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Study of Zinc Electroplating on Steel

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Abstract— Electroplating or Electrodeposition is a process which uses electric current to deposite a more reactive material over a less reactive material. In Zinc Electroplating, Zinc is deposited over steel, where zinc acts as a sacrificial element which enhances Steel's life.Electroplating is an economical process, often used to protect steel with Ultimate Tensile Strength of 1500 MPa or less. The Zinc Process Plating is widely affected by process parameters such as temperature, current, voltage, etc. As the time in Zinc Plating Bath increases, the thickness of coating of Zinc over Steel increases. Also, increase in the distance of workpiece from the centre leads to decrease in plating thickness.

Index Terms— Electroplating, Zinc, Steel, Hydrogen Embrittlement, Salt Spray Tests, Alkaline Bath, Passivation, Top Coat, Hull Cell, Cathode.

1 INTRODUCTION

Electroplating or Electrodeposition is a process which utilises electric current to reduce cations of a suitable and desired material from a solution (called Electrolyte) and coat that material over some other material to enhance its life by protecting it from Corrosion. In this case, Zinc is coated over one of the most common Engineering material; Steel.
There are three type of Zinc Electroplating processes commonly used throughout the world;

i. Acid Chloride
ii. Alkaline Cyanide
iii. Alkaline Non-Cyanide

These process differs on the basis of there Throwing Power, Cathode Efficieny, Deposition Mechanism, SST Life, and affinity to Hydrogen Embrittlement. However, our major focus is on the Alkaline Non-Cyanide Process.

2 ELECTROPLATING BACKGROUND

Most of the Electroplating Processes exists to enhance the properties and life of Base Metals. Almost every of the metal can be plated, provided that the reactivity series is followed. As discussed earlier, three major electroplating processes exists predominantly, viz; Acid Chloride, Alkaline Cyanide and Alkaline Non-Cyanide. The key player in every of the Zinc Electroplating process is Zinc in the form of Zn2+ which gets reduced to Zn0 at the cathode end.
In general, Zinc Coatings are done on Carbon Steels. Moreover, adding to this, a successful zinc plating process requires proper pre-celaning of the material as well as post plating treatments.
Though, post plating treatments such at baking is required for steel having tensile strength of 1500 MPa or higher. This is done in order to ensure that the hydrogen embrittlement is perfectly cured.

2.1 FARADAY'S LAWS

Electroplating is a chemical deposition of a tacky coating upon another metal (acting as an electrode) to enhance its properties and safeguards its life. Electroplating Process follows Faraday's Laws.
Faraday's First Law states that, "The amount of chemical changed produced by an electric current is proportional to the amount of current that passes." So, by measuring the quantity of electricity passed, one can easily measure the amount of chemical change that will happen.
Faraday's Second Law states that the quantity of different substances liberated by a given quantity of electric current are proportional to their chemical equivalent weights.

2.2 ELECTROPLATING BACKGROUND

Electroplating is a simple process of deposition of one metal (or sacrificial metal) over another. In this process, the metal to be coated is made as an electrolyte (ZnSO4 in case of Zinc Plating). The cations associate with the anions in the electrolytic solution. Furthermore, these cations are reduced at the cathode to deposite on the Anode (i.e Base Metal).
For Example, in Zinc Plating over Steel, The Zinc is made anode, while Steel is made cathode. So, over passing of current, Zn2+ from ZnSO4 will be deposited on Steel, and the remaining SO42- will react with Zn2+ in the regeneration tank to form ZnSO4 again and the process continues.
However, pretreatment of the work piece in Degreasing tanks to remove the layers of oil, dirt or any other contaminants that could affect the plating process is an essential pre-requisite for achieving a bright, thicker and longer plating.

3 ALKALINE NON-CYANIDE PROCESS

The Alkaline Non Cyanide Zinc Electroplating Process is a reliable and cost efficient methodology that is widely used in Industries. Its process is similar to Acid Chloride Plating.
The Chemistry that is involved in this process is shown by below equations:

$$[Zn(OH)_4]^{2-} \longrightarrow [Zn(OH)_3]^- + OH^-$$

$$[Zn(OH)_3]^- + e^- \longrightarrow [Zn(OH)_2] + OH^-$$

$$[Zn(OH)_2]^- \longrightarrow Zn(OH) + OH^-$$

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$$Zn(OH) + e^{-} \longrightarrow Zn + OH^{-}$$

The major limitation to this process is the presence of high level of carbonate ions found in the solution after a use of one month. However, the carbonate ions can be eliminated by dropping the temperature of Zinc Bath to 2 to 5°C so that the carbonate ions will settle down and can be drained out easily.

The following table shows the requirements of Zinc, NaOH and other additives to improve the outcomes of Zinc Plating Process.

CHEMICAL	RANGE
Zinc Metal	8-15 g/L
NaOH	120-150 g/L
Other Additives	As recommended by Manu-facturer

4 Standards Available/Used in Industries

Following international standards are available and are widely referred and followed in Industries doing Zinc Electroplating:

i. ASTM B633-11
ii. IS 1573:1986
iii. ISO 4042
iv. BS EN ISO 14713:2009
v. DIN EN 12329
vi. ISO 2081:2015

5 Pre-plating Treatments

5.1 Degreasing

Degreasing refers to the process of removing the layers of oils, greases, dirt, and other contamination that would potentially affect the plating process. There are a multiple of sub processes involved in degreasing, namely, Pre-Degreasing, Hot Degreasing and Anodic Cleaning.

5.2 Acid Treatment

Post Degreasing, The workpiece is treated with Conc. Acid (40%-50% HCl) to further remove the contaminants from the surface to be plated. This would prepare the surface for better coating.
One of the biggest disadvantages of this process is the fumes of acid created during the treatment. These fumes are very toxic in nature and affects the life of persons engaged in the process. Hence, well equipped PPEs (Personal Protective Gears) such as Masks and Rubber Hand Gloves are essential while operating acid treatment plants.

5.3 Treating with Base

After treating the workpiece with concentrated acids, the job is treated with some basic mediums to nullify the effect of acid over the surface of the workpiece. This acid could lead to acidification of the Zinc bath, and also affect the life of the Zinc Plated Workpiece.
Generally, NaOH is used to treat material post acid treatments.

6 Post Plating Treatments

6.1 Hydrogen Embrittlement

Hydrogen Embrittlement, as the term says, is the brittlement of steel due to the addition of Hydrogen (H2) into its microstructure through an aqueous or gaseous medium.
Hydrogen Embrittlement is a phenomenon which causes loss of ductility and strength, and making it brittle. It is responsible for a surprising number of delayed failures and problems with parts made up from Drawing or Extrusion, especially if they undergoes secondary surface treatment operations such as Plating.
Hydrogen Embrittlement is also called Hydrogen induced cracking or Hydrogen attack. Materials which are more vulnerable, including high strength steels, Titanium based materials, and Aluminium alloys are more susceptible to this phenomenon.

6.2 How Hydrogen Gets Out?

Hydrogen absorption is not a permanent condition. If cracking or material failure does not occur and the environmental conditions are altered in a way that no Hydrogen is generated on the surface of the metal, the Hydrogen will evolve out of the metal naturally and the metal's ductility will be restored.
Performing a relief to curb embrittlement, or to bake the metal at certain elevated temperature is a powerful method in eliminating hydrogen before it could make some damage. For this, the key players are time and temperature, which, if are not maintained properly, could also lead to more damages. Another important variable is concentration gradient or the movement of the atoms.
Following table shows the Bake-Out requirements for high strength steel parts:

Tensile Strength (MPA)	Hardness (HRC)	Time (Hrs.)
1000-1200	31-36	10-12 Hours
1300-1500	36-47	12-18 Hours
1600-1700	47-49	20+ Hours
1700-1800	49-51	22+ Hours

For more information, readers are advised to refer ASTM B850-2009, Standard guide for Post-Coating Treatments of Steel for reducing the risk of Hydrogen Embrittlement.

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7 Factors Affecting the Process

Listed below are the factors which should be taken care of in order to achieve a good, thick and lustrous Zinc Plating:

- Operating requirements such as Bath Analysis, Hull Cell Testing and other Tests should be done frequently.
- Analyze, Maintain and Dump Acid and other cleaners on a regular basis.
- Preventive maintenance of Machinery should be done every quarter in order to reduce operational costs and reduce productivity loss.
- Manufacturer shall be consulted in order to determine the additives, degreasing cleaners, chemicals for post plating treatments (Such as Passivation and Top Coat).

8 Types of Chromate Coatings

- **Yellow Chromate**: Chromate film, intended for protection is yellow in colour. It is available in both; Hexavalent Chromium and Trivalent Chromium. However, the shade of Trivalent Chromium in iridescent.
- **Bright (Clear) Chromate**: Chromate processing creates a corrosion protective film on a zinc plating while also acting as a chemical polishing agent. This chemical polishing action is used to give gloss to plating. Methods of treatment are classified into chemical polishing and alkali liquid treatment. In the chemical polishing method, the creation of corrosion protective film is rather suppressed. In the alkali treating method a corrosion protective film is produced and then treated by the alkali solution to have a glossy surface. The corrosion protective performance of this bright chromate is Inferior to the yellow chromate.
- **Black Chromate**: After plating, the chromate film is formed with a processing solution containing chromic acid and an additive of black color treatment chemical (silver nitrate, etc.). Black chromate does not provide any significant abrasion resistance.
- **Olive (Green) Chromate**: After plating, a chromate processing solution containing special anions is used. A thick film-type coating can be obtained with good resistance to corrosion. The coating is also called green chromate.

9 Salts Spray Tests

The Salt Spray Test (SST), also known as Salt Fog Test or simply Fog Test is a standard and popularly known corrosion method, used to measure the corrosion resistance of a material or surface coatings/platings. Usually, the tested materials are metals, although stones, ceramics and polymers can also be tested using modern techniques. Salt spray tests are an accelerated corrosion tests that produces a corrosive attack on the surface on the metal (or coating) to check the corrosion limits. The appearance of corrosion products is generally evaluated after a period of time, in a regular interval. Common type of corrosion products are:

i. White Rust Corrosion Products
ii. Red Rust Corrosion Products
iii. Black Spots Corrosion Products
iv. Finger Print Corrosion Products
Etc.

ASTM B117 was the first standard was recognized internationally as a SST Standard, and was published in 1993.
Other International Standards that are used, are:

i. ISO 9227
ii. JIS Z 2371
iii. ASTM G 85
iv. IS 9844

9.1 Types of Salt Spray Tests

a. Neutral Salt Spray (NSS)
b. Acetic Acid Salt Spray (AESS)
c. Acidified Salt Fog Test – Non Cyclic
d. Acidified Salt Fog Test – Cyclic
e. Sea Water Acified Test
f. SO2 Salt Spray Tests
g. Dilute Electrolyte Salt Fog/Dry Test.

9.2 Salt Solution

The Salt Solution Shall be prepared by dissolving 5% of NaCl (Common Salt) in 95% of water (H2O). Careful attention should be given to the chemistry of the salt, which should not contain any impurity more than 0.3% by mass. Household Salt (which includes Iodine or other Halides) should not be used in preparing the brine solution.

Following Table shows the maximum allowable content for impurity level in NaCl (Sodium Chloride) used for SST Tests.

IMPURITY DESCRIPTION	ALLOWABLE AMOUNT
Total Impurities	≤ 0.3%
Halides (Excluding Chloride)	≤ 0.1%
Copper	< 0.3 PPM
Anti-Caking Agents	0.00%

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