# Chrom□ting

## The Thick Layer Passivation for Zinc and Zinc Alloys Free of Hexavalent Chromium

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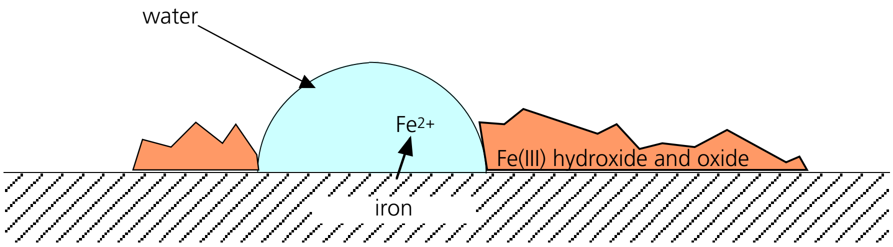
## Topics



- Corrosion and Corrosion Protection
- Cathodic Corrosion Protection of Steel
- Properties of Conventional Chromates
- Application, Properties and Corrosion Protection of Chrom□ting
- Outlook

- steel is dissolved in salt and air containing water while oxygen is reduced and hydrogen is evolved, and forms iron oxide/hydroxide which precipitates as a voluminous corrosion product on the surface = **Red Rust**
- iron oxide layers are not protecting against further corrosion, in contrary to chromium oxide on metallic chromium or aluminium oxide on aluminium



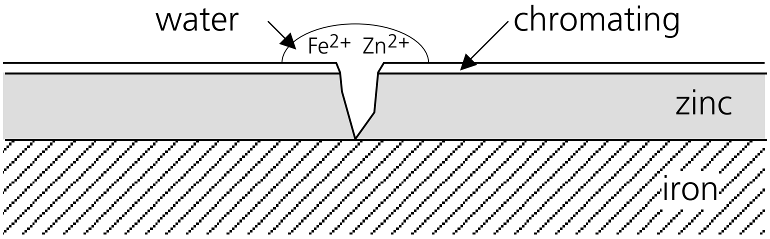

- corrosion protection is provided:

| | |
|---|---|
| **barrier layers** | oil, conversion layers, lacquer, combination, metallic layers |
| **„redox buffer“** | less noble layers, conversions layers with different oxidation levels, organic corrosion protectors |
| **duplex layers** | combination of both |





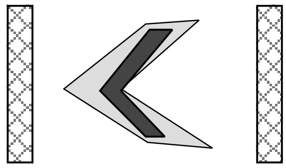
- this is the typical method to protect steel and other iron material, because in the electrochemical series of elements, iron is more positive than zinc, and this means
- zinc is less noble than iron and represents the anode in the galvanic element - iron is the cathode
- thus, iron will be - as the more noble metal - protected cathodically, until the zinc is corroded completely
- **mechanism:**




$Zn / Zn^{2+}$ : $Zn \longrightarrow Zn^{2+} + 2\,e^-$

$Fe / Fe^{2+}$ : $Fe^{2+} + 2\,e^- \longrightarrow Fe$

- basic task is the protection of the base metal against rust and consequently also against hydrogen induced embrittlement
- side purposes are a decorative function (brightness, colour) as well as tribological properties
- higher layer thickness and more even metal distribution are extending the cathodic corrosion protection



- zinc alloys (Co, Fe, Ni, Sn) are more noble than pure zinc and extend also its cathodic corrosion protection
- in addition to the cathodic protection, the zinc layer is passivated by a chromate layer, which is improving strongly the corrosion protection (by its barrier effect)
- the colour is defined by the chromating: possible tints are transparent-blue and transparent-green (trivalent) as well as yellow, black and olive green (hexavalent)

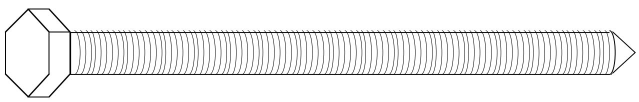




## metal distribution

**conventional** cyanide-free alkaline zinc process

15,1 15,5 17,5 12,3 11,8 17,0 20,9 µm

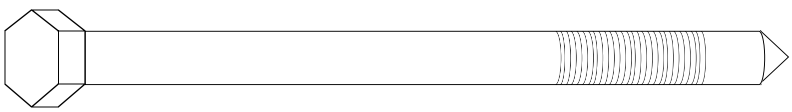


9,9 13,8 14,2 14,2 15,6 15,1 14,1 µm

**new** cyanide-free alkaline zinc process

**conventional** cyanide-free alkaline zinc process

11,9 7,0 8,6 7,1 6,6 9,6 11,1 µm



9,9 9,5 9,6 9,3 9,3 9,6 9,6 µm

**new** cyanide-free alkaline zinc process

## zinc

mechanism: cathodic protection
parameters: thickness, metal distribution, trace metals (e.g. alloys)

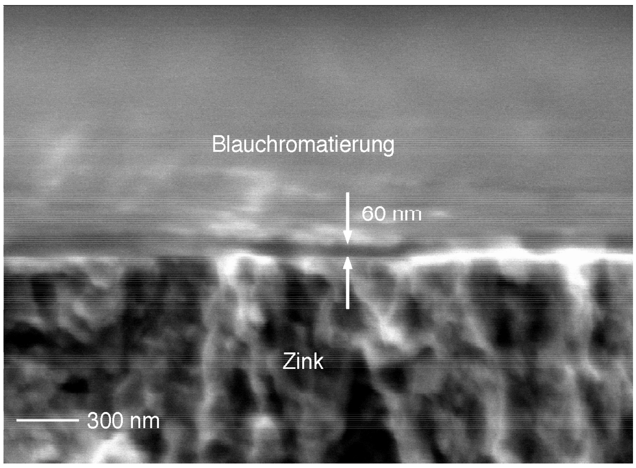
## passivation

mechanism: barrier effect, specific effect of chromium(VI)
parameters: ?

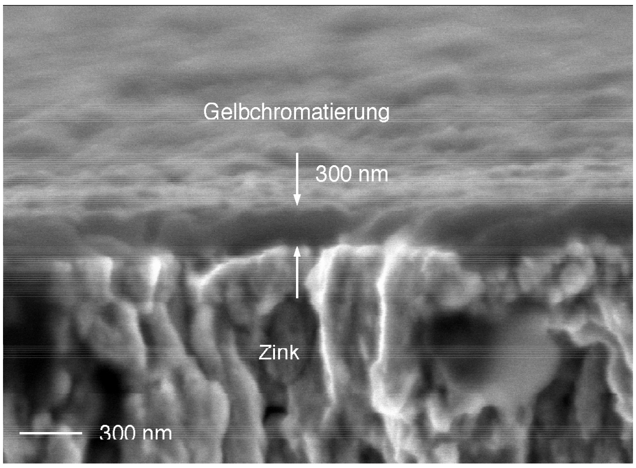
| type | chromium(VI) in the chromate layer in $mg/m^2$ | layer thickness in nm | corrosion protection in hours salt spray test until first white corrosion |
|---|---|---|---|
| blue (trivalent) | 0 | 25-80 | 20-40 |
| yellow | 80-220 | 250-500 | 200-300 |
| olive-green | 300-400 | 1000-1500 | 400-500 |
| black | 80-400 | 250-1000 | 150-300 |








edge of a broken steel sheet, bright zinc plated and trivalent **blue passivated,** at a magnification of 40,000x

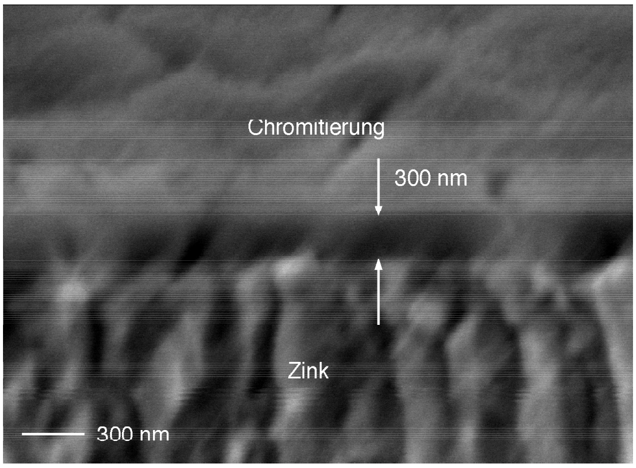



edge of a broken steel sheet, bright zinc plated and hexavalent **yellow passivated**, at a magnification of 40,000x

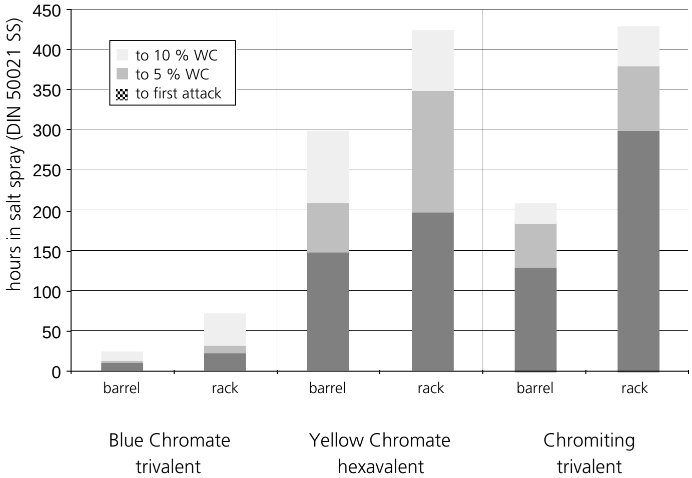
- if chromium(VI) had a specific corrosion protecting effect, we shall always expect a disadvantage with trivalent chromates with regard to its anticorrosive properties

## Properties of Chromiting 9

- if the corrosion protection of a chromate layer was based on it barrier effect only, then trivalent passivations with the same layer thickness should provide the same corrosion protection as hexavalent passivations




edge of a broken steel sheet, bright zinc plated and trivalent **chromited**, at a magnification of 40,000x




Corrosion Protection in Comparison



## Application: Chromiting in Comparison to Yellow Chromate 10

| | trivalent Chromiting | hexavalent yellow chromate |
|---|---|---|
| **make-up:** | 12.5 Vol%<br>= 10 g/l Cr(III) | 1 Vol%<br>= 2 g/l Cr(VI) |
| **pH-value:** | 1.8-2.2 | 1.6-1.8 |
| **temperature:** | 60 °C | room temperature |
| **contact time:** | 60 s | 20 s |
| **heating:** | necessary | in winter season |
| **exhaust:** | necessary | recommended |
| **rinsing:** | 3 steps | 2 steps |
| **activation:** | recommended | |
| **agitation:** | rack agitation/barrel rotation and/or air agitation | |
| **tank material:** | (insulated) plastic tanks or steel tanks with plastic inliner | |

## The Green Alternative

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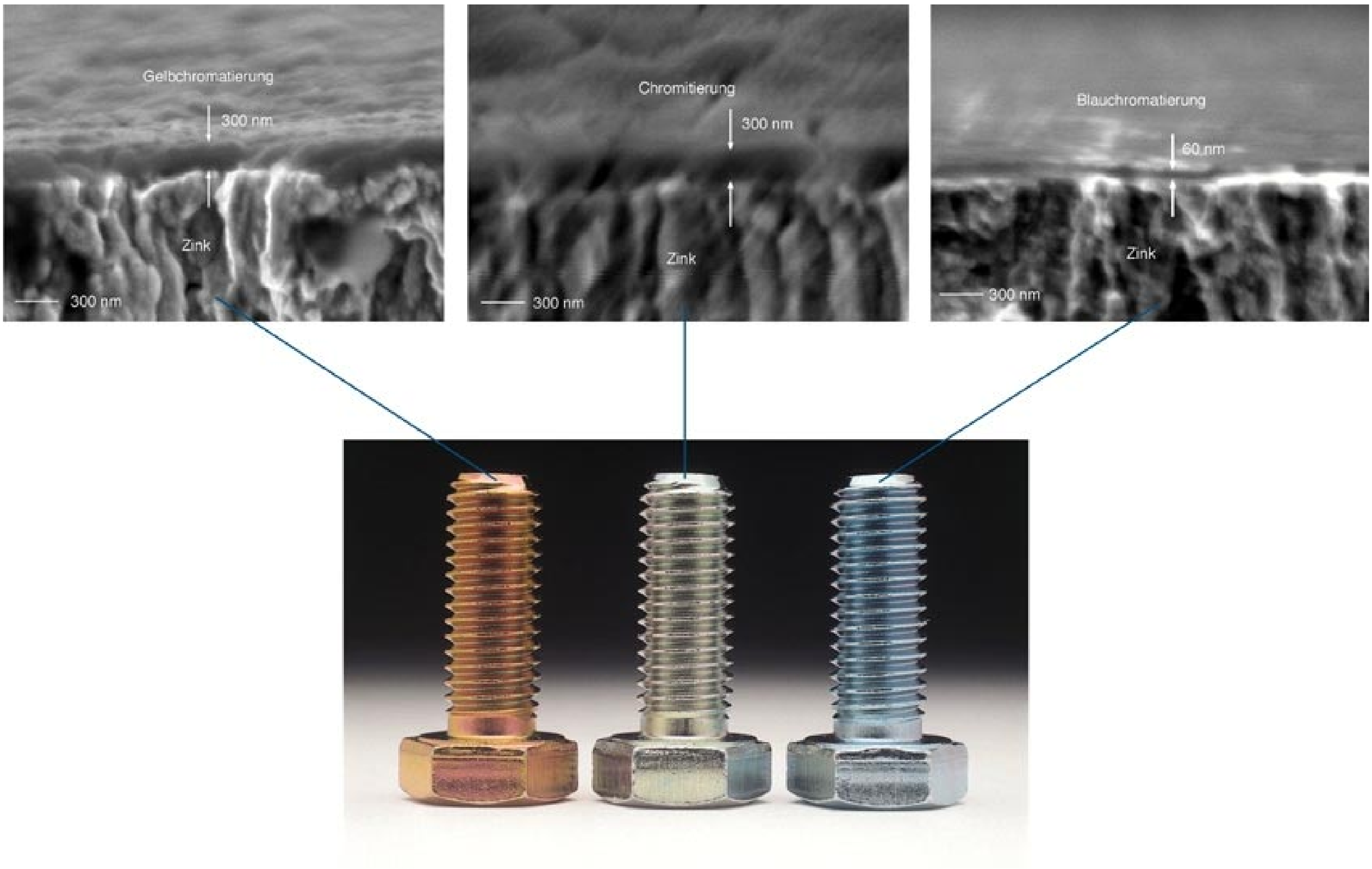




## Sputter Profiles in Comparison

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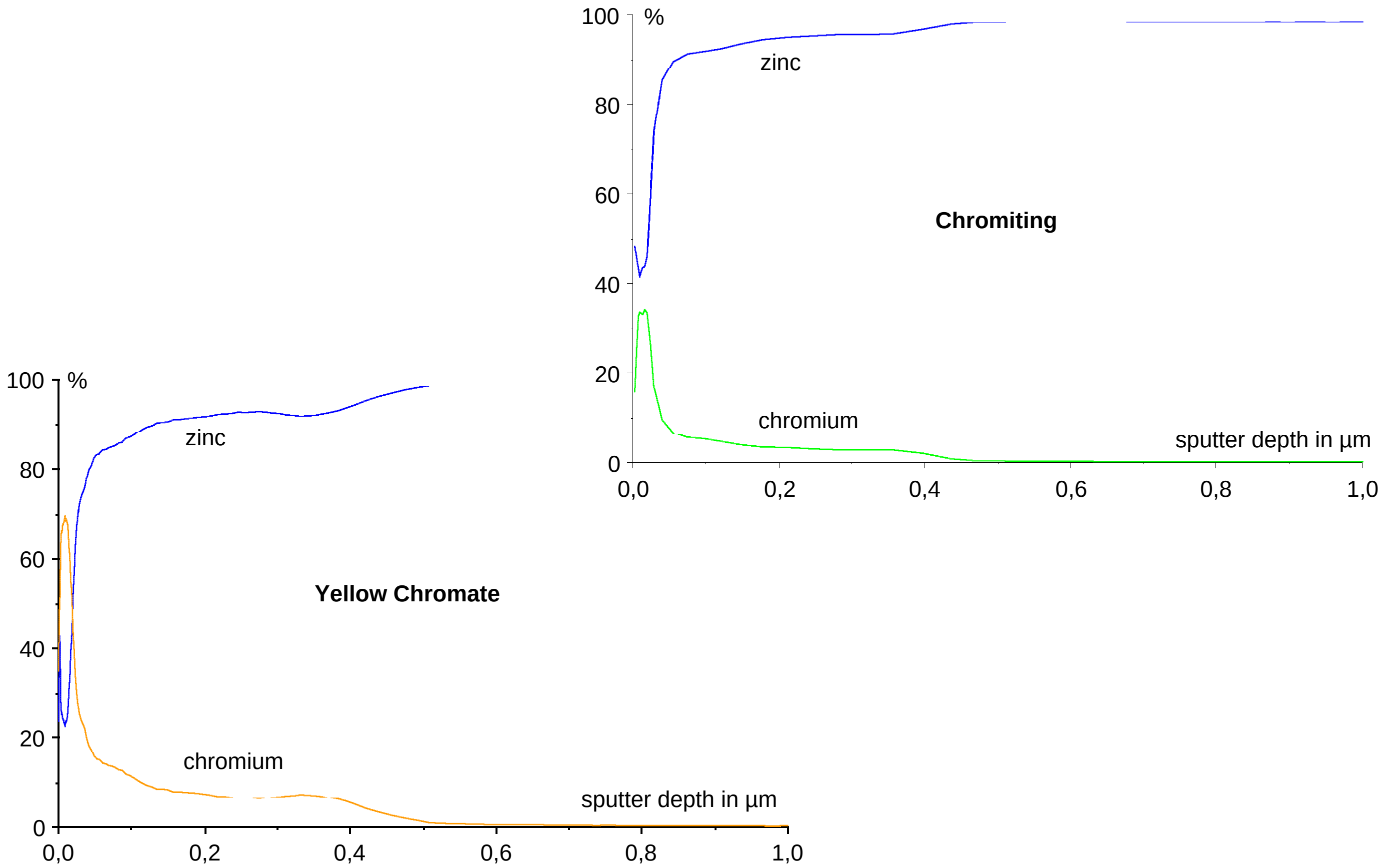


## Chromiting Layer Thickness Measured with Different Methods 13

### Layer Thickness in nm

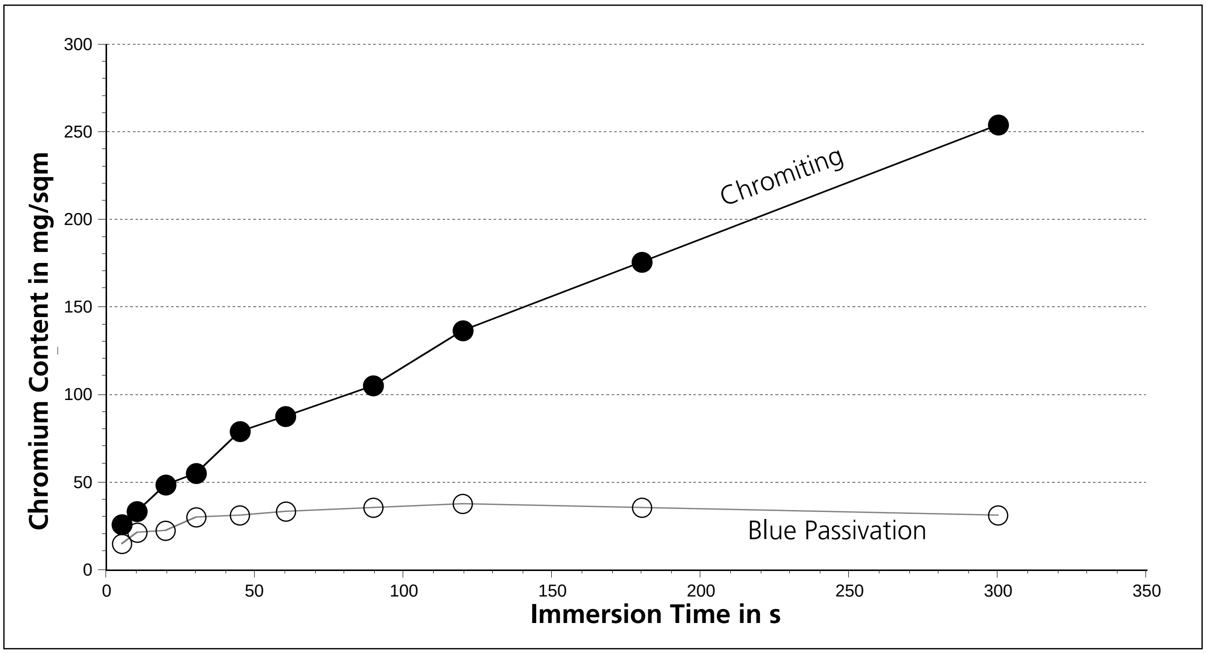
ellipsometry, glow discharge spectroscopy (GDOES) and scanning electron microscopy

| | immersion time in s | temperature in °C | pH-value | scanning electron microscopy | glow discharge spectroscopy | ellipsometry |
|---|---|---|---|---|---|---|
| **Chromiting** | 60 | 60 | 2.0 | 300 | 312 | 353 |
| | 120 | 60 | 2.0 | | 400 | 440 |
| | 60 | 60 | 2.5 | | 195 | 230 |
| | 90 | 60 | 2.5 | | 295 | 300 |
| | 120 | 60 | 2.5 | | 435 | 400 |
| | 60 | 100 | 2.0 | | 360 | 580 |
| in comparison: | | | | | | |
| **Blue Chromate** | | | | 60 | 60 | 100 |
| **Yellow Chromate** | | | | 300 | 440 | 395 |



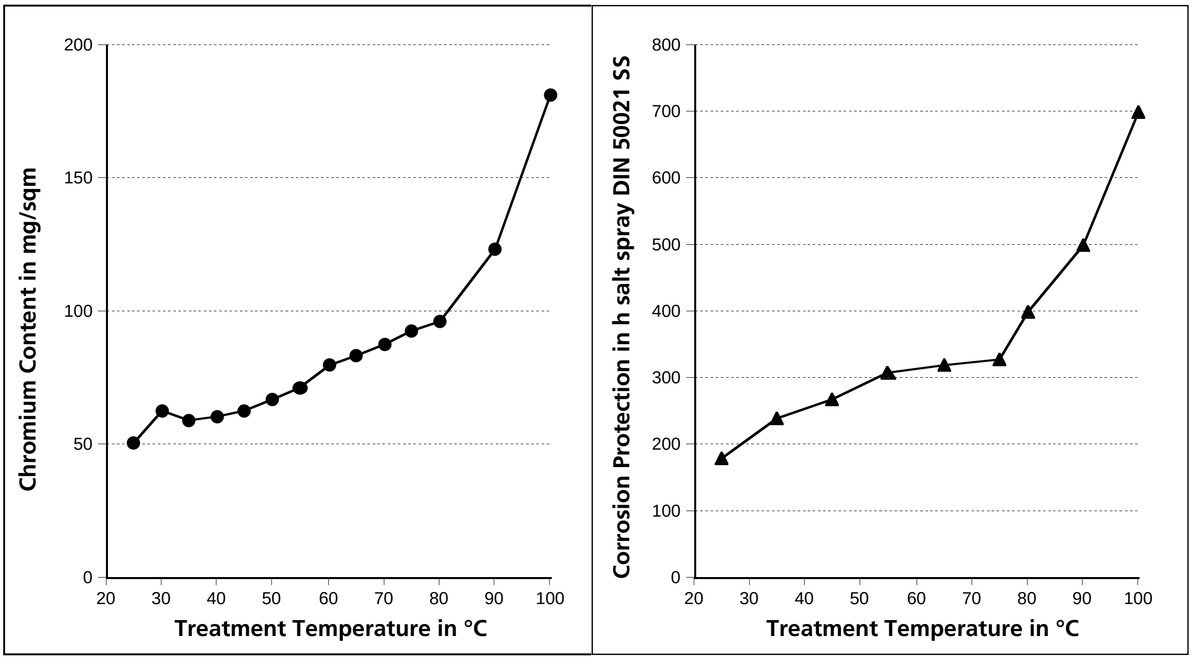
## Chromium Content in the Chromiting Layer 14

### depending on the immersion time



## Chromium Content and Corrosion Protection


### depending on the treatment temperature






## German "Qualitätsförderkreis Chromitierung" (just founded)


▼ old members **Collini**, **Holder**, **Vollmerhaus**
new: **Holzapfel**, **Huster**, **Kronenberger**, **Zeschky**

▼ application of Chromiting, Black Chromiting and possible further developments

▼ exchange of experience (trouble shooting)

▼ commitment to keep narrow parameter ranges for the coating

▼ development and guarantee of common standards
(measuring procedures, setting and guaranteeing process safety, reproducibility)

● **task: to provide capacity in a sufficient volume and in constantly high quality**

## Colour Effects 17

### 1. Chromiting on Zinc

The natural colour is transparent and significantly green iridescent. This colour is no body colour caused by pigments, but a layer thickness related interference colour. A significantly green layer has a thickness of 100-700 nm.

This colour will disappear completely after an organic sealing with SurTec 552 or 555 (different refraction index than the passivation itself).

### 2. Chromiting on Zinc/Iron or Zinc/Nickel

The colour of Chromiting on zinc/iron is stronger iridescent and slightly darker. Also here it is disappearing to a great extent by an organic sealer, resulting in a colour similar to that of titanium. On zinc/nickel, a thinner Chromiting layer appears dark blue - iridescent; thicker layers are looking yellowish-green. After sealing, a uniform grey shade is formed.

### 2. Chromiting on Other Surfaces

On zinc/cobalt, the colour is similar to zinc/iron, but the layer composition of zinc/cobalt is less uniform and so is its colour. On hot dip zinc, it is opaque greyish green, on zinc dye cast often spotted (copper!).



## Outlook: Other Colours 18

### What About Black Chromitings?

- black layers on zinc/iron are possible with a variation of Chromiting; its further optimisation is a current project
- black layers on zinc/cobalt are possible with the same solution (but less uniform)
- for zinc/nickel there is no Black Chromiting up to now

### Dyeability

- high-coloured dyes can be used to tint the layer; blue, yellow, "brass" and pinkish-red are already tested
- black dyes (as for aluminium) are to weak in colour to result in an opaque black colour

▼ minimal traces (between 1-3 mg/m$^2$) of chromium(VI) are always present in high amounts of chromium(III), due to the chemical equilibrium

▼ the analysis of chromium(VI) traces in chromium(III) bulk is not trivial

● a theoretical replacement for chromium(VI) in passivations must fulfil a series of criteria:

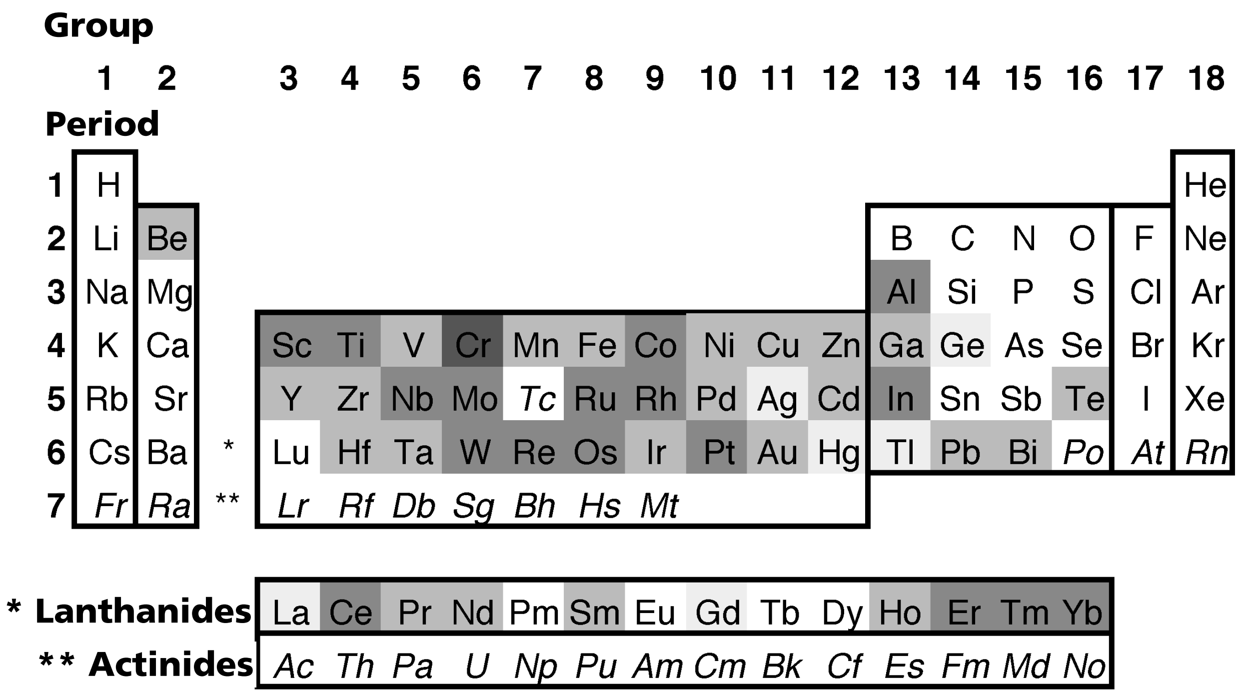
**Chemical Properties**
- good water solubility in acidic pH (a conversion layer always requires a prior etching)
- the formation of oxides, insoluble in water, acids **<u>and</u>** lyes

**General**
- availability (mass production)
- recyclability
- low raw material costs
- known toxicology of all possible oxidation levels





the solubility of element oxides is coded in greys.
light grey = insoluble in water; grey = insoluble in acids **<u>or</u>** lyes; dark grey = insoluble both in acids **<u>and</u>** lyes



## Conclusion

- Chromium(III) is the best alternative to Chromium(VI), other - more appropriate - elements are not in sight

- with trivalent thick layer passivations (Chromiting), the requirements of the EU End of Life Vehicles Directive are easily met
  (2 g chromium(VI) per car are allowing 600 to 2000 $m^2$ passivated surface)

- in collaboration with the VDA, chemical suppliers are developing an analytical method for the detection of chromium(VI) in passivations