one or more of the molybdenum ligands has been reduced from Mo(VI) to Mo(V), can be used for a spectrophotometric determination.

Cost Analysis

New technology must be equal to the method it is replacing (preferably better), and must not be more expensive to use. The cost analysis presented here is based on current knowledge of the new method, and on available information concerning prices and discounts for the chemicals involved.

About 65 percent of the costs involved in a passivation process are payrolls and investments.[4] These costs would remain the same if chromate treatments are replaced with molybdate-based treatments.

The remaining 35 percent of costs are for chemicals, water, heating and waste processing. The price for one L of the molybdate-based solution is about seven times more than the price for one L of (yellow) chromate solution. The molybdate-based treatment also requires a bath temperature of 60 °C, while chromate works at room temperature. Because a bath temperature of 60 °C will make water evaporate quickly, a supply of fresh water is necessary. The water can be taken from the first rinse bath after the passivation process, allowing extensive recycling of the chemicals. Recycling the active components can make it possible to eliminate most costs concerning waste-treatment and water cleaning. Because disposal of wastewater is about 10-15 percent of the total costs, it maybe possible to make up the difference in chemical and heating costs.

The cost of the passivation process will probably increase 0-10 percent by replacing yellow chromate passivation with molybdate-based passivation. This estimate depends on the accuracy of estimates, how increased interest in molybdenum will affect price levels of the chemicals, and future regulations concerning he use of chromates.. ❑

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An important part of the chemistry in the molybdate-based solutions involves hetero poly-acids formed bY molybdenum and phosphorus at low pH values. These rather large molecules are made up by four ligands, containing molybdenum, surrounding each Phosphorus atom. The hetero polyacids are usually written as $H_3[P(Mo_3O_{10})_4] \cdot x\ H_2O$, but a number of different conformations with molar ratios (Me/P) of 1, 10, 9, 8, 8.5 and 6 are known to exist.

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