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The Effect of Hydrogen on the Zinc Coating Quality Produced through the Hot-dip Galvanizing Process.

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Abstract- *Hot-dip galvanizing is a process of creating an alloy coating of zinc on steel parts by their immersion in a zinc melt. This operation involves a complex series of diffusion processes, elementary metallurgical reactions, and thermodynamic transformations. In terms of appearance, thickness, structure, and other characteristics the final coating is the result of the influence of several factors. A precondition for successful galvanizing is perfect wetting of the zinc-coated part by the zinc melt. Therefore, parts intended to be galvanized are subjected to chemical pre-treatment before galvanizing to achieve a pure metallic surface and, then, their activation. The parts are first degreased and then pickled. Pickling removes scale, oxides, and corrosion products, as well as other soluble impurities from the surface. A perfectly clean metallic surface of a degreased part is achieved by subsequent pickling in an inorganic acid. The most frequently used pickling agent in commercial galvanizing plants is hydrochloric acid, typically at a concentration of up to 14%. The hydrogen in hydrochloric acid gradually penetrates during the pickling process and forms an interstitial solution in it. A part of the hydrogen inside the steel remains in the atomic form, and after completion of the pickling, it escapes from the substrate again. However, some atoms combine to form molecules in places of lattice imperfections and vacancies, inclusions, etc., and significantly increase their volume.*

Keywords- *Pickling Process, Hydrochloric Acid, Hydrogen, Hot-dip galvanizing, Zinc Coating.*

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I. INTRODUCTION.

Hot dip galvanizing is a corrosion protection process where iron or steel is immersed in a bath of molten zinc at about 450°C, creating a durable, metallurgic ally bonded zinc coating. This coating provides lasting protection against corrosion and oxidation through a combination of barrier and cathodic protection. Some mass production items are suited to be galvanized in continuous systems Besides high productivity such lines offer the benefit of accurate setting of the process parameters. It allows you to efficiently check the basic parameters of the coating such as appearance, structure, and thickness [1]. Aluminum is generally added to the zinc bath in continuous galvanizing as it takes priority in reacting with the substrate to form a thin, consistent, iron- aluminum alloy layer. That layer prevents further iron diffusion and its reaction with zinc suppresses the formation of brittle iron-zinc alloy phases so that the coating generally consists of relatively malleable pure zinc. This produces favorable mechanical properties for further forming of galvanized metal sheets. The thickness of the zinc coating on the surface of a continuously galvanized strip is approximately 10 to 35 µm [2]. Integrated steel plants producing both hot and cold-rolled flat products, a significant proportion of cold-rolled sheet products are galvanized for use in construction and automotive sectors.

Continuous hot dip galvanizing operation entails joining, cleaning, annealing and cooling of cold-rolled steel strip before hot dipping in molten zinc bath at 455-460°C followed by post-treatment processes involving air wiping, chromate passivation, temper-rolling and, finally, coiling. The quality requirements of galvanized sheet products encompass a prescribed uniform coating weight/ thickness, “spangle” size, surface finish and formability along with adequate peel-off resistance and adherence of the coating with the steel substrate [3-6].

The purpose of pickling is to achieve a perfectly and chemically clean metallic surface of the steel is to facilitate the metallurgical reaction that produces the alloy coating. The surface of the steel part usually covered with scale and corrosion products Figure-1, which can be efficiently removed by pickling, usually in hydrochloric acid. During this process the iron oxides become gradually separated from the base material. The shares of individual iron oxides may be different in the scale layer. To efficiently remove w ü stite, which is always closest to the substrate, the pickling solution must get access to it. Scale predominantly consisting of magnetite Figure-2requires very long pickling times. Parts on the surface where w ü stite predominates, which dissolves readily in the pickling solution Figure-3, need relatively short pickling times to achieve a clean metallic surface. In modern metallurgical plants, scale is removed from the surface of rolled products with the use of efficient methods and the occurrence of strongly scaled metal sheets is relatively rare. The w ü stite layer of the scale dissolves first, as ferrous oxide is most readily soluble in the pickling solution.

During pickling, reaction of pure iron with the hydrochloric acid cannot be excluded, which produces hydrogen. This might produce harmful effects in the steel and any coating applied onto it. Therefore, inhibitors are often added to pickling baths to inhibit the reaction of iron with hydrogen chloride and so reduce the rate of saturation of the substrate with hydrogen. This study aims to indicate the harmful of hydrogen resulting from hydrochloric acid using in pickling to remove scales, oxides, and corrosion products on the Zinc coating quality.

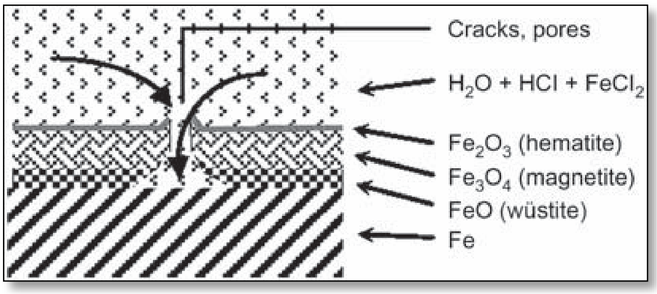
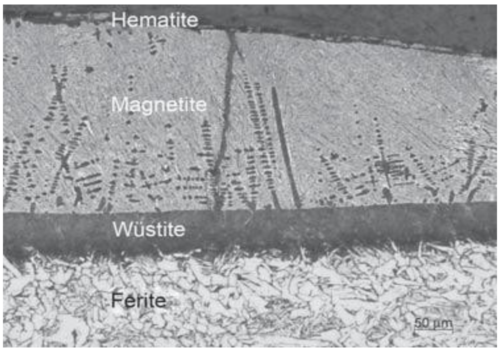


Figure 1: Principle of Scale Removal by a Pickling Solution.



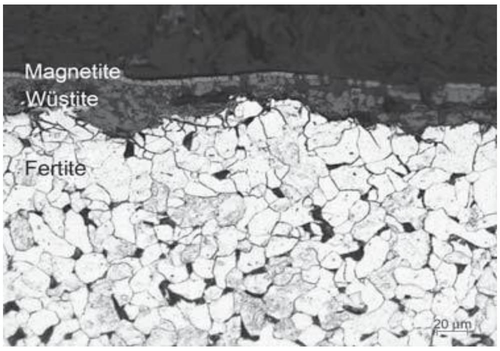


Figure 2: Scale with a high Proportion of Magnetite **Figure 3: Scale with a high Proportion of Wu¨stite.**

II. MATERIALS AND METHODS.

Cold rolled low carbon steel sheet with a relatively clean surface is welded to form an endless strip and it is continuously degreased .and pickled. Then it passes through a furnace where, in a reducing atmosphere, the material is subject to full annealing and oxides are removed from its surface. In a protective atmosphere, the clean metallic strip is then immersed in a galvanizing bath and exits in a vertical orientation through mechanical air knives that wipe the coating surface. After leveling, the strip is wound up into coils, Figure-4 diagram of a line for continuous sheet metal galvanizing.

The Chemical Composition of low carbon steel alloy as showed in Table -1.

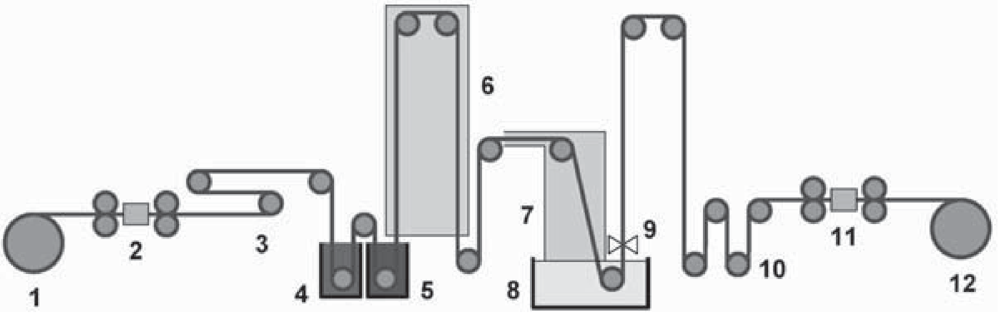


Figure 4: Diagram of a line for Continuous Sheet Metal Galvanizing.

1.Strip unwinding, 2. Welding, 3. Levelling loop, 4. degreasing, 5. Pickling, 6. Full Annealing, 7. surface activation in a reduction atmosphere, 8. Zinc bath, 9. air wiping knives, 10. levelling, 11. Shearing,12. Winding the galvanized strip into a coil.

Table 1: Chemical Composition of Low Carbon Steel Alloy used.

Element	C	Si	Mn	S	P
Chemical Composition %	**0. 17**	**0.03**	**0.35**	**0.018**	**0.019**

III. RESULTS AND DISCUSSIONS

In this part of the study, the researcher will focus on the influence of hydrogen generated from hydrochloric acid used in the pickling to clean the surface of steel sheet from scales, oxides and corrosion products on the Zinc Coating, the influences of hydrogen as the following:

1. Blisters and Foam

Blistering of the zinc coating is caused by hydrogen escaping from steel during the galvanizing process. Given its very small dimensions, atomic hydrogen penetrates into various materials very easily Figure - 5 Cross-section of a blister. From places with a higher hydrogen partial pressure it passes to places where its partial pressure is lower. Therefore, during pickling hydrogen penetrates into steel where its quantity is relatively lower than in the pickling solution and later, especially when the steel is heated in the zinc melt, escapes from the steel again. At the same time, the layer of the originating alloy phase ζ in the coating represents an area of frequent imperfections in the crystalline structure. In such places atomic hydrogen quickly recombines. As the hydrogen emerges, when the layer of zinc adhering to the surface of the part solidifies, a barrier is formed against escaping of recombined hydrogen and blisters can appear in the coating. The cause of foam formation is also hydrogen escaping from the substrate, which is in this case blocked by a mushy substance formed on steel containing silicon in the Sandelin area Figure -6 Foam in the Galvanized Coating formed on Steel.

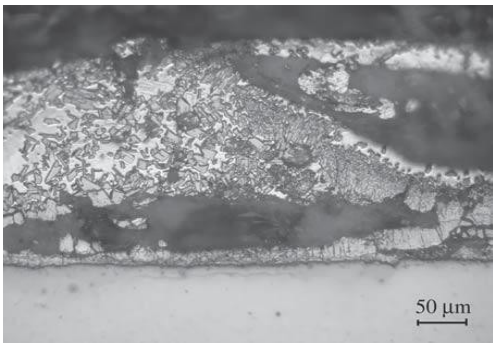


Figure 5: Cross-Section of a Blister.

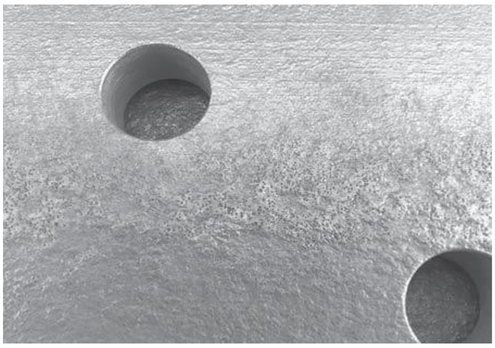


Figure 6: Foam in the Galvanized Coating formed on Steel.

2. Defects of Organic Coatings

Atomic hydrogen, which penetrated into steel during pickling, only escapes from it partly during the immersion in the zinc bath. A considerable amount is released from steel later a few days after the galvanizing. Every next heating of the substrate accelerates this process. This may cause problems, e.g., during baking of powder coatings applied on the galvanized coating. Baking of an organic material causes its sintering and this barrier blocks free escape of hydrogen, which recom- bines in the porous zinc coating and due to increasing of its volume causes formation of bubbles and craters in the organic material layer.

3. Hydrogen Embrittlement and Hydrogen Corrosion.

Hydrogen that recombined in substrate defects achieves a pressure of up to several hundreds of megapascals. During the hot-dip galvanizing process this pressure rises even further and the yield point of the material is locally exceeded. A higher risk of hydrogen embrittlement is present in steels with a higher yield point, which put up increased resistance to possible plastic deformations, show a difficult relaxation capability, and, in extreme cases, a brittle fracture may occur.

Hydrogen that combines with free carbon precipitated at grain boundaries, producing methane, causes “hydrogen corrosion.” Methane is not capable of further diffusion and accumulates in the place of its generation where it causes strong stress. Welds and heat-affected weld areas exhibit an increased risk of hydrogen corrosion. Figure -7 Principle of steel hydrogenation during pickling.

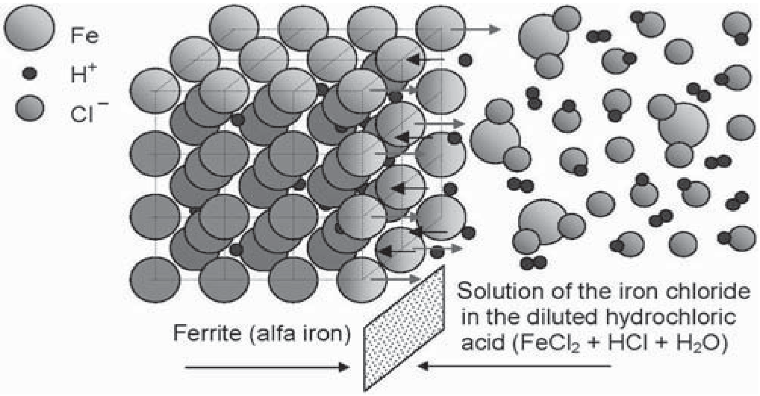


Figure7: Principle of Steel hydrogenation during Pickling.

IV. CONCLUSIONS.

The following conclusions have been drawn from this study:

1. The formation of a blister is caused by hydrogen escaping from the substrate and recombining in numerous discontinuities of the growing coating, where it increases its volume.
2. The cause of foam formation is also hydrogen escaping from the substrate, which is in this case blocked by a mushy substance formed on steel containing silicon.
3. Baking of an organic material causes its sintering and this barrier blocks free escape of hydrogen, which recombines in the porous zinc coating and due to increasing of its volume causes formation of bubbles and craters in the organic material layer.
4. Hydrogen that combines with free carbon precipitated at grain boundaries, producing methane, causes "hydrogen corrosion.".

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