Some Aspects of Modern Zinc Plating (Process & Equipment)

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A presentation of a new multiflexible electroplating equipment for plating zinc and zinc/iron combined with 4 different conversion coatings, 3 different sealer systems and heat treatment to eliminate hydrogen embrittlement. The new equipment, with a capacity of 4000 metric ton/y is able to produce more than twenty useable combinations of zinc coating, conversion-coating and sealer. Furthermore the equipment is designed for waste minimization.

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Introduction:

Zinc and zinc alloy coating of steel is one of the most common ways to prevent steel from corroding in natural environments. At the same time it represents the most effective and economic way to protect steel against corrosion.
In practice the steel is protected by the zinc coating through a barrier effect and a galvanic effect, in which zinc acts as the sacrificial anode whilst the steel acts as the cathode.
In most natural environments zinc corrodes much less than steel. In the literature a factor 10-100 times is reported. The reasons for this phenomenon are that the zinc layer builds up "a natural conversion coating" consisting of alkaline corrosion products of the type $ZnCO_3$ $*3Zn(OH)_3*H_2O$, and furthermore that the overvoltage for hydrogen is higher for a zinc surface**.**

In cases where the zinc coating has been removed or is defective leaving the steel exposed to the galvanic action between steel and zinc, zinc can protect the exposed steel from corrosion. This type of protection depends on factors such as the compositions of the electrolyte, the thickness of the electrolyte and the distance between zinc and steel. In practice a very thin layer of electrolytes ($\leq$ 500 µm) on top of a zinc coating is able to protect a defect in the zinc layer (several mm. in width).

Improved corrosion resistance of a zinc coating it self can be achieved in different ways:

- Alloying the zinc with transition metal elements like cobalt, nickel, iron and manganese.

- Improvement of the passivation of the zinc layer by applying a conversion coating.

- Protecting the zinc and the passivation layer by application a sealing system.

The effect of the corrosion protection for the zinc alloy coating depends on the transition element selected for the alloy, the conversion layer on the top and the corrosion environment.
In the case of a zinc/nickel alloy (8-12% Ni) the corrosion protection evaluated in a neutral salt spray is about 600% better compared with the pure zinc coating. One of the reasons, for the improved corrosion resistance in this case is a change in the potential for the Zn/Ni alloy to a more noble value than the corrosion potential of pure zinc and at the same time a higher hydrogen reduction overpotential. The corrosion protection for a zinc/cobalt alloy (0.8% Co) is about 300% better compared with the pure zinc coatings. When evaluating the coatings in an acid salt spray, the zinc/cobalt alloy will be the best and the zinc/nickel alloy will show very bad results. The reason for the bad results for zinc/nickel is explained by a dezincification of the coating and the formation of a more noble nickel alloy phase.

During the last 10 years zinc/iron alloys especially with a very low content of iron (less than 1%) have become very popular. The corrosion protection mechanism behind these types of coatings is explained by a change of properties in the chromate conversion coating and not from the properties obtained by changing the alloy composition of the zinc layer.
In neutral salt spray the evaluation result of a zinc/iron coating with a chromate conversion coating is several times better than a conventional zinc coating. Only few evaluations of corrosion protection properties have been carried out for different zinc coatings "in situ" and this gives different results compared with accelerated testing (1).

Passivation of zinc and zinc layers has been in use since the forties and has been based upon chromate conversion coatings of different types. During the nineties, a lot of effort has been given to reduce or eliminate the use of chromate conversion coatings because of the risk for chromate allergy and cancer. At the moment only few alternatives have been introduced, but they do not have the same properties with respect to the self repair effect as known from chromate conversion coatings. However some of the new alternatives have shown quite good results especially in acid environments compared to the chromate conversion coatings (2).

Since the eighties a large selection of sealer systems has been introduced commercially as topcoat for the chromate conversion coatings. Different types of sealers have been used to either reduce corrosion, or to reduce friction, or to cope with both the aforementioned factors. The sealers are normally based on an organic resin in an aqueous dispersion and from time to time corrosion inhibitors (such as chromate) or friction reducing agents such as PTFE are added.

The philosophy behind the design of the plating line:

From a practical point of view it is becoming more and more complicated to supply the market with zinc coatings because of all the new coating systems and different specifications from customers based upon the new possibilities.

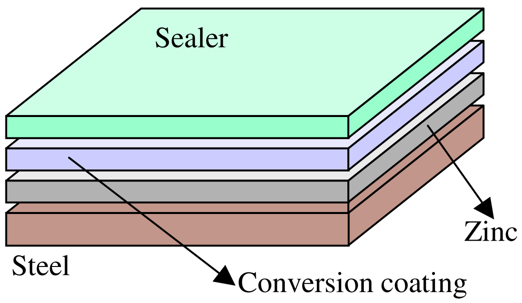

Figure 1. A combination of two types of zinc, four types of conversion coatings and three types of sealers give 24 combination of the zinc coating system.

To overcome this problem the Arvid Nilsson Group Inc. in Denmark decided in 1996 to develop a new concept for electroplating of zinc.
The development of the concept was carried out as a collaboration project between the Department of Manufacturing Engineering at the Technical University of Denmark and the Arvid Nilsson Group Inc.

Before development of the new plating line was undertaken, a list of demands to the new equipment was made.

- Environment (internal/external)
- Low production of waste for disposal connected to the production.
- Reduced water consumption.
- Lifecycle considerations (low zinc consumption and longer life span for the zinc coatings)
- Application of the best chemical process technology for improvement of the coating quality and reduction of the environmental problems.
- Flexibility and a high degree of automation
- The plating line should be certified to quality system according to ISO 9002 and an environmental management system according to ISO 14001.

A consequence of the list above was that cyanide-containing processes had to be completely eliminated. At the same time it was “a must” to select coating systems (zinc, conversion coating and sealer) in a way, that they could improve the properties for fasteners in advanced application such as the automotive industry. Furthermore it should be easy to change process chemistry quickly if there was a demand for a new coating. Great attention was given to the possible replacement of chromate conversion coatings. It was important, that one would be able to produce and supply customers with different types of chromate conversion coatings and non-chromate conversion coatings combined with different sealers at the same time.

Lifecycle considerations with reference to low zinc consumption and improved corrosion protection without use of chemicals, which could cause both external and internal environmental problems was also decided to be a part of the project, and this should continually be evaluated.

Finally a low formation of waste and a future possibility for separating the waste in different types was decided (zinc containing, chromium containing etc.). That would make a future recycling of waste (sludge) possible and reduce the demand for disposal. A strategy to strip zinc coatings from rejected fasteners without making waste was also decided to be incorporated in the new plating line. Normally zinc coatings are stripped in the pickling bath, but in this case it was decided to strip the rejected parts anodically by electrolytic treatment in a zincate electrolyte.

Description of the plating line:

The result of the project became a multiflexible computer controlled electroplating line for plating zinc and zinc-iron combined with four different conversion coatings and three different sealer systems.

Furthermore a “in line” heat treatment prior to chromating was incorporated to eliminate the risk of hydrogen embrittlement for high strength steel. The plating line was designed for 4000 ton steel/year.

The pre-treatment part of the plating line was designed in a conventional way and carried out in double drums. The different process steps were followed by a sequence of multiple rinse steps:

- soak cleaner
- pickling
- anodic cleaner

The zinc plating parts of the plating line were designed conventionally with both an acid zinc process (6 steps) and a zinc/iron process (3 steps) with different activation processes to match. A combination of pure zinc and zinc/iron (on top) resulting in a duplex zinc coating can also be produced. The plating drums were provided with a feature for variable rotation speed to make it possible to control the coating distribution on the fasteners.

Figure 2. A view over the zinc plating line with integrated centrifuges in the post-treatment processes. The centrifuges can be seen in the front of the picture.

Figure 3. A centrifuge basket under automatic transportation with fasteners before the chromating process step.

Because of the type of production (mass finishing of fasteners) it was decided to carry out the post-treatment (conversion coating and sealer) in an integrated centrifuge line separated in one part for conversion coating and a second part for sealer coatings.

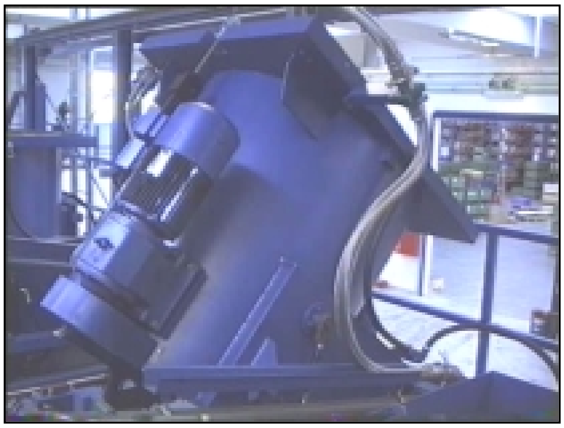

Figure 4. The centrifuges are tilted under the chromating process, and the centrifuge basket with the components are turned slowly around to secure good distribution of chemical conversion solution.

Automatic transporting of the fasteners from the drums to the centrifuge baskets was a critical point because of the risk of thread damages. Much attention was paid to this problem, and it was solved by transferring the fasteners to a water filled centrifuge basket.

The conversion coating part consists of four different process selections, which can be operated at one time and easily be replaced by one or more new processes. The small amount of process solution about 350 liters can be pumped from a closed storage tank to the centrifuge basket where the chemical conversion process takes place. After the process has finished the solution is drained back from the basket in the storage tanks and the surplus chemicals are centrifuged from the components followed by a counter flow rinse and several centrifuge operations. This feature saves a large amount of rinse water compared with traditional plating lines with drums.

The second part of the post-treatment (sealing) consists of three different sealers that can be applied separately to any of the different zinc and conversion coatings. The plated parts had to change centrifuge basket, to eliminate contamination with resin in the conversion coating process in the first part of the post-treatment line.

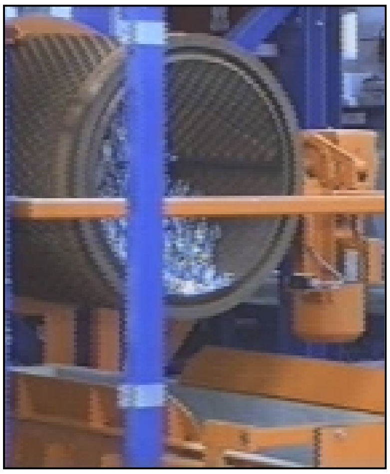

Figure 4. Emptying of a centrifuge basket after post-treatment.

Controlling of the plating line:

All articles are registered in a database with information about the product. Based on knowledge of the specifications, the surface area in dm^2/kg and the geometry of the product, a specific program is formulated and the following parameters are used:

1. Pre-treatment in the barrel line
   - Soak cleaner
   - Current density in anodic cleaner
   - Pickling

2. Zinc treatment in the barrel line
   - Zinc process
   - Current density
   - Treatment time

3. Minimum and maximum barrel weight

4. Rotation speed of the barrel.

5. Treatment in the centrifuge line
   - Heat treatment
   - Type of chromate
   - Sealing

All the procedures in the process flow can be combined with each other.

Energy consumption and environment experience from the plating line.

In the design phase, there was focus on the consumption of water and energy in the plating line. To reduce the water consumption optimized counter flow rinses were used after all the processes. Furthermore two ion-exchanger systems were incorporated in the line to secure the quality of the final rinse water after the plating and the chromating processes and to reduce the amount of rinse water from the tap. Finally a selective ion-exchanger was incorporated after the filter presses to remove the last traces of metals in the wastewater.

The wastewater from the line is separated in the following fractions:

- Chromium containing water
- Alkaline concentrate
- Acid concentrate
- Alkaline and acid rinse

This gives several advantages. Chromium containing wastewater can be separated from the rest, which gives a reduced chemical consumption, by the wastewater treatment. Usually the pH-value in this fraction is around 2.5, meaning that reduction of hexavalent chromium can take place immediately without any pH-adjustment.

Figure 5. The wastewater treatment is carried out in batches and ion exchange of the rinse water is used to secure the quality of the final rinse water.

The acid and the alkaline concentrates are used to neutralize each other and for adjusting the pH-value to 9, where the precipitation of metal hydroxides occurs. Since the solution is chromium free, a reduction of hexavalent chromium is not required. Once again chemicals are saved for pH adjustment.

After separation of metal hydroxides in the filter presses a selective ion-exchanger is used to remove the rest of the heavy metals in the wastewater. The pH-value is adjusted to 6 to optimize the efficiency of the ion-exchanger. Finally the pH value in the water is adjusted to 7. Before it is discharged, it goes through a 7 m^3 tank from where it is reused for rinses in the pre-treatment.

The concentration of metals in the wastewater is continuously measured by atomic absorption. The concentration of zinc and chromium is usually between 0.00 ppm. to 0.25 ppm. The total water consumption is approx. 0.10 litre/dm^2 plated surface, corresponding to 13 m^3/day.

Figure 6. Two filter presses are used to make it possible to separate chromium and non chromium containing sludge. All the wastewater is filtrated and finally treated by an selective ion exchange to eliminate zinc and chromium. Typical values of Zn and Cr is usually between 0.00 and 0.25 ppm.

The metal hydroxides are separated in two fractions as well, a fraction without chromium and a fraction containing chromium. Unfortunately, there are no possibilities for reuse of the metal hydroxides today, but in the future a consistent separation of the waste in different types (chromium, zinc and iron) will make it attractive to recycle heavy metals and avoid disposal. The iron from pickling is neutralized in the same system, but used pickling solution could be reused in the production of iron chlorides, which is used for elimination of phosphates in sewage to avoid eutrophication in seas and rivers.

The total amount of hydroxides generated by the plating process is approx. 2.5 kg/ton with a dry matter of approx. 40 %.

The electrical energy used for rectifiers, heating, cooling, ventilation, pumping etc. is approx. 280 kWh/ton.

Conclusion:

From a practical point of view it is becoming more and more complicated to supply the market with zinc coatings because of all the new coating systems and different specification from customers based upon the new possibilities.

A new multiflexible concept has now been introduces in a large scale and has shown that a high flexibility does not need to make the process expensive and reduce productivity. The new concept has been tested in practice and has shown that it has been possible to produce over 20 different coating combinations on the plating line at one time. The plating line is controlled by an effective computer system.

The application of centrifuges in the post-treatment processes has reduced the consumption of rinse water in the chromating process, because it has been possible to remove the process chemistry effectively from the fasteners by using the centrifuge technique. The application of a combination of traditional plating with centrifuges has expanded the flexibility of the plating line without reduction in quality or productivity.

References:

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