

# Replacement of Hexavalent Chrome Passivations on Galvanized Steel

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## Abstract

Most automotive producers will ban the use of hexavalent chrome passivations for all parts beginning in the year 2003 and other industries will follow soon this ban. Therefore, the hexavalent chrome passivations now used on galvanized steel for construction, furniture and other applications is expected be banned in the near future. New passivation systems based on trivalent chrome can replace the current hexavalent processes with the same or, if needed, a much higher coating weight. Depending on the coating weight, the corrosion protection can be similar or even higher.

The new passivation coatings are harder, more scratch resistance and are contain less water compared to the old hexavalent chrome passivation coatings. Because of the lower water content, these new coatings are more heat resistant.

Unlike the hexavalent chromate coatings which are colored, the trivalent passivation coatings are colorless but have an iridescent appearance changing from colorless to green depending on the thickness. The application of a colorless topcoat to these trivalent coatings gives back the original appearance of the zinc coating.

These trivalent chrome passivation systems are well established in conventional barrel, rack and continuous tube plating operations for the replacement of hexavalent chromates. These new systems are tested for both hot dip and electrogalvanized steel in many instances.

## 1. Introduction

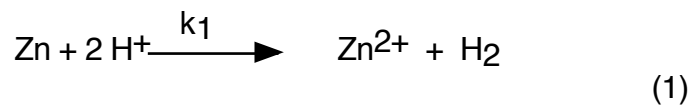
In the year 2000, the EU community released the "End of Life Vehicles Directive" which allows only 2 g hexavalent chrome per vehicle from July, 2003 onwards. Every two years this amount will be compared with the latest technology and possibly adapted. Due to this regulation, car manufacturers in Europe, US and Japan will stop using hexavalent chromates in the year 2002. The electronic industry is planning the same for the year 2006. Hexavalent chrome is known to be carcinogenic, while trivalent chrome and metallic chrome not. The EU-Directive bans the hexavalent chrome but not the trivalent or metallic chrome. The passivation of galvanized steel with hexavalent chrome is used for two reasons; first to achieve a significant increase in corrosion protection, especially for construction and furniture (>72 h salt spray for the beginning of white rust) or second as a temporary protection during shipment if the usage of a corrosion protecting oil is not possible. The coating weight of the passivation depends strongly on the application parameter, the thicker, the higher the corrosion protection. In continuous strip plating, the yellow passivations (based on chromic acid) are applied by dip, spray or roll coating (no-rinse coating) with and without further organic topcoats.

Alternative systems for replacement must be free of hexavalent chrome or other toxic compounds. The corrosion behavior and the properties as an adhesive layer must be similar or better, but the appearance can be different. Trivalent chrome passivations are known as a non toxic system for many years, however in the past, they could not fulfill the corrosion requirements.

Recently developed so called “thick layer passivations” based on trivalent chrome can produce passivation layers with the same or an even better corrosion protection.

## 2. New “Thick Layer Passivations” based on trivalent chrome; theoretical aspects

Independently whether a hexavalent or trivalent chrome passivation is used, the first reaction is the same:



The acidic passivation solution dissolves the zinc. Due to the consumption of acid in front of the zinc layer, the pH-value increase, see fig. 1:

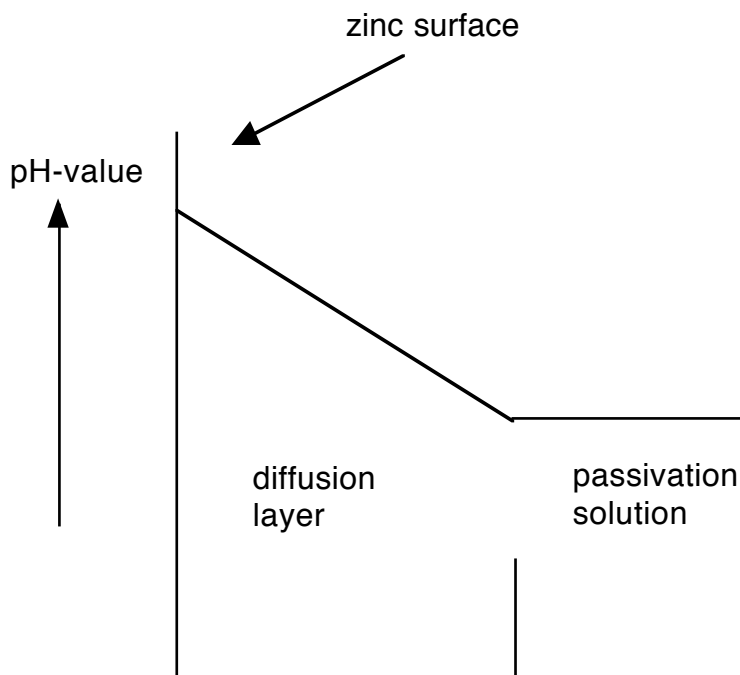
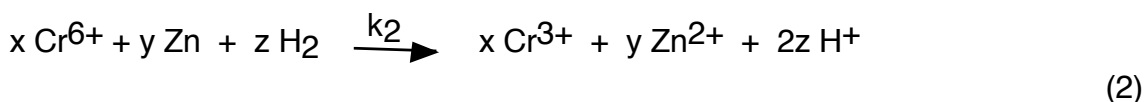


Fig. 1.: pH-value increase in front of a zinc layer in a passivation solution

In case of a hexavalent chrome passivation, the  $\text{Cr}^{6+}$  is reduced to  $\text{Cr}^{3+}$  by zinc and hydrogen (produced in reaction eq. 1), see eq. 2:

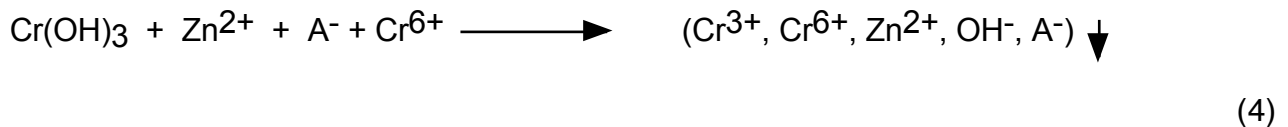


The Cr<sup>3+</sup> intermediate has two reaction paths:

1. Complexing (hex aqua etc.) the trivalent chrome and moving into the electrolyte or,
2. precipitates as chrome hydroxide due to the pH-shift on top of the zinc surface as seen in fig. 1, see eq. 3:



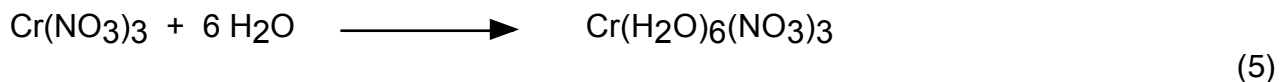
During precipitation of the chrome hydroxide zinc cations and anions as well as hexavalent chrome are incorporated in the layer, see eq. 4:



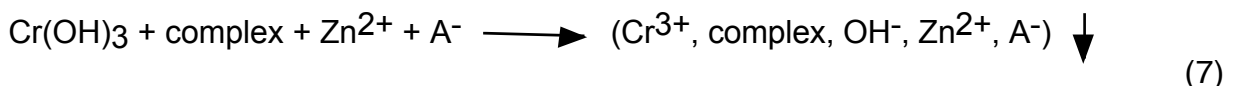
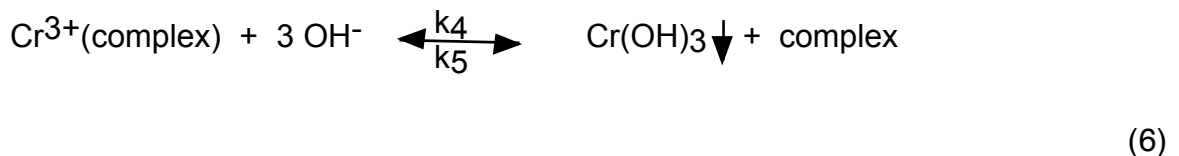
$k_1, k_3 > k_2 = \text{Cr(III)-intermediate}$  is only in a low concentration.

It is interesting to realize that even in a hexavalent chromate the reaction takes place via trivalent chrome and the Cr(VI) is only incorporated during precipitation. The Cr(VI)/Cr(III) ratio in the solution is very important, if the Cr(III) concentration gets too high a new make up of the passivation is necessary.

In opposite to the hexavalent chrome passivation where an non complexed trivalent intermediate is created the Cr(III) in a hexavalent free passivation is almost complexed, at least as a hex aqua complex as shown in eq. 5:



The Cr(III)-complex precipitates on the zinc surface because of the pH-shift (eq. 1, fig. 1) to build a passivation layer as described in eq. 6,7:



For a hexavalent passivation the reaction speed limiting step is the creation of the Cr(III)-intermediate (eq. 2). For the trivalent chrome passivation it is the reaction of the complex (eq. 6). Therefore the complex is most important example:

Complex = water: Very weak complex; the reaction speed ( $k_4$ , eq. 6) is high and the passivation layer becomes powdery with a bad adhesion.

Complex = fluoride (as usual for thin layer blue passivations): Very strong complex; the

reaction speed ( $k_4$ , eq. 6) is low, and the layer is thin.

In case of a thick layer trivalent chrome passivation the complex is stronger than water but weaker than fluoride:

$$k_4, \text{ water} > k_4, \text{ thick layer passivation} > k_4, \text{ fluoride}$$

An increase of the passivation solution temperature increases the reaction speed  $k_4$ .

In contrary to the hexavalent chromating process, the service life of a trivalent chromiting process is only limited by impurities like iron, copper etc.

### 3. Experimental

To test the properties of a thick layer trivalent chrome passivation zinc plated steel samples (10  $\mu\text{m}$  acid sulfate zinc) with a dimension of 21 cm x 15 cm were passivated in spray and dip applications.

#### Passivation Parameters

|                       |  |
|-----------------------|--|
| Passivation solution: | 12.5 Vol% SurTec 680 Chromiting <sup>®</sup> |
| Temperature:          | 40, 55 and 70 °C                             |
| contact time:         | 2, 4, 6, 8 and 10 s                          |
| pH-value:             | 1.6-1.9                                      |

#### Process

- degreasing of the zinc plated steel samples
- rinsing with DI-water
- spray (0.5 bar) or dip (stirring) application
- rinsing with DI-water (optional)
- organic top coat (optional)
- squeeze
- drying

A salt spray test is used (DIN 50021) to determine the corrosion behaviors.

### 4. Results

A longer contact time and a higher temperature of the passivation solution leads to a thicker passivation layer during spray application as shown in fig. 2.

The corrosion protection increases with the temperature as shown in fig. 3. At 70 °C a rather high corrosion protection is achieved (120-140 h to 3 % white rust) by only 2-6 s contact time. Also at 55 °C salt spray results > 72 h to 3 % white rust can be reached at a contact time of 4-6 s. At low temperature (40 °C) only a temporary corrosion protection (24 h to 3 % white rust) is achieved. The coating weight at 55-70 °C is comparable to a yellow passivation with a corrosion protection >48 h. For a temporary corrosion protection (having white rust 24 h) the coating weight of a hexavalent chromate is lower (5-10 mg/m<sup>2</sup>) and comparable with the trivalent passivation at 40 °C.

As the layer thickness increases with a higher contact time as shown in fig. 2 the corrosion protection reaches a maximum. This is due to an increase of cracks in the layer with an increasing thickness.

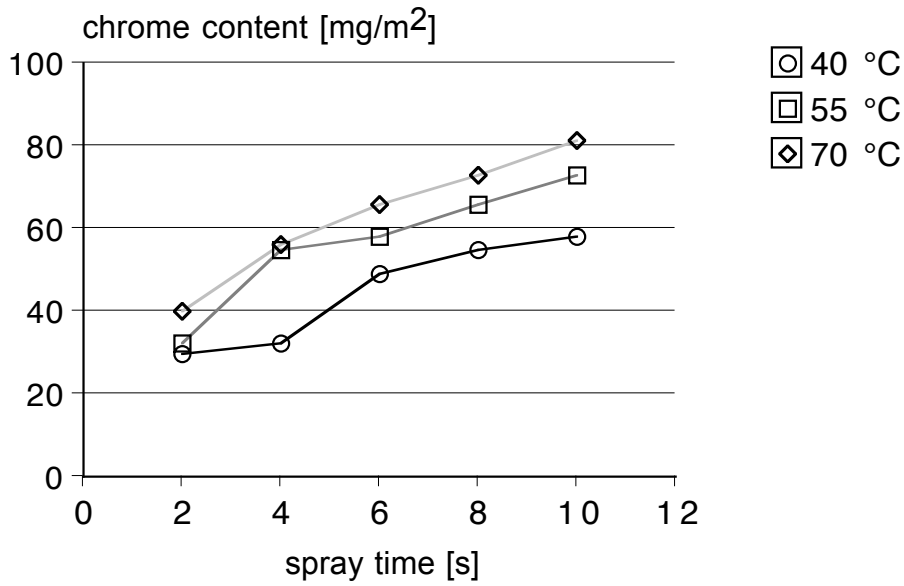


Fig. 2.: Coating weight vs. contact time and temperature for spray application. No activation before passivation, rinsing after passivation

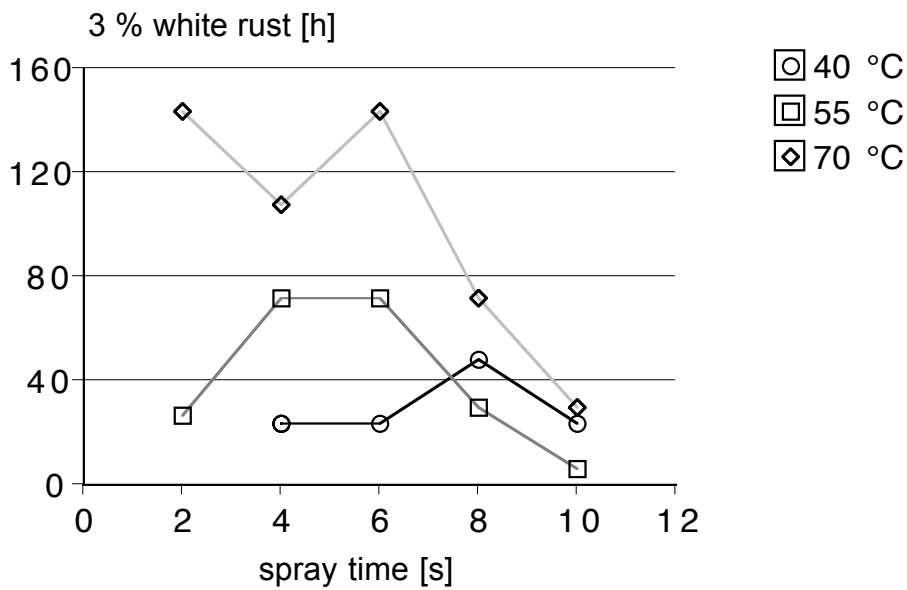


Fig. 3.: Corrosion protection (salt spray hours to 3 % white rust) vs. contact time and temperature for spray application. No activation before passivation, rinsing after passivation

Due to a longer reaction time if no rinse is used (only squeeze rolls) the coating weight is higher for the same application time as shown in fig. 4. (compared to fig. 2).

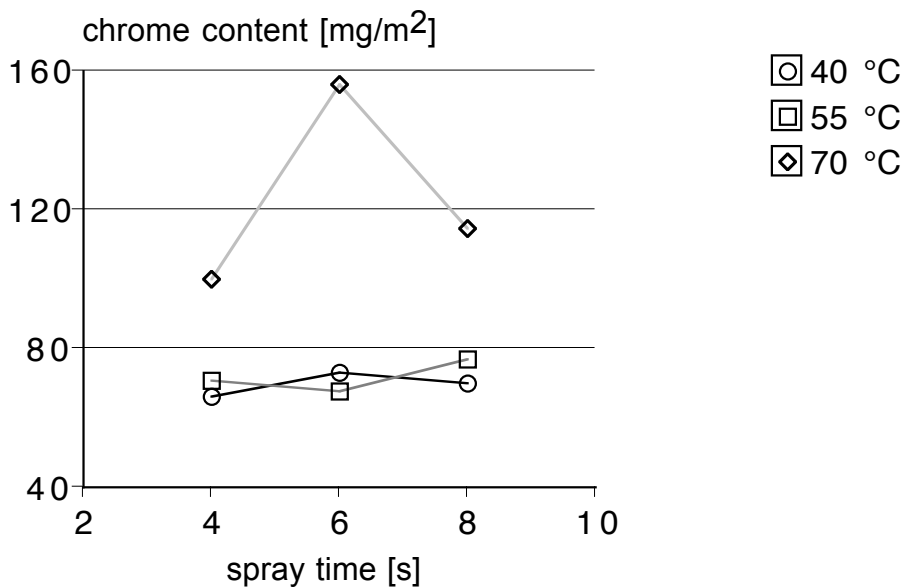


Fig. 4.: Coating weight vs. contact time and temperature for spray application.  
No activation before passivation, **no rinsing after passivation**

This higher coating weight leads to a slightly higher corrosion protection except at 40 °C as shown in fig. 5 (compared with fig. 3).

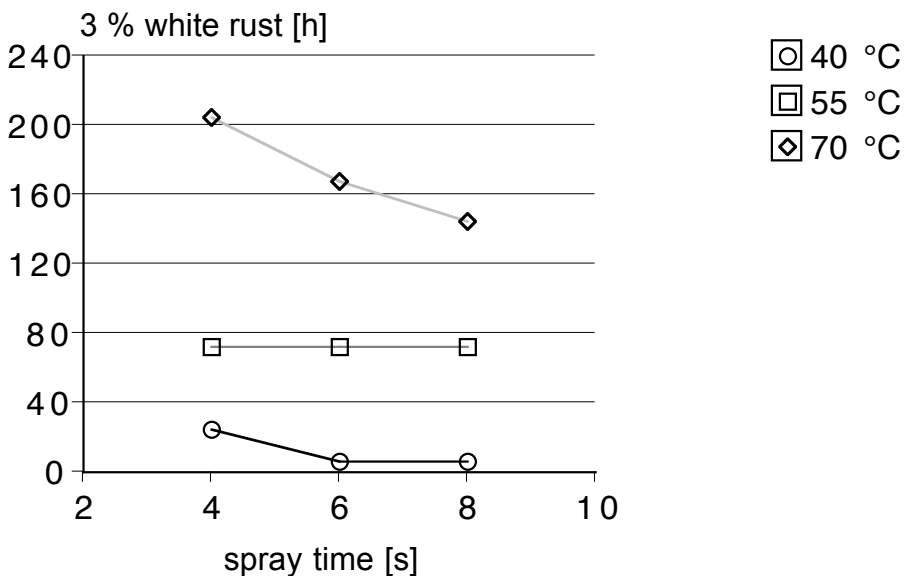


Fig. 5.: Corrosion protection (salt spray hours to 3 % white rust) vs. contact time and temperature for spray application.

No activation before passivation, **no rinsing after passivation**

Due to a lower diffusion layer caused by stronger turbulences a spray application leads to a higher reaction speed compared to a dip application. This leads to a higher coating weight and corrosion protection as shown in fig. 6 and 7.

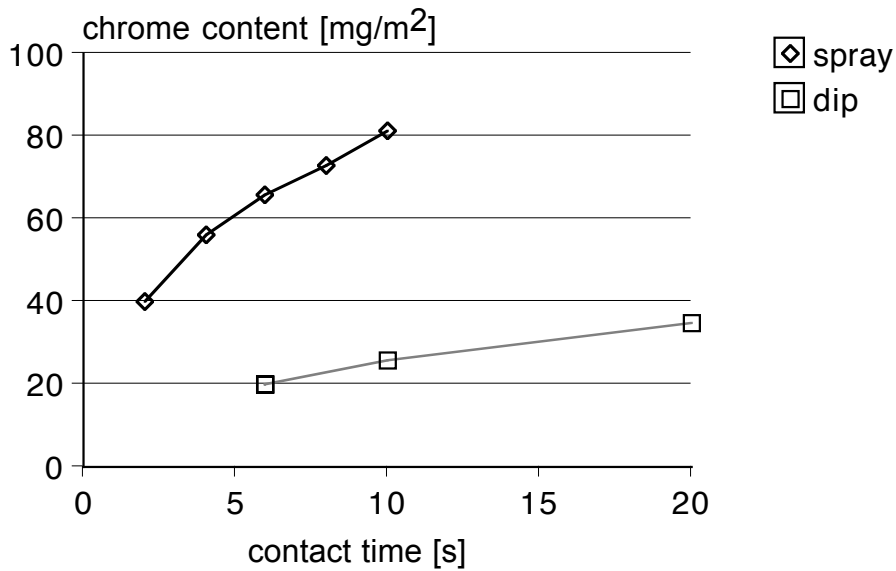


Fig. 6.: Coating weight of spray and dip application vs. contact time. Temperature 70 °C, no activation, rinse after passivation

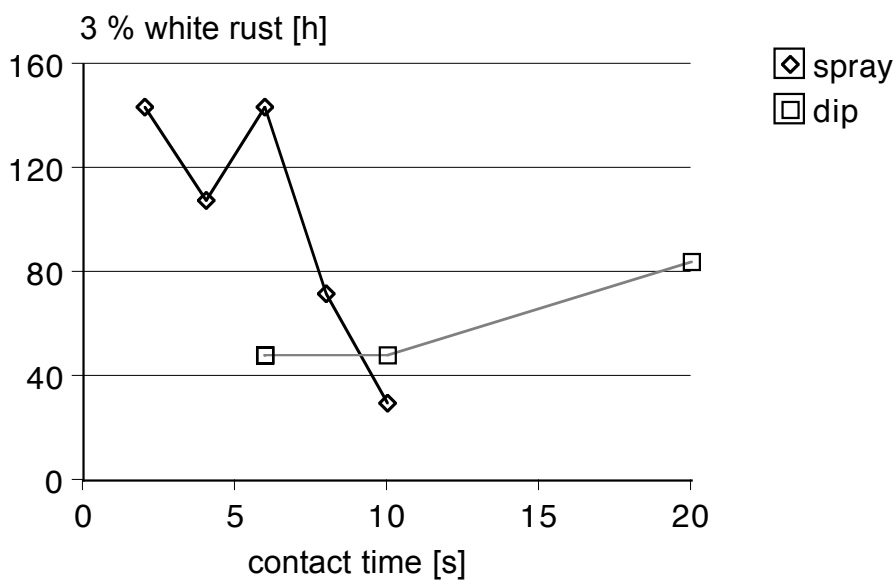


Fig. 7.: Begin of white rust for spray and dip application vs. contact time. Temperature 70 °C, no activation, rinse after passivation

An organic top coat like for example an anti finger print can increase the corrosion protection strongly for spray and dip application (see table 1).

| Process | Temp. / °C | Time/s | post treatment | WC 3% /h |
|---------|------------|--------|----------------|----------|
| Dip     | 70         | 6      | -              | 48       |
| "       | 70         | 6      | X              | 144      |
| "       | 70         | 10     | -              | 48       |
| "       | 70         | 10     | X              | 168      |
| Spray   | 70         | 6      | -              | 144      |
| "       | 70         | 6      | X              | 484      |

Table 1: Variation of passivation parameter

12.5 Vol% SurTec 680, pH 1.8

post treatment: Anti finger print, 1 g/m<sup>2</sup>, different supplier

activation: 2 s in 0.5 % nitric acid

As it could be seen in fig. 4 and 5, no rinsing after the passivation leads to a higher coating weight and corrosion protection in salt spray testing. On the other hand, as it could be seen in the introduction, a trivalent passivation needs in contrary to a hexavalent chromate, ligands for complexing the Cr(III). If there is no rinse after passivation, these ligands will dry on the surface which will lead to an accelerated corrosion during the stack test.

Process parameter for the stack test  
one cycle:

- 6 h 20 °C, 90 % rel. humidity
- 6 h 35 °C, 90 % rel. humidity
- 6 h 35 °C, 40 % rel. humidity
- 6 h 20 °C, 40 % rel. humidity

100 cycles were done.

The different passivation parameters are leading to the following relative corrosion behaviors:

with rinse >>> no rinse

70 °C > 55 °C > 40 °C

with corrosion protecting oil >> no corrosion protecting oil

All samples with no rinse after passivation show white rust and blackening after 100 cycles, samples with rinsing and an application temperature of 70 and 55 °C show no white rust and no blackening.

### Appearance

With an increasing coating weight, a hexavalent chrome passivation has a yellow appearance (transparent - yellow) because of the yellow color of hexavalent chrome. For a trivalent chrome passivation, an iridescent color changing with an increasing layer thickness from transparent - blue - red - green is observed. Because of the iridescent color and not a "body" color (caused by Cr(VI) pigments), an original matte silver zinc finish appears after application of a colorless organic top coat.

## 5. Practical Test

Due to the promising lab results, a trial in an electrogalvanizing line was done. After zinc plating (vertical cells), rinsing, surface conditioning, zinc phosphating and rinsing, the usual hexavalent chrome passivation was replaced by a 12.5 Vol% SurTec 680 (trivalent chrome passivation). The application was a low pressure spray with 4-5 s contact time followed by squeeze rolls, rinsing, drying, anti finger print and drying. The result were as follows:

- Compared to the old hexavalent chromate better corrosion protection 76 h instead of 30 h for beginning white rust is observed
- slightly bluish-yellowish appearance
- brighter surface than before
- adhesive power for the anti finger print is the same
- because of the lower pH-value of the trivalent chrome passivation (pH 1.8) compared to the hexavalent chromate (pH 4) in use an efficient rinsing was important to prevent the drag in of passivation solution into the anti finger print because of coagulation at a low pH.

## 6. Conclusion

The new thick layer trivalent chrome passivation leads to the same or even higher corrosion protection compared to a usual hexavalent chromate with the same short contact time. Depending on the application parameters (contact time, temperature and concentration), the coating weight and therefore the corrosion protection can be adjusted to customer requirements: for example a low coating weight for temporary protection (transportation, 24 h salt spray) or a high coating weight for a high corrosion protection (computer boxes, furniture etc., >72 h salt spray). In combination with an organic top coat, the original zinc color is given back, and a further increase of the corrosion protection is observed. An efficient rinsing after passivation is necessary to prevent a dry up of the passivation solution which will reduce the corrosion protection (stack test) or a drag in into an organic top coat which will may lead to coagulation. In opposite to the hexavalent chromate, the rinse water can be recycled into the passivation solution to balance drag out losses and evaporated water. This will also reduce the consumption of the passivation chemistry. Because the Cr(VI)/Cr(III) ratio is not important for a trivalent chrome passivation solution, its service life for spray or dip application can be longer compared to a hexavalent chromate bath.

## 7. Literature

1. P. Hülser, Rolf Jansen, Andreas Möller and Horst Hahn, *Metalloberfläche* 10 (1996)
2. P. Hülser, "Chromiting, chromium(VI)-free Passivation Basecoat for Deltacoll on Zinc and Zinc Alloys", International MKS-specialist conference, 4-5 Nov. 1999,