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EFFECT OF CONVENTIONAL AND NON-CONVENTIONAL (ECO-FRIENDLY) FLUXES ON HOT DIP GALVANIZING - A REVIEW

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Abstract — *Galvanizing is very common practice now a day for corrosion prevention through modification of surface of the metal to be protected. In this process, the various techniques are used from which one of the most common is hot dip galvanizing. Before hot dip galvanizing, fluxing is to be done of metal surface. Again, the fluxes having many categories like conventional flux and non – conventional flux. Non – conventional flux has many plus points compared to the conventional flux which is discussed in this paper elaborately.*

Keywords *— Hot dip galvanizing, corrosion, coating, fluxing, passivation, etc.*

I. INTRODUCTION

Corrosion is destruction of metal or deterioration of proportion of material due to chemical and electrochemical reaction with its surrounding environments [1]. Corrosion plays an important role in destructing of materials and hence its protection is utmost important.Many techniques are available for corrosion controls like: surface coating, surface cladding, surface heat treatment, diffusion treatment, cathodic protection, surface finish, etc. Fromall these technique the corrosion prevention coating is quite common. The surface can be treated by immersion coating, which is very effective processto prevent atmospheric corrosion. Coating helps to break the contact between material and atmosphere and result disconnection of corrosion circuit. Coating also provided cathodic protection as well as barrier protection to ferrous metals. The well-established process is zinc galvanizing.This zinc galvanizing includes the processes like electrodeposition, cladding and hot dip galvanizing which are mainly used for metal surface coatings [2]. Hot dip galvanizing is one of the oldest methods for surface coating of metal in which metal is immersed in molten metal bath of low melting point metals, mostly zinc, tin, lead and aluminum [3]. There are two methods of hot dip galvanizing, batch and continuous. Using these methods a thin layer of molten zinc is applied to the metal surface. The continuous process is a more advantageous process for coiled products such as sheet, wire and tube, whereas the batch process is normally used for bulk products. During hot dip galvanizing four phases are form such as gamma, delta, zeta and eta. Eta is ductile phase while gamma, delta and zeta are brittle Fe-Zn phase [4]. To make hot dip galvanizing effective and efficient, various fluxes are being used. These flames are mainly of two types namely conventional and non-conventional fluxes.Alloying elements like aluminum, nickel, cadmium, copper, lead and tin are controlling the melt and improve the coating properties [5]. The main purpose of this paper is to understand the effectiveness and important of the fluxes. The general practice is to use both conventional flux and non – conventional flux for fine tuning of the surface properties of the metal.

II. HOT DIP GALVANIZING

Hot dip coating is a process in which an adherent protective coating is applied to a metal by immersing it in a hot liquid bath of the coating metal. Hot dip galvanizing provided barrierprotection of the ferrous metals against corrosive media,resistance to mechanical damage. The common steps of hot dip galvanizing are shown in figure1 as well as discussed below.

2.1. Pretreatment of Hot Dip Galvanizing

In the hot dip galvanizing process surface cleaning and surface preparation is most important part for determining the good quality coating. Oil, grease, dirt and oxidation products generally sticking with steel surface affect the adhesion, continuity and quality of the coating. So surface pretreatment is necessary to impart the quality of coating.

2.1.1. Alkaline Degreasing and Rinsing

Oils, greases and other saponifiable compounds are removed mostly with mixture of basic sodium salts [6]. It is followed with rinsing in a water bath to avoid transfer of degreasing solvent to the next stage [7].

2.1.2. Acid Pickling and Rinsing

The pickling process focuses on removal of surface oxides and mill scale. The pickle acid consists of a mineral acid which is an aqueous solution of usually hydrochloric acid (HCl) or sulfuric acid (H_2SO_4). The acid concentrations and pickling temperatures vary from galvanizer to galvanizer, but they should remain within a narrow range. To avoid attack of the base metal, an inhibitor is sometimes used [6].
The work is again rinse in a water bath after undergoing chemical cleaning by pickling and this is doneto minimize the transfer of any acid residues to subsequent stages of the process [7].

2.1.3. Fluxing

The requirement of a process called fluxingis to dissolve any oxide films which are formed on the steel after pickling but before galvanizing and to make sure that a clean metal surface will come in contact with the molten metal zinc. The fluxing methods used include the wet process and the dry process. The wet process involves steel being passed through a layer of molten flux which floats on the surface of the molten zinc. The dry process also called prefluxing process which involves immersing of steel in an aqueous flux solution and drying before galvanizing. Both cases involve a flux composed of zinc ammonium chloride ($ZnCl_2 \cdot 2NH_4Cl$) because both processes have certain advantages.Selection of a method is based on an individual choice and the types of material to be processed [6].

2.1.4. Drying

The flux tank steel articles for galvanizing are dried and will become coated with a thin film of flux after the immersion process is complete [7]. Drying is done between temperature ranges of 110°C-120°C. Above 150°C the important ingredient hydroxy acid produced due to decomposition of ammonium chloride and combination of zinc chloride. Below 100°C the moisture trapped in flux and transferred in the galvanizing bath [8].

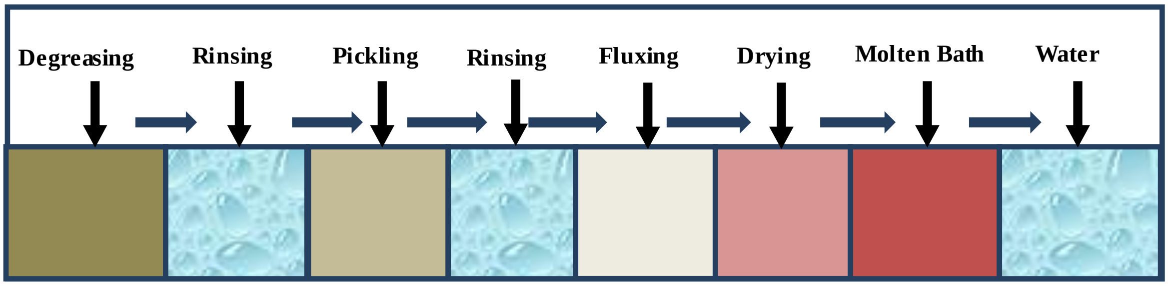

Figure 1: Steps for hot dip galvanizing [8].

2.2. Galvanizing Bath

Galvanizing bath consist of molten metal of Zn along with Cd, Pb, Al, Sn as addition to enhance various properties of galvanized coating the process is carried out at 450–460°C with respected to different gauge sheet of low carbon steel [6].

2.3. Post treatment of Hot Dip Galvanizing

The protection of the zinc coated coils against white rust during storage and transportation is achieved by a thin and uniform film of oil which is employed by advanced spray oiling system.This system is incorporated in the line or through a process called chromating [9].

2.3.1. Passivation

In chromating process, the spraying of hot chromic acid on the sheet or the sheet goes through the achromic acid tank followed by the hot air drying process. Hence a thin layer of a zinc chromate forms on the zinc coated surface which improve further corrosion resistance of coating .This chromate coating thickness will depends on the pH, temperature and the concentration of the chromate solution [9].

2.4. Factors affecting on hot dip galvanizing

2.4.1. Temperature

When steel is immersed in molten zinc at the galvanizing temperature range 450–490°C, The different layers have been form according to the Fe–Zn phase diagram as shown in figure 2. The phases are formed zinc saturated α-iron, Γ phase layer, Γ1 phase layer, δ phase layer, ζ phase layer and η phase layer. Immersing the steel article in molten zinc the sequential nucleation of the Fe–Zn phases occurs at the interface beginning with ζ phase layer, followed by δ phase layer, then the Γ phase layer after some incubation time. Galvanizing coating thereby also depend upon temperature which is depend on the thickness of metal sheet being coated. Increase in coating thickness can be observed below 480°C, while the same reduces as the temperature increase above 480°C significantly. During 500-530°C, a little change can be observed. The coating thickness is also depends on immersion time at the same temperature [10].

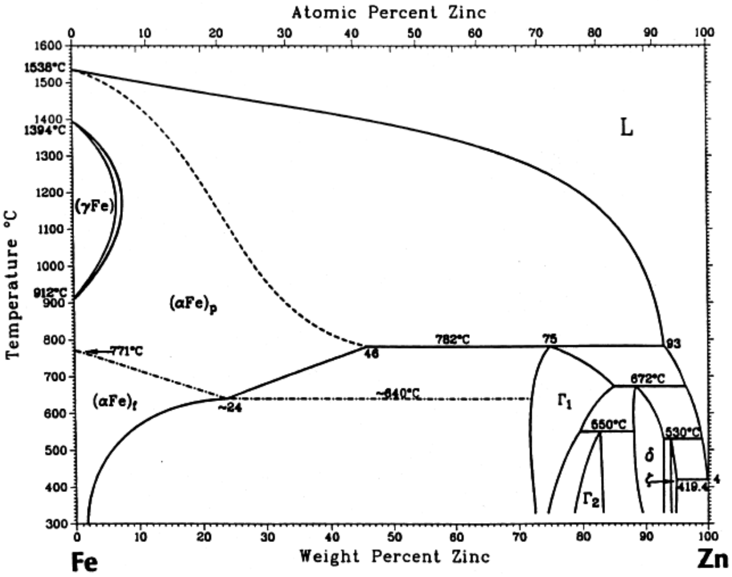

Figure 2: Fe-Zn equilibrium phase diagram [4]

2.4.2. Alloying Elements

The small amount of alloying element affects the corrosion resistance of metal significantly.The additions of the alloying elements mainly influence the first period of crystallization. Alloying elements can delay the interfacial reaction between zinc and iron which indirectly can induce growth of different layers and favors the growth of the outer η-phase layer. Some alloying elements as discussed below;

Aluminum, in low concentrations up to 0.3 wt. % has been influence the coating properties such appearance, mechanical properties, and durability.Also it is known for significant changes in the microstructure of the coating andto affect the formation of certain phases.

Nickel, additions generally reduce the reaction between zinc and steel. Thus zinc bath inhibit further growth of the ζ-phase after an initial formation, resulting in a decrease of the coating thickness.

Aluminum and Nickel, additions in which first Al is inhibit the formation of Fe-Zn phases. The latter Ni hinders the formation of the undesirable ζ-phase, which consists of numerous tiny and brittle crystals. Both elements enhance the formation of the outer η-phase, which offers more galvanic protection due to the low content of iron. The η-phase also improves the quality of the coatings.

Lead, additions strongly alter the crystallographic orientation and the surface morphology of the eta phase. Small amount of lead is used for spangle formation. Moreover lead additions delay the fast thickening of the solid layer, as it lowers the surface tension and promotes a planar growth. Thus lead seems to improve the quality of the coatings and to produce thinner layer.

Copper, reduces the segregation at grain boundary and resistance to intergranular corrosion. Copper is known to favor the crystal growth of the δ-phase, which exhibits a localized high concentration inside this phase. It is possible that copper atoms act as effective heterogeneous nucleation sites for the δ-phase.

Copper, Tin and Cadmium,at relatively high concentrations of the order of 1 – 2 wt. % has been found to affect significantly both the appearance and the structure of the coatings.

Tin,additions there are no influence in the grain orientation of the galvanized coatings. But it enhances the appearance of coating surface [5].

2.4.3. Effect of Fluxes on Hot Dip Galvanizing

During galvanizing manyflux reactions occur which are as follow [11],

- Dissolution of metallic iron

$$Fe + 2NH_4Cl = FeCl_2 + H_2 + 2NH_3$$
$$FeCl_2 + 14Zn = ZnCl_2 + FeZn_{13} \text{ (zeta dross)}$$

Giving an overall reaction

$$Fe + 2NH_4Cl + 14Zn = ZnCl_2 + FeZn_{13} + H_2 + 2NH_3$$

- Dissolution of metallic zinc

$$NH_4Cl_{(solid)} + Zn_{(molten)} = H_2 + NH_3 + ZnCl_{2\,(molten)10}$$

- Dissolution of zinc oxide

$$NH_4Cl_{(solid)} + ZnO_{(molten)} = H_2O + NH_3 + ZnCl_{2\,(molten)}$$

- Oxidation of flux

$$2NH_3 + Zn + (O) = Zn(NH_2)_2 + H_2O$$
$$Zn(NH_2)_2 + 2HCl = ZnCl_2 + 2NH_3$$

2.5. Mechanism of Hot Dip Galvanizing

During hot dip galvanizing, depending upon temperature and immersion time, various phases can be form starting from the inner most gamma layer, delta layer, zeta layer and the outer most eta layer. This layer sequence and their thickness can be seen from figure 3.

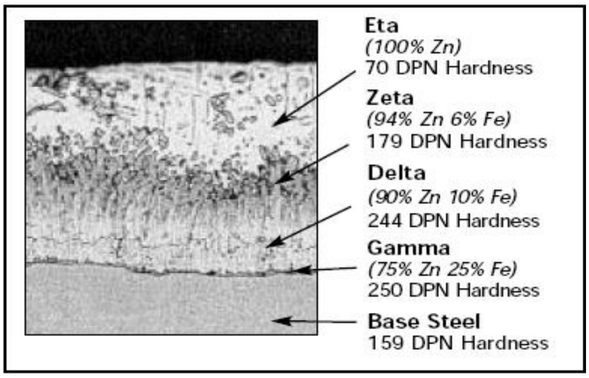

Figure 3: Microstructure of galvanized layer [12]

2.5.1. Fe-Zn Phase Formation

According from Fe-Zn phase diagram (as shown in figure 2), when the iron is immersed in molten zinc at the galvanizing temperatures range (450-490 ° C). Immersing the steel article in molten zinc the sequential nucleation of the Fe–Zn phases occurs at the interface beginning with ζ-phase layer, followed by δ-phase layer, then the Γ-phase layer after some incubation time [4].

2.5.2. Fe-Zn Phase Characteristics

The Fe-Zn characteristics can be understood by following table 1.

Table 1: Properties of alloy layers of hot dip galvanized steels[5]

Layer	Alloy	Iron, wt.%	Melting point (°C)	Crystal structure	Diamond pyramid micro hardness	Alloy Characteristics
Eta (η)	Zinc	0.03	419	Hexagonal	70-72	Soft, ductile
Zeta (ζ)	$FeZn_{13}$	5.7-6.3	530	Monoclinic	175-185	Hard, brittle
Delta (δ)	$FeZn_7$	7.0-11.0	530-670	Hexagonal	240-300	Ductile
Gamma (Γ)	Fe_3Zn_{10}	20.0-27.0	670-780	Cubic	-	Thin, hard brittle
Steel base metal	Iron	-	1510	Cubic	150-175	-

III. FLUXING PROCESS

After pickling and rinsing process the surface of steel article is extremely active and which is quicklyoxidizes to form thin layer of oxide. Oxide are hinders the coating formation but also increasing the costs galvanizersdearly by increasing the dross generation. To make the steel surface active andfree of oxides therefore using active chloride salts as a flux. This can he achieved in two ways:

Prefluxing, is used in dry galvanizing process in which process the article to be galvanized is treated in watersolution of zinc chloride-ammonium chloride mixture at about 70- 80°C for about a minute and then dried in drying oven at 100 – 120°C prior to dipping in galvanizing bath.
In-situ fluxing, is used in wet galvanizing process in which process a solid mixture of zinc chloride-ammonium chloride is added on the top of the molten zinc bath. The article to be galvanized directly passes to the galvanizing bath after pickling, rinsing and drying.
There are two broad categories of the fluxes used, such as conventional flux and non - conventional flux.

3.1 Conventional Fluxes

The mainly zinc chloride and ammonium chloride are used as a conventional fluxes in the hot dip galvanizing process to remove the impurities such as oxides, chlorides, sulphates and sulphides from the steel and molten zinc bath surface [8].
The fluxing operation includes production of hydrochloric acid and zinc hydroxy acid by extremely important reactions, of the decomposition of NH_4Cl and combination with $ZnCl_2$.

$$NH_4Cl \rightarrow NH_3 + HCl$$

$$ZnCl_2.2H_2O + HCl \rightarrow \underbrace{\{HCl(OH)_2\}H_2.ZnCl_2}_{\text{Zinc hydroxy acid}}$$

Zinc hydroxy acid being extremely acidic, quickly reacts with oxides present on the molten zinc layer and steel surface to form corresponding chlorides.
Only NH_4Cl as flux in galvanizing will not function properly as solid NH_4C1 sublimes below 100°C and does not decompose into hydrochloric acid and ammonia. To ensure that NH_4Cl decomposes into the two components, it should be dissolved in its solvent whose boiling temperature is above 100°C. Hydrated $ZnCl_2$ is the appropriate & most used solvent for decomposition of NH_4Cl and to form zinc hydroxy acids. The acids produced are stable at the top of the molten zinc (temperature 350°C) and act extremely well as flux.

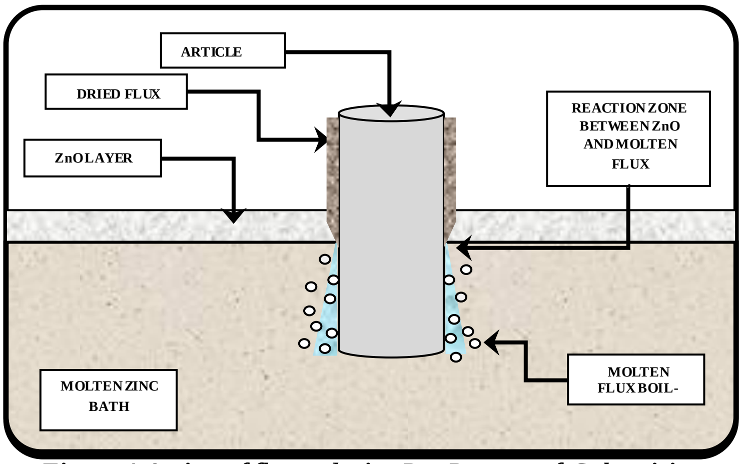

Figure 4:Action of fluxes during Dry Process of Galvanizing

As above show the figure 4, the article which is to be galvanized is first treated with an appropriate concentration of flux. The articles is then dried at about 110-120°C. During this process of dipping of the articles in molten zinc bath, the flux melts at the top of bath (temperature 350°C). The preflux starts boiling with rise in temperature (the articles going deeper into the bath) and hydroxy acids are formed. The acid will react withZnO on the molten zinc surface and iron on the steel surface to provide cleaner surface for galvanizing.

3.1.1. Drying of Prefluxed Articles

The drying of prefluxed articles should be done at 110 -120°C but below 150°C to trapped the moisture which may transfer in the galvanizing bath and will cause formation of steam in the process. This in turn will blow away the film of flux formed on the steel surface which may cause black spots.

3.1.2. Ratio of NH_4Cl-$ZnCl_2$ in Fluxes

The concept of ammonium chloride number (A.C.N.) for fluxes was introduced. A.C.N. is defined as:

$$A.C.N = \frac{\text{Weight \% of ammonium chloride}}{\text{Weight \% of zinc chloride}}$$

In early eighties, it was suggested that an A.C.N. value of 1.75 to 2.5 was the most appropriate for effective fluxing.

The boiling point of flux having ACN of 1.75 - 2.5 is to be maintained at about 350°C and sufficient hydroxy acids are formed which will resultin an efficient fluxing.The above flux composition provides excellent result as far as quality of galvanizing product was concerned. No black spot appeared during the galvanizing [8].

3.2. Non-Conventional Fluxes

Corrosive attackedis observed of NH_4CI on the steel and molten zinc. NH_4CI is extremely corrosive to steel, generating a high rate of dross and thicker coating during galvanizing. Evolution of white fumes of NH_4CI which is dangerous for human body and highly polluted to the environment.[8] So go for non-conventional fluxes which can give thin coating , enhance brightness and fewer fumes evolved during galvanizing. Some non conventional fluxes are $NiCl_2$, $CdCl_2$ and $SnCl_2$ [13].

3.2.1. $NiCl_2$

Use of $NiCl_2$ as flux will improve of the coating brightness, reduce of the coating thickness and inhibition of the Sandelin effect.

Due to Ni addition in the preflux bath, it will enhance the growth of small-sized crystallites of the ζ-phase instead of the columnar growth usually encountered whichresults in reduction of the coating thickness [13].

3.2.2. $CdCl_2$

The use of $CdCl_2$ as flux will generate fumes which is less volatile than fume generate in conventional flux and also produce similar morphology of coating which is form by conventional flux [13].

3.2.3. $SnCl_2$

Tin (Sn) is beneficial when it is dissolved in molten zinc up to 1.8%. Sn is similar to Ni,it also improves brightness and reduces the coating thickness. However its excessive addition, apart from its cost which is much higher than the zinc cost, leads to the formation of inclusions with the eutectic composition of the Zn/Sn alloy with reduced corrosion resistance.

Sn addition seems to be inert with regard to the coating structure [13].

IV. CONCLUDING REMARK

From the above discussion regarding the effect of conventional and non conventional fluxes on hot dip galvanizing, the following concluding remarks can be extracted out.

- Galvanizing is a process to reduce corrosion of low carbon-low alloy steel by providing thin, adherent, compact and uniform coating of Zn.
- The quality of Zn coating is greatly influence by temperature, bath composition, pre and post treatment process.
- Conventional fluxes with $ZnCl_2$& NH_4Cl produce good quality coating but also produce hazardous and toxic fumes during the process.
- Non - conventional fluxes can be used with less skill and good economy of the process can be maintained.

Looking from above concluding remark, one can easily make replacement of conventional fluxes with various non – conventional fluxes like $NiCl_2$, $CdCl_2$ or $SnCl_2$ as they are very essential for environment pollution and health related issues of person working in the industries due to which non – conventional fluxes are sometimes known as *"a eco – friendly fluxes"* also.

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