

Introduction

The surface of zinc and zinc alloy-coated steel sheet can be treated using one or more of many methods. **This GalvInfoNote deals with surface treatments used to impart resistance to storage staining.** Other treatments are used for different reasons, namely:

- Improving uniformity of appearance (see GalvInfoNote 2.8)
- Treatments for enhancing formability (see GalvInfoNote 2.9)
- Preparing galvanize for field painting (see GalvInfoNote 2.11)
- Pretreatments for metallic-coated sheet (see GalvInfoNote 2.12)
- Treatments for resistance to handling and fingerprint marks (see GalvInfoNote 2.13)

While anti storage stain treatments are always applied directly on the hot-dip line after the metallic coating has been applied, some of the others listed above can also be carried out on separate process lines/facilities, or in the field.

There are a number of surface treatments available to improve resistance to storage stain. First, the reason for the formation is storage stain is explained.

Storage Stain

Storage stain is a corrosion product that is typically white, but which can also take the form of a grey or black deposit on the surface. Since the most common form of discoloration is white, storage stain is often called **white rust**. It can occur when sheets of galvanized steel that are in close contact (in a coil or stacked in lifts/bundles) get wet, either by water intrusion, or by condensation from moist air trapped between the sheets. The discoloration is due to the corrosion products that form after zinc reacts with moisture in the absence of free air circulation. Refer to GalvInfoNote 3.2 for more information on storage stain.

White rust on storage stain-damaged galvanize is initially zinc hydroxide, and turns to zinc oxide when left to dry in the open air. The white rust inside a wet stack or coil will eventually turn black if left unchecked. When storage stain on galvanize turns black it usually means that iron has become part of the corrosion product. When iron becomes involved, enough zinc has been consumed to expose the steel substrate and the remaining zinc is of little, if any, protective value.

The stain that forms on water-damaged galvanized steel is grey to black in color due to the iron in the coating. See GalvInfoNote 3.3 for more information on stained galvanized steel. The corrosion products that form on water damaged zinc-aluminum coatings often have a black to grey appearance – the result of hydrated aluminum hydroxide formation.

Chemical Treatments – Chromate Based

To reduce the susceptibility of metallic coated steel sheet to storage stain, the practice for many years has been to treat it with an aqueous solution of chromic acid, chromium salts and mineral acids to produce a thin-film coating on the surface. This inorganic chemical or “passivation” treatment is applied near the end of the coating line. The solution dissolves a very small amount of the coating metal and forms a protective film containing complex chromium and metal compounds¹. Traditional chromium

based treatments contain chrome in two valence states, trivalent (Cr^{+3}), and hexavalent (Cr^{+6}). The presence of Cr^{+6} designates these as "chromate" passivates. The formation mechanism of a chromate coating is a dissolution and precipitation process similar to what occurs during phosphating. The thickness and color of chromate coatings depends mainly on the chromate concentration, pH, and dipping time. They are usually applied so thin that they are essentially invisible. Thicker chromate coatings may have a yellowish or greenish appearance and could be anywhere from 0.1 to 0.6 μm thick. The total chromium content of a normal, invisible coating is usually 1-2 mg/ft^2 , with less than half as hexavalent chromium in a complex mixture of metal salts and oxides.

Protection of the zinc is afforded through barrier and passivation effects. The complex chromium oxide acts a barrier while the hexavalent chromium contained in the film serves to re-passivate exposed metal. Water that comes in contact with the film dissolves the hexavalent chromium, forming a chromate solution, which then forms a fresh passivation film on the surface. This is the reason for the "self healing" ability of chromate passivation films. This self-healing attribute is limited under wet conditions. The result is that chromate passivate films do not prevent the eventual formation of storage stain if the water is allowed to remain between contacting surfaces. In any case however, even when the sheet is kept dry, Cr^{+6} eventually oxidizes to Cr^{+3} .

Chromate passivation films are generally not considered paintable without the use of extreme removal procedures. Also, they cannot be effectively phosphate treated.

Any type of chromium passivation interferes negatively with the spot weldability of galvanized sheet. Chrome "poisons" the copper electrodes, softening them, and reducing tip life. For this reason, almost all galvanized sheet intended to be fabricated using automated spot welding equipment, is ordered and produced as non-chemically treated (unpassivated).

Due to health, safety, and environmental concerns, the use of hexavalent chrome is being discontinued². This move began with the European Union RoHS Directive to eliminate hexavalent chromium and other substances from essentially all new electrical and electronic equipment by July 1, 2006. This regulation is being used as a model in many other countries. It is significant that these regulations do not prohibit the use of chromium; rather they prohibit the use of chrome in the hexavalent state². The use of chrome in other valence states, e.g., Cr^{+3} , is acceptable. As a result, the development of passivates to replace chromate is evolving in two directions: products containing trivalent chromium (Cr^{+3}), or products entirely free of chromium.

Trivalent Chromium Passivation Treatments

The use of trivalent chromium products allows the retention of some of the advantages of chromium-based systems yet avoids the use of hexavalent chromium treatments². These products have been in use for several decades and are less costly than non-Cr based passivates. Obtaining all the benefits of chromate is difficult to achieve with trivalent Cr so the latter must be applied at heavier coating weights to obtain the same corrosion protection as the former. Trivalent treatments can be applied successfully on both flood/squeegee and chemcoater application systems. Many of these treatments are paintable.

Henkel, a GalvInfo Sponsor, now produces a Cr^{+3} passivate, called Bonderite[®] 6020, that can be utilized at coating weights as low as 2.0 mg/ft^2 , has improved paintability, and has been approved by major electronic manufacturers.

Chromium-Free Passivation Treatments

Chrome-free coatings are manufactured from both organic and inorganic materials that can contain many different ionic species, including molybdates, tungstates, vanadates, titanates, and fluorides. While they can be applied using flood/squeegee and chemcoater units, the application parameters have been found to be more critical compared to those for Cr^{+6} systems and coating weights need to be as high as 30

mg/ft². Corrosion performance tests compare favorably with hexavalent systems with excellent formability. Paintability, however, is similar to chromate passivation.

Henkel, produces a chromium-free passivate, called Passerite[®] 5004, that is being used in several galvanize mills to achieve RoHS compliance.

Another non-chromium product has been developed by Henkel² to replace Cr⁺⁶ containing acrylic coatings. Thick acrylic coatings are used on zinc and aluminum-zinc coated sheet, not only as passivates, but as clear protector films to avoid handling marks and to keep the sheet brighter for a longer period. The Henkel product is known as Granocoat[®] 342 and is an inorganic system containing vanadium, cerium, zinc, molybdenum, and titanium reacted with fluoride and phosphate. The thickness is as high as 250 mg/ft² and is applied using a roll coater at ambient temperatures. The paintability is improved over hexavalent-based treatments.

Is it Passivated?

It is sometimes necessary in the field to find out if coated sheet has been passivated. In most cases it is not possible to visually determine this. There are a variety of methods for detecting passivation.

- Surface passivation can be quickly evaluated with 5% hydrochloric acid. A drop will “fizz” on unpassivated zinc surfaces but show little reaction on passivated zinc.
- The amount of chromium on the surface can always be tested by using chemical stripping and laboratory analysis but the standard of the industry is to use x-ray fluorescence; for example the Cianflone PortSpec.
- Analysis for the presence of chromate can also be performed by placing a drop of a diphenylcarbohydrazide solution on the surface of the sheet and observing if there is a color change or not. If the drop remains clear, no hexavalent chromium is present. This test is described in ASTM D 6492 – Detection of Hexavalent Chromium on Zinc and Zinc/Aluminum Alloy Coated Steel, available at www.astm.org .
- Another quick method of finding out if galvanized sheet has been passivated, with chrome or non-chrome treatments, is to use a simple condensing humidity test. Place a 4” square of the galvanize sheet as a lid on a beaker containing 140°F water and leave for 15 minutes. If the underside remains shiny it is passivated. If it is stained to any degree it is not passivated.

Oils

An alternative to using passivation treatments is to apply oil to the sheet surface. Specially formulated oils are used that contain rust inhibitors, which are usually polar products designed to strongly adsorb onto metal surfaces. They are effective in providing protection from humidity rust due to their ability to prevent moisture from condensing between the laps of a coil or sheets in a bundle. They are not effective, however, in preventing the penetration of bulk water, e.g., rain, between laps.

Oil also has the benefit of being easily cleaned off at a paint line, so some temporary protection can be given to metallic-coated sheet without the risk of contaminating the cleaning and pretreatment chemicals with chrome. For added protection, and/or to assist lubrication during forming, passivated sheets can also be oiled.

A source of additional information on mill-applied surface treatments for storage stain protection can be found in Appendix X2 of ASTM A 924/A 924M Standard Specification for General Requirements for Steel Sheet, Metallic-Coated by the Hot-Dip Process, available at www.astm.org.

¹ Zhang, Xiaoge Gregory: Corrosion and Electrochemistry of Zinc, Plenum Press, New York, 1996, pp. 16-17.

² Cape, Tom, et al: Non-Hexavalent Chromium Coating Technologies for Galvanized Steel, Galvanizers Association Conference, Montreal, QC, 2007

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