GalvInfoNote **2.7**

Galvanizing – The Use of Chemical Fluxes

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Introduction

As discussed in GalvInfoNote 2.1, "The Continuous Hot-Dip Galvanizing Process for Steel Sheet Products", it is absolutely necessary to have the steel sheet free from any surface oxide as it enters the molten zinc coating bath. On high-speed processing lines, where running at speeds of up to 600 feet/min [180 m/min] is common, the sheet is in the coating bath for times as short as 2 seconds. In order to develop the alloy layer essential for good adhesion between the steel and zinc coating, the incoming sheet has to be very clean and oxide-free.

Hydrogen Gas Cleaning for Continuous Galvanizing

The most common method used today for obtaining a super-clean surface at coating bath entry is to have an aqueous alkaline cleaning section (sometimes with an electrolytic assist) ahead of the annealing furnace. The annealing furnace gas atmosphere contains a small amount of hydrogen (typically 5-6%) and is kept as free of oxygen as possible to assist with hydrogen-reduction of the oxide layer. Nitrogen is used as the inert carrier gas to maintain adequate internal pressure within the furnace. As the sheet is heated to high temperatures in the furnace to anneal the steel and obtain the desired mechanical properties, the hydrogen gas reacts with any remaining iron oxides to produce a very clean surface; one that can be readily wet by the liquid zinc bath metal. In this manner, the zinc and steel are able to develop a complete alloy bond in a very short time.

Other Gas Cleaning Methods

Some lines also have a non-oxidizing cleaning furnace section between the wet cleaning and annealing sections. Other lines omit the wet cleaning section, but have a non-oxidizing cleaning furnace before the annealing furnace. Non-oxidizing furnaces burn off surface hydrocarbons and provide some reduction of surface oxides, while heating the sheet to temperatures just below the annealing point.

The chemical reaction in the furnace is shown by the following:

$$\text{Iron oxide} + \text{Hydrogen } (H_2) \longrightarrow \text{Iron (Oxide-free surface)} + \text{Water } (H_2O)$$

To prevent re-oxidation after being annealed and cooled to the approximate temperature of the zinc bath, the moving sheet is kept under the protection of the hydrogen-containing atmosphere between the end of the furnace and the coating bath. This is accomplished via a fixed enclosure (usually referred to as a "snout") between the furnace and the molten zinc bath. The upper end of the snout is bolted tightly to the furnace, and its lower end submerged into the coating bath, ensuring that the steel never encounters air prior to immersion into the molten zinc. It is at the snout where the pressurized atmosphere gas is introduced and forced to flow back towards the entry end of the line, against the movement of the steel sheet. This ensures that gas with the most reducing potential is in contact with the sheet just before it enters the molten zinc.

Flux Cleaning Method for Continuous Galvanizing

There is one other method for providing a clean oxide-free steel surface to a galvanizing bath, viz., the use of chemical fluxes. It is an older, and now a far less common method than the process described above, but is a proven means of obtaining very good coating adhesion. The flux galvanizing process is also used in the after-fabrication, batch galvanizing industry for articles such as structural shapes, pipe, etc. Refer to GalvInfoNote 2.3 for information on batch galvanizing.

The normal procedure for continuous flux galvanizing of steel sheet involves a cleaning/degreasing step, often using a similar aqueous alkaline cleaning solution to that used for the hydrogen cleaning process. Following this is an acid-pickling step (usually hydrochloric acid) to remove surface oxides. After pickling and during the time that the sheet is rinsed and dried, a very thin oxide layer reforms on the steel surface. The reason this happens is that oxide-free low carbon steel reacts very quickly in air to form a thin surface oxide layer. It is essentially impossible to prevent this reaction. This oxide layer does not perceptibly change the appearance of the steel surface, although the surface may be slightly darker than an absolutely oxide-free surface. The color is not the usual black or red iron oxide normally associated with rusting, but a thin oxide is present. This thin film must be removed in order to get rapid, complete wetting of the steel by the molten zinc. Therefore, one more step is needed ahead of the coating bath.

Since flux coating lines do not have an annealing furnace as part of the process (the sheet's mechanical properties are obtained in annealing and skin passing operations ahead of the galvanizing line), hydrogen cleaning is not possible. Instead, chemicals are used to dissolve the last vestiges of oxide. These chemicals are called fluxes, much like the fluxes used for processes such as soldering. They are simply compounds capable of dissolving the oxides of iron.

For galvanizing, the most common flux used, and one that has been around for many years, is based on the inorganic chemical "zinc ammonium chloride". The weight ratios of zinc chloride to ammonium chloride can be adjusted to meet individual customer needs. Typically, these solutions also contain special proprietary wetting agents, anti-foaming agents, and possibly other viscosity-adjusting additions. Zinc ammonium chloride fluxes are used for all types of galvanizing - after-fabrication galvanizing as well as continuous sheet, wire, and tube galvanizing operations.

As flux is a relatively low melting temperature inorganic chemical, the steel sheet cannot be heated to high temperatures ahead of the galvanizing bath. If the steel temperature becomes too hot, the chemical flux will be burned, detracting from its performance. This means the sheet must enter the galvanizing bath at a temperature considerably below the zinc metal temperature (860-875°F [460-470°C]). The zinc pot therefore has to have a much higher heating capability than a typical coating pot used on lines that have in-line annealing. This high heating capability, combined with the need to remove the "spent" flux from the surface, usually leads to a less efficient use of the zinc metal than for coating lines that utilize in-line annealing and hydrogen cleaning. Flux fumes are also generated and must be collected by hoods located above the zinc pot. Another feature of flux coating lines is that the coated product has natural small, flat spangle – even with lead-bearing zinc. This is a result of the fast, post-pot cooling resulting from the sheet's low pot entry temperature.

In the continuous sheet galvanizing process, the flux can be applied as a "preflux", that is, applied from a water-based solution that contains the dissolved flux chemicals, or it can be applied as a "top flux", that is, a molten flux layer floating on top of the galvanizing bath. In some cases, both types of flux application are used.

Continuous galvanizing using fluxes has been a commercial process for many years. In fact, before the development of continuous galvanizing, the zinc coating of steel sheet was done by operators immersing sheets, one at a time, into a bath of molten zinc. Zinc ammonium chloride fluxing was part of that operation. The movement to continuous galvanizing, using fluxes as a part of the process, was a natural outgrowth of the one-sheet-at-a-time process.

Flux galvanizing lines were also known as "Cold Galvanizing Lines", or "Wheeling Lines" (the first steel company to use them), or "Cook-Norteman Lines" (the process developers).

The downside of flux lines in the case of flat products, however, is that the steel must be annealed and temper rolled prior to galvanizing. The development of “hot” sheet galvanizing lines that can both anneal and galvanize in one step, at a much lower operating cost, has brought an end to flux lines in North America and in many other parts of the world.

Summary

The flux-galvanizing process served as a viable process for the continuous galvanizing of steel sheet. Although it has its own unique processing problems, such as the formation of flux fumes and flux ashes that need to be handled as waste products, it is a method of galvanizing without the usually larger capital expense of the typical inline annealing furnace and hydrogen cleaning method. For most producers of galvanized sheet, the inline annealing of steel sheet is preferred, as it has lower operating costs. However, for smaller manufacturers who want to purchase steel sheet and apply a zinc coating for corrosion protection, a flux galvanizing line is still an alternative process – one that usually requires less capital expenditure, even though there are small “hot” line designs now available with capital costs that compete with cold flux galvanizing.

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