2017 Award Nomination

Title of Innovation:
Multi-functional surface passivation treatment

Nominee(s)

(Jingjuan Cao, Haitao Lu, Weifeng Zhu, Shanghai Xingyu-Ecosil Surface Material Co. Ltd. Shanghai, China; Danqing Zhu, Ecosil Technologies LLC, Fairfield Ohio, The United States)

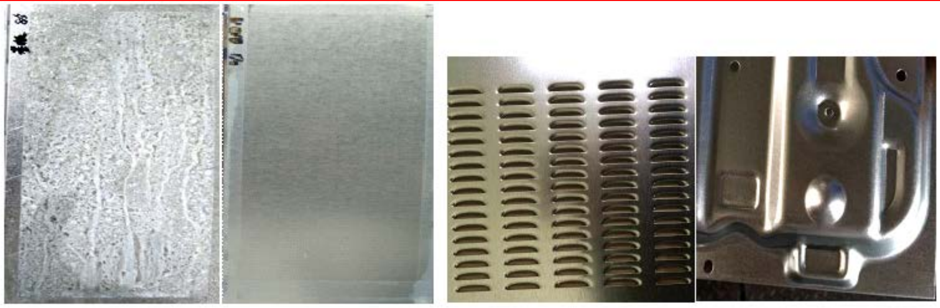
Category:
Chemical Treatment

Dates of Innovation Development:
(January 1st 2014)

Web site: http://www.xingyu-ecosil.com/ and www.ecosiltech.com

Summary Description:

This environmentally-friendly Multi-functional surface Passivation Treatment (MPT) has been developed to provide galvanized steels with outstanding corrosion resistance, surface lubricity for downstream metal forming applications and other favorable properties. The MPT is applied onto galvanized steel sheets by rolling or spraying to rapidly form a thin hybrid film (~1 μm) that is highly water-resistant to prevent water/dissolved corrosive species from attacking the metal surface during transit or storage. Non-toxic corrosion inhibitors incorporated in the film provide a "self-repairing" characteristic, and water-dispersible polymeric additives provide excellent lubrication property and other favorable properties to the galvanized steel surface. The MPT technology also enables downstream users to achieve a significant cost reduction by eliminating the use of metal forming oils and degreasing chemicals and by minimizing the resulting waste water treatment cost. The MPT products have been launched into the market in 2015 with an example part shown in the following photographs.



(a) (b) (c) (d)

Corrosion performance and formability of MPT-treated hot-dip galvanized (GI) steel;
(a) Untreated GI after 48-hr Salt Spray Test (SST) showing 100% white rust,
(b) MPT-treated GI after 120-hr SST retaining shiny metal surface,
(c) and (d) MPT-treated GI steel sheets to form microwave oven back panels after stamping /pressing without application of metal forming oil

Full Description:

1. What is the innovation?

Background Carbon steel rusts in the air due to the moisture which facilitates oxidation on the metal surface. A common way to protect steel is to galvanize the steel surface with a zinc alloy coating. When exposed to the atmosphere for 6-12 months, with dry and wet cycles, a thin passivation layer of zinc carbonates forms on the galvanized steel surface that significantly slows down the corrosion rate of the steel. However, a freshly-galvanized steel surface is still vulnerable to corrosion, as there is not sufficient time to form the passivation layer. Historically, a hexavalent chromium (Cr(VI))-based passivation treatment is applied onto the freshly-galvanized steel surface to provide corrosion protection for the steel during transit or storage. However, the use of Cr(VI)-based treatment has been highly-restricted due to the major carcinogenic concern related to Cr(VI). Cr(VI)-free passivation treatments have thus been developed in recent years, but the performance of these replacements has not been satisfactory to downstream users.

The innovation presented here is a new generation of chrome-free surface passivation treatment, called **M**ulti-functional **P**assivation **T**reatment (MPT), for galvanized steels. This MPT technology has been jointly developed by *Shanghai Xingyu-Ecosil Surface Material Co., Ltd (Shanghai China)* and *Ecosil Technologies LLC (Fairfield OH, USA)*. Compared to the early generation of Cr-free passivation treatment, MPT greatly enhances the corrosion resistance of galvanized steels and also imparts other positive properties such as excellent surface lubricity to the galvanized steel. The following highlights the positive features of MPT:

- Exceptional corrosion protection performance
- Excellent surface lubricity for enhanced formability of galvanized steels in forming applications without the need of metal forming oils
- Environmentally-friendly formula
- Enabling downstream users to achieve significant cost reduction by eliminating the need for metal-forming oils and subsequent degreasing processing
- Other favorable properties include paint adhesion, chemical/solvent resistance, anti-fingerprint properties, and heat resistance

MPT is a “drop-in” product, which can be applied onto a moving galvanized steel sheet surface using existing spray or rolling application equipment on continuous galvanizing lines. The MPT film thickness is approximately 1.0 μm. A short baking step at 180°F (Peak Metal Temperature, PMT) for 10 sec is used to quickly cure the film on the galvanizing line. The MPT chemistry is suitable for a variety of freshly-galvanized steel sheets such as hot-dip galvanized steel, electro-galvanized steel, Galfan®, Galvalum® and ZAM®.

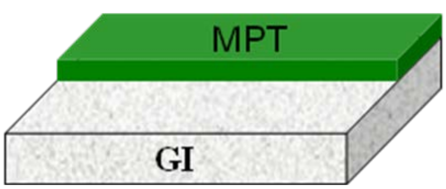
PMT treated galvanized steel sheets have many applications in markets where excellent corrosion protection and formability properties are desired. A few examples of potential applications for PMT treated galvanized steel sheets are shown in Figure 1. These include steel panels of refrigerators, washers and microwave ovens in the home appliance market, metal panels on copiers, printers and computer chassis in the office appliance market, and interior materials for construction and architectural markets.

(a) (b) (c)

Figure 1. Applications of PMT treated galvanized steel sheets; (a) washer frame, (b) microwave oven frame and (c) a computer frame

2. How does the innovation work?

The unique approach used for formulating MPT is shown Figure 2. Three major components are included in the MPT formula: organofunctional silanes, non-toxic leachable corrosion inhibitors and water-dispersible polymeric additives. Each of the three components is responsible for different properties, as stated in Figure 2.



Coating weight: 0.8 to 1.5 g/m^2
(Coating thickness: 0.8 to 1.5 μm)

<u>MPT major components and their functions</u>

- **Organofunctional silanes**
  - Form a highly-crosslinked siloxane film to provide a superior physical barrier to prevent corrosion
  - Form metallo-siloxane covalent bonds with metal hydroxyl groups to provide excellent adhesion to the metal surface
- **Non-toxic, leachable corrosion inhibitors**
  - Provide a "self-repairing" function
  - Passivate the metal surface
- **Water dispersible polymeric additives**
  - Add excellent surface lubrication property
  - Add other favorable properties such as flexibility, anti-fingerprint and chemical/solvent resistance

Figure 2. MPT: major components and their functions

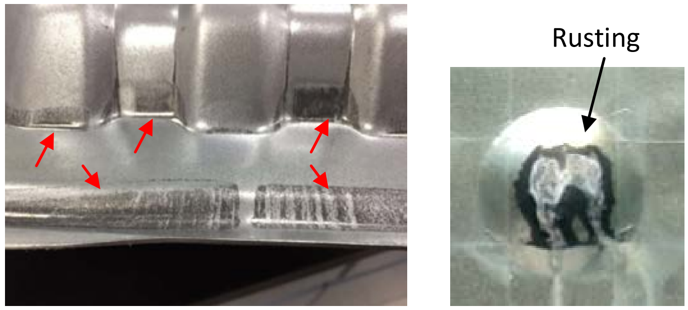
The MPT formulation is an acidic emulsion with a 15% solid content. It is often applied onto a freshly-galvanized steel sheet on a continuous galvanizing line by rolling. The MPT-coated galvanized steel sheet is baked in an oven for 10 to 12 seconds at PMT of 180°F. Upon baking, silanol (Si-OH) groups in the wet MPT film react with metal hydroxyl groups (Me-OH , Me stands for metal) to form strong, covalent metallo-siloxane (Si-O-Me) bonds, while other Si-OH groups crosslink to form a highly water-resistant siloxane (Si-O-Si) thin film on the metal surface. The siloxane layer serves as a physical barrier to retard water and dissolved corrosive species from attacking the metal surface, while the metallo-siloxane bonds ensure the siloxane layer is bonded tightly to the metal surface. Leachable corrosion inhibitors such as phosphates in the MPT wet film react with the zinc metal to form an additional passivation layer to prevent corrosion. If the MPT-treated galvanized steel surface is damaged due to scratching during transit or storage, these leachable corrosion inhibitors migrate to the damaged sites and re-grow a passivation layer in place to stop corrosion. Compatible water-dispersible polymeric additives such as acrylic resin and PTFE dispersion impart excellent lubricity, flexibility, and other favorable properties to the MPT film.

3. Describe the corrosion problem or technological gap that sparked the development of the innovation? How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?

There is an immediate market need for high performance Cr-free passivation treatment because today's downstream users of the sheet metal are not satisfied with the performance of existing Cr-free passivation treatments. Feedback from these users indicates two major drawbacks of these Cr-free passivation treatments:

- *Inadequate corrosion protection* in adverse weather conditions of high humidity or heavy rain. Application of rust-inhibitive oil onto Cr-free passivated galvanized steel surface is thus often required.
- *Low formability* during subsequent metal forming processes such as stamping, punching and drawing. Therefore, application of metal forming oil and a subsequent degreasing/rinse process are needed. This leads to a large volume of waste water generated from the degreasing and rinsing process.

Figure 3 demonstrates the above issues. Figure 3(a) shows a passivated galvanized steel part after metal forming. Black belts (indicated by red arrows) are visible after forming. These are the areas where the passivated galvanized steel surface has been heavily scratched and damaged during the forming process due to lack of surface lubrication. Figure 3(b) shows a deformed passivated galvanized steel surface after exposure in a salt spray test (SST, ASTM B117) for 72 hrs. The deformed area ("dome") rusts heavily, indicating that the damaged passivation film can no longer protect the metal surface from corrosion. To resolve the above issues related to the prior generation of Cr-free passivation treatments, this developmental work was aimed to develop a high performance, multifunctional Cr-free passivation treatment that would provide galvanized steel surfaces with both enhanced corrosion protection performance and exceptional formability.



(a) (b)

Figure 3. (a) “Black belts” (indicated by red arrows) occurred on a passivated galvanized steel sheet after forming; (b) deformed passivated galvanized steel surface after exposed in SST for 72 hrs

4. Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the innovation

A number of MPT formulas have been optimized in laboratory tests. Based on the lab test results, one MPT formula was down-selected and tested in several line trials at Panzhihua Iron and Steel Company in Sichuan Province, China. The following section summaries the results for both lab tests and line trials.

Laboratory test results MPT formulations were tested on galvanized steel (GI) panels, benchmarked against the cleaned-only GI and Passivation Treated (PT) GI. The tests used for performance evaluation are listed in Table 1. Both PT and MPT formulations were rolled onto cleaned GI surface by using a draw down bar. The dry film thickness was controlled at around 1 μm.

Table 1. Performance tests used for evaluating MPT treated GI

Test items	Description
Corrosion resistance	1) 500-hr salt spray test for flat GI (ASTM B117) 2) 72-hr salt spray test for deformed GI (after cupping test) 3) 3-week wet stack test for flat GI
Chemical resistance	1) NaOH alkaline resistance test; 2) H_2SO_4 acid resistance test
Solvent resistance	1) Ethanol resistance test; 2) MEK resistance test
Heat resistance	200°C baking for 20 min, inspect color change of MPT treated GI surface
Fingerprint resistance	Vaseline wipe, inspect color change of MPT treated GI surface
Coefficient of Friction	Measured by tribometer

Table 2 shows SST results for GI panels with different passivation treatments. The untreated GI shows white rust after 48 hrs of SST and red rust after 96 hrs. The PT treated GI starts to show white rust after 120 hrs of SST and a few red rust spots after 500 hrs. The MPT treated GI is the best performer in the SST, showing no white rust after 120 hrs and no red rust after 500 hrs.

Table 2. SST results for GI panels with different passivation treatments

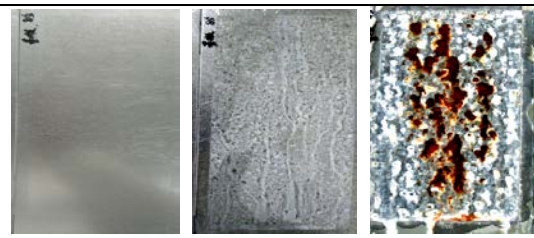
Untreated	 0 hr 48 hr 96 hr
PT treated (0.8 μm)	 0 hr 120 hr 500 hr
MPT treated (0.8 μm)	 0 hr 120 hr 500 hr

Figure 4 shows 72-hr SST results for the deformed GI panels treated with different passivation treatments. Before SST, the treated GI panels were deformed to form a dome on the panel surface using an Erickson cupping tester. It is seen in Figure 4(a) that the PT-treated GI displays a large amount of white rust on the dome (deformed area), while the MPT-treated GI shows no rusting. This result demonstrates that MPT provides excellent corrosion protection for GI even after the metal sheet has been deformed.

(a) (b)

Figure 4. 72-hr SST results for deformed GI panels with different passivation treatments;
(a) PT treated, and (b) MPT treated

The 3-week wet stack test results for GI flat panels with different passivation treatments are shown in Figure 5. Prior to the test, the GI panels were sprayed with de-ionized water. Two wet GI panels were stacked tightly together and were then placed into a humidity chamber (100°F, 90%Rh) for exposure of 3 weeks. This test is to simulate a typical transit or storage conditions in high humidity. In Figure 5, the untreated GI panel exhibits 100% uniform corrosion (Figure 6(a));

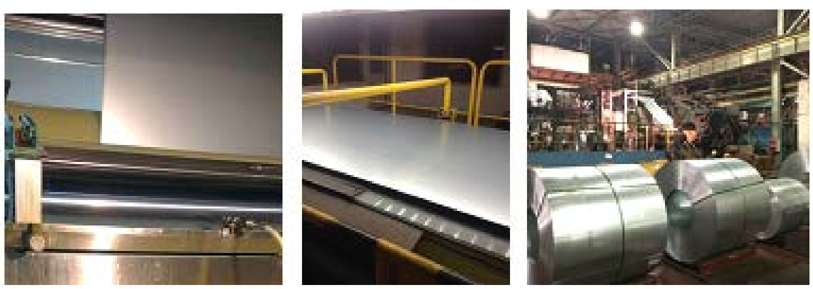
the PT treated GI surface exhibits dark grey corrosion spots (Figure 6(b)); the MPT-treated GI surface has no corrosion (Figure 6(c)).

(a) (b) (c)

Figure 5. 3-week in-house wet stack test results for GI flat panels with different passivation treatments; (a) untreated, (b) PT-treated and (c) MPT treated (both PT and MPT film thickness was 1 μm)

The co-efficient of friction (CoF) values were measured for both MPT-treated GI and PT-treated GI surfaces using tribometer. The CoF value for the PT treated GI surface was 0.53, while that for MPT-treated GI surface was 0.08. This indicates that MPT greatly enhances the formability of GI sheets by reducing the CoF of GI surface.

<u>Field trial test results</u> A down-selected MPT formulation was tested in field trials that were carried out on a continuous galvanizing line at Panzhihua Iron and Steel Company. Figure 6 shows the on-site galvanizing line and MPT-treated GI coils.



(a) (b) (c)

Figure 6. A line trial at Panzhihua Iron and Steel Company; (a) MPT rolling-applied onto a moving galvanized steel sheet, (b) MPT-treated GI sheet after baking, and (c) MPT-treated GI coils

These MPT-treated GI coils were shipped to a client's plant for formability testing without application of metal forming oil. This plant makes microwave oven parts such as side panels. MPT-treated GI sheets were punched or stamped to form the desired shapes (Figure 7). No cracks or black belts as exhibited in Figure 3(a) were observed during the forming process. This demonstrates that MPT can provide GI sheets with sufficient formability without the need of metal forming oil.

(a) (b) (c)

Figure 7. Formability test in a downstream client's plant (a microwave oven manufacturer); (a) uncoiling MPT-treated GI coil; (b) punched back panel and (c) stamped panel

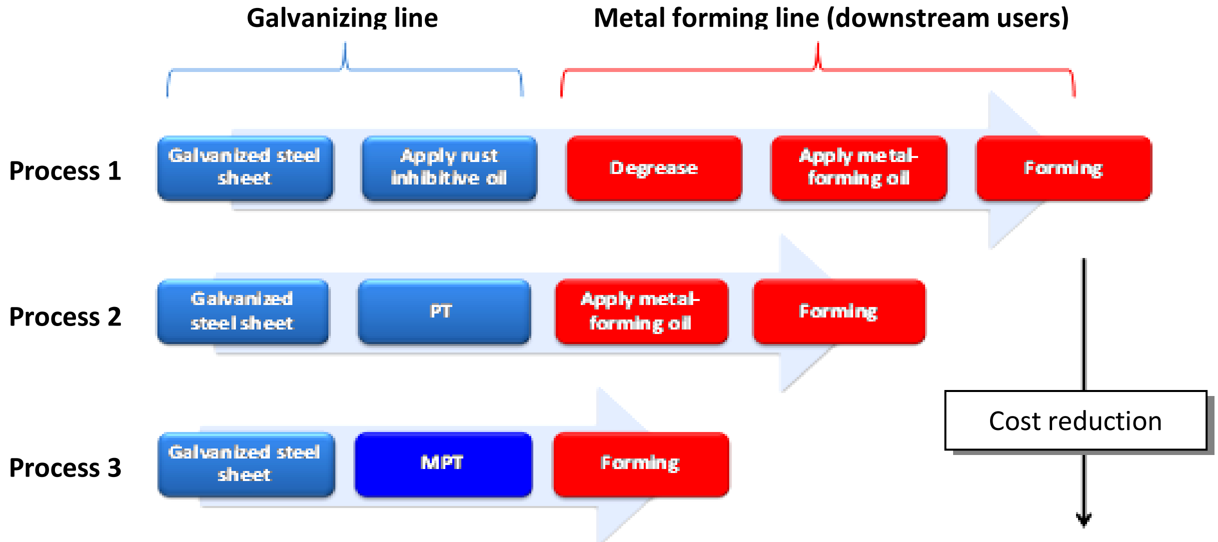
5. How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)?

In addition to its exceptional technical performance, the MPT also provides end users with maximized cost saving and added efficiency since both metal forming oil and degreasing agents are no longer needed. Consequently, no waste water is generated from these two process steps. Figure 8 schematically compares the MPT process with other currently-used processes.

In Process 1, freshly-galvanized steel sheets have rust inhibitive oil applied for corrosion prevention at the finish end of galvanizing line. When delivered to downstream sheet users', the rust inhibitive oil on the GI surface must be cleaned off by using degreasing agents and rinse water. After that, metal forming oil is applied onto the cleaned GI surface for the subsequent forming process. The metal forming oil also needs be cleaned off afterwards. As a consequence, a huge amount of waste water is generated from Process 1 that is always a problem for the users to deal with.

Process 2 is a simplified process. Instead of using rust inhibitive oil, a solid thin passivation film (PT) is applied onto GI. Metal forming oil can be directly applied onto the PT-treated GI surface prior to the forming process. Process 2 helps the sheet metal users reduce cost by eliminating the cleaning step of rust inhibitive oil. Since the metal forming oil also needs to be cleaned off after forming, waste water is still generated from Process 2.

With the use of MPT in Process 3, the process is simplified greatly. MPT-treated GI sheets can be directly subject to the forming process to form desired shapes without the need of metal forming oil. No cleaning step is needed after forming and therefore no waster water is generated from Process 3, which permanently resolves the waste water problem for the metal sheet users.



PT: Passivation Treatment
MPT: Multi-functional surface Passivation Treatment

Figure 8. Comparison of the MPT process with other currently-used processes

6. Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome?

The MPT technology has been commercialized and the related products have been in commercial applications since early 2015 in China.

7. Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.

There are no patents on this work. The proprietary formula information is a trade secret.