HOT DIP GALVANIZING

M. Mohan Rao

Department of Metallurgy, Indian Institute of Science, Bangalore-12

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Galvanizing–the application of a zinc coating to ferrous products-is one of the most popular and reliable methods of protecting these products against corrosion under a wide variety of service conditions. The life of a galvanized coating may vary from 5 to 40 years depending on the nature of the environ ment. Applications range from small components like bolts and nuts to large transmission line towers, railway electrification schemes, bridges etc. The process of galvanizing and the various factors governing the success of the process are reviewed in this article.

The Process

The process consists of two basic steps: first the pretreatment, which implies the preparation of the surface to accept the coating and second the application of the zinc coating. The coating may be done 1.) by the hot dip galvanizing process in which the work piece is dipped in a bath of molten zinc or 2) by the electro-galvanizing process in which the zinc is deposited by an electrolytic process. The details involved in the two basic steps for a successful application of the hot dip galvanizing process will now be presented in some detail.

The Pretre itment

The manner in which surfaces are prepared influences the type and quality of the galvanized coating and hence, the need for efficient pretreatment for good galvanizing cannot be overemphasized. Pretreatment may involve one or more of the following operations.

1. Degreasing and/or paint removal.
2. Shot or Grit Blasting.
3. Pickling and
4. Fluxing

The choice of the operations required for any work piece would depend on the nature of the object and the degree of its contamination.

Where contamination with oils, greases or paints is heavy, degreasing or paint removal has to be carried out. Important methods of degreasing or paint removal are vapour degreasing, treatment with cold or hot alkali solutions and immersing the article in the molten zinc bath through a thick flux blanket. If the contamination is light, it may be possible to go to pickling without degreasing. Vapour degreasing in trichloroethylene is very effective in removing oils and greases but is usually too costly for use in general galvanizing since this requires expensive and specialized plants. Hot alkali solution containing from 0.10 to 0.15 Kg of caustic soda per liter of water is a powerful cleansing agent for all oily surfaces and can also effect some paint removal. Degreasing should immediately be followed by a rinse first in hot water and then in cold water.

After degreasing, the surface to be galvanized may either be pickled or grit blasted. In castings where burnt-on sand is present pickling is not very effective and shot or grit blasting may be used. This method of cleansing while suitable for smooth, flat surfaces cannot be used for complicated shapes where the shot does not make contact with the whole surface.

In pickling the components are immersed in a solution of acid, hot or cold. The galvanizer has a choice of hydrochloric acid or sulphuric acid for pickling although mixtures of the two acids may also be used Hydrofluoric acid and fused caustic soda have also been used in pickling castings The choice between hydrochloric acid and sulphuric acid is not very clear and the following advantages and disadvantages may be cited for each choice.

Advantages of Hydrochloric Acid

1. Hydrochloric acid can be used at room temperature 18 to 21°C, with pickling rates comparable to those obtained with sulphuric acid at 60°C. The heat evolved during pickling is sufficient to maintain a constant temperature of 18-21°C.
2. A greater chemical dissolution of scale is obtained with hydrochloric acid with only slight attack on the iron base.
3. In view of the lower temperatures used, there is

considerably less penetration of hydrogen by diffusion.

4. Iron salts can be tolerated upto 100-120 g/l and cleaner pickled surfaces are obtained with less pickling residues and iron salts on the surface.

Disadvantages of Hydrochloric Acid

1. Hydrochloric acid can be regenerated from the spent liquor but the recovery systems are expensive.
2. Hydrochloric acid requires for transportation and storage containers lined with acid resistantmaterial.
3. Below 15°C, the pickling rate is very slow ard heating of the acid will be necessary While heating improves the pickling rate, at temperatures of 50-60° the acid will emit fumes which need to be processed.

Advantages of Sulphuric Acid

1. The pickling rate with sulphuric acid is slow at room temperature and improves with increasing temperature. This makes for better control of the pickling rate Since sulphuric acid does not fume excessively at high temperatures, it can be used at 80° C with a pickling rate higher than that for hydrochloric acid at room temperature.
2. The regeneration of acid and recovery of iron sulphate is easy.
3. Sulphuric acid can be transported and stored in containers of mild steel.

Disadvantages of Sulphuric Acid

1. Heating of the acid is required to obtain pickling rates comparable with those of hydrochloric acid.
2. Greater diffusion of hydrogen into the steel
3. Pickling residues are more adherent.

Pickling with hydrofluoric acid has been used for cleaning castings with burnt-on sand. The pickling time depends on the strength of the acid, decreasing with strength. A gelatinous laver is formed on the casting surface and must be removed with a water rinse.

The burnt-on sand can also be removed by treatment with molten caustic soda at 450-500°C followed by removal of the adhering alkali residues with a water rinse. Very good results are claimed for this process.

The pickling operation is followed by fluxing with zinc ammonium chloride. the objective of which is to protect the surface from contamination and also to ensure cleaning of the surface at the instant of contact between zinc and the steel. There are two methods of fluxing. In the dry method the cleaned surface is dipped into an aqueous bath of flux. The thin layer of flux adhering to the surface is dried prior to introduction of the piece into the bath of molten zinc. In the wet process the cleaned surface is dipped into molten zinc through a molten flux blanket.

Hot Dip Galvanizing

In order to better appreciate the factors which contribute to a successful galvanizing process, the reasons for the protective action of zinc need to be considered. In the first instance the zinc coating acts as a barrier between the base steel or iron and the environment. When the coating is scratched to the base metal, the base is still protected sacrificially since zinc dissolves at the crack in preference to iron. Hence protection against corrosion will last only so long as the zinc coating is present. Thus, the object of a galvanizing process would be to obtain a uniformly thick coating of zinc. It may be pointed out that an identical thickness of coating will last for shorter durations in severe industrial atmospheres than in cleaner rural areas. It would therefore be appropriate to specify the thickness of coating required for any work piece bearing in mind the life expected of the piece and the conditions of the exposure. The thickness of the coating in galvanizing is expressed in terms of weight per unit area, and the minimum usually specified is about 610 g/m^2. Needless to say thicker coatings will offer better protection but there are also disadvantages to thicker coatings. These and the factors effecting the thickness of the zinc coating are dealt with below.

1. Composition of the Base Metal :

In galvanizing the coating forms in several layers. The top surface layer is pure zinc (η) and the layers below are various zinc-iron alloys formed by diffusion The pure zinc layer covers a zinc iron (approximately $FeZn_{13}$) or ζ layer Beneath this, there is an iron rich phase (δ). The thickness and the composition of the alloy layers is strongly dependent on the composition of the base metal. The alloying elements usually present in steel compositions used for galvanizing are carbon, silicon, sulphur phosphorous and nitrogen. The effect of these on the thickness of the coating has been extensively

studied. It has been shown that increase in carbon, results in increased thickness of coating, other process variables remaining the same. The ratio of the zeta to the delta increases with increasing carbon content. At the higher contents the amount of delta decreases significantly with the existence of the zeta phase.

In the case of silicon, for short immersion times, the alloy layer thickness decreases, while for longer immersion times, the thickness increases with increase of silicon content. The zeta phase is the predominant phase in the alloy layer. Fracture along the zeta/delta interface is a possibility since this interface becomes irregular with increasing silicon content.

Nitrogen and sulphur do not have any effect on the thickness of the coating. Phosphorous accelerates the growth of the alloy layer. Phosphorous suppresses the formation of the delta phase below 0.06% P.

While it is true that the thicker the coating the better the protection the alloy layers being brittle are sensitive to shock and impact. Where ductile coatings are required as in structural applications, the formation of the alloy layer needs to be minimised. From a study of the effect of individual elements, the dependence of the alloy layer thickness on steel composition has been empirically given as.

$$t\,(mm) = 0.0059 + 0.00056\,(time) + 0.007\%C - 0.0058\%\,Si + 0.019\%P + 0.16\%N.$$

It may be noted that the overall effect of silicon is a negative effect.

2. Surface Roughness :

Thick galvanized coatings can be obtained if the surface of the steel prior to introduction into the bath of molten zinc is rendered rough. This can be achieved by grit blasting. Cold worked surfaces as such do not have an influence on the thickness of the coating. It may therefore be inferred that internal stresses do not play a significant role in the galvanizing process. Machined or emeried surfaces have been shown to produce an increase in the weight of zinc in the coating.

3 Galvanizing Temperature :

In the choice of galvanizing temperature only a very narrow range between 430°C and 460°C is available to the operator. The lower temperature limit is set by the melting point of zinc which is only 10°C below the minimum limit. Above 460°C, it has been observed that the life of the galvanizing pot is severely affected. However, even in this temperature range, the thickness of the coating increases with temperature. A widely used temperature is 450°C.

4. Bath Composition :

The presence of common impurities like lead, cadmium and iron in the molten zinc bath have no adverse effect on the corrosion resistance of the coating obtained although ductility may be affected. In order to improve the appearance of the coating the presence of lead between 0.15—0.2% is essential. Deliberate additions of tin (0.1%) and antimony (0.1%) also serve the same purpose. In order to develop a ductile coating aluminium additions between 0.05%-0.15% have proved useful. This is used in the continuous sheet and strip galvanizing.

5. Dipping Time

A longer dipping time leads to a thicker coating, because of the formation of a thicker alloy layer. It has been observed that this effect is not very significant in mild steel but is more pronounced in silicon steels.

Thus, it is possible to control the nature and thickness of zinc coatings within certain limits by varying the magnitude of the individual effects. However, each case should be considered both from a technical and economic point of view. Where additional protection is required, the galvanizing may be followed by a chromating process, or a chromating process and painting. Experience has shown that a coat of paint on a galvanized surface increases the life expectency of the surface significantly besides imparting aesthetic appeal to it.

The chromating treatment consists in immersion of the galvanized surface into a 20% solution of acidified sodium dichromate at room temperature. The pH of the solution and the chromate content are critical parameters in the process. The process results in the formation of a passivating chromium oxide - metal oxide film on the surface.

Steel is also given a zinc coating by a variety of other processes such as :

i) Electrolytic Process and

ii) Sherardizing Process.

In the electrolytic process, a prepared surface is placed in a plating tank in which pure zinc from zinc anodes is plated on to the surface. The thickness may be controlled by controlling the current density and the time of deposition The plating can also be done on a continuous basis. A variety of plating baths have been developed like, cyanide baths, acid sulphate and chloride baths, fluoborate solutions and pyrophosphate baths. A discussion of the compositions and the other process variables is not within the scope of this review.

Sherardizing is a process specially suited for small fabricated items such as nuts, bolts and screws. In this process, the cleaned parts are heated in an airtight container in close contact with zinc dust to near the melting point of zinc. The zinc impregnates the steel surface resulting in a thin uniform coating.

In conclusion, it need only be said that zinc galvanized steel is a material which provides a combination of strength, corrosion resistance and formability. It can be readily joined by processes such as welding or soldering.

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