

Chromiting[®], chromium(VI)-free Passivating Basecoat for Deltacoll on Zinc and Zinc Alloys

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1. Introduction

Chromating zinc plated surfaces has been a commercial corrosion protection process for several decades (1st patent application 1936 by E.J. Wilhelm).

The additional passivation of electroplated zinc and/or zinc alloy coatings results in significantly greater passivity of the metallic surface in response to external corrosive influences. The precise corrosion protection action, however, has not yet been clearly explained. It is assumed, that the relatively thick layer (up to several hundred nanometers) of chromium(III) hydroxide acts as a barrier against external corrosive substances. In addition, in-built hexavalent chromium acts as a self-healant, which diffuses to damaged areas and actually recreates the protection layer via a reduction process.

Because of its highly carcinogenic effect, chromium(VI) and conventionally produced chromate coatings are disappearing from the market and being replaced by safer products.

Notable car manufacturers like GM are now forbidding the use of chromium(VI) passivators from the year 2002 in specifications. The "End of Vehicles Life" Directive from the European Parliament forbids the use of chromium(VI) and/or regulates the quantities used from 1st January 2005.

It is therefore necessary to find a chromium(VI)-free passivator to replace conventional chromatings (especially yellow chromate).

Table 1 lists currently commercially available chromating processes. With the exception of the trivalent blue chromate, which has poor resistance in thin layers, all other processes contain chromium(VI). The table shows that corrosion resistance increases with the thickness of the coating layer.

Type	chromium(VI) content in the coating layer in mg/m ²	Coating thickness in nm	Corrosion protection in the salt spray test in h up to the first appearance of white rust **2
Blue (trivalent) * 1	0	25-80	20-40
Yellow	80-220	250-500	200-300
Olive	300-400	1000-1500	400-500
Black	80-400	250-1000	150-300

*1 Hexavalent blue chromate is obsolete and is not taken into consideration here

**2 damaged chromate layers without added protection from, e.g. sealants, waxes.

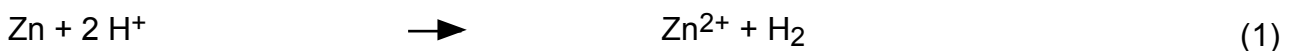
Table 1. Current chromating processes for zinc

2. Chromiting; Chromium(VI)-Free Replacement for Yellow Chromate

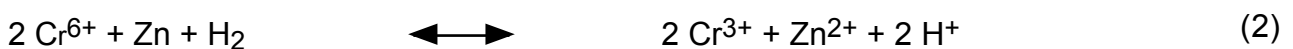
Chromium(III) is not carcinogenic and there are no restrictions on its use as a passivator. It therefore represents a good basecoat replacement for chromium(VI). In addition, trivalent chromium has the advantage over new processes that its environmental effects have been thoroughly investigated.

Up until today, however, it has not been possible to achieve corrosion protection results to match that of yellow chromating on the basis of trivalent chromating, which is primarily based on the thinner layer thicknesses.

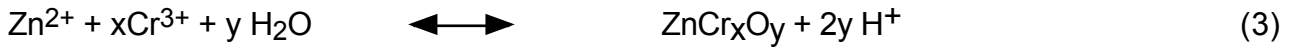
If we look at the reaction equation that results in the formation of a chromium layer, we see that the first step is an acid attack on elementary zinc in the passivating solution:



The proton consumption leads to an increase in the pH value on the surface.



This Cr(III) intermediate reacts to form an insoluble zinc/chromium oxide layer due to the pH increase on the surface before a stable complex can form.



In this way chromium(VI) is built into the layer.

Reaction step (2) does not occur in trivalent chromating. As chromium(III) in solution is always present in stable complexes, reaction (3) takes place significantly more slowly than in hexavalent passivation. Chromiting® has provided the first opportunity, via the selection of suitable process parameters as well as the selection of a suitable chromium(III) complex, to achieve a coating thickness comparable to that of yellow chromate (Figs 1-3).

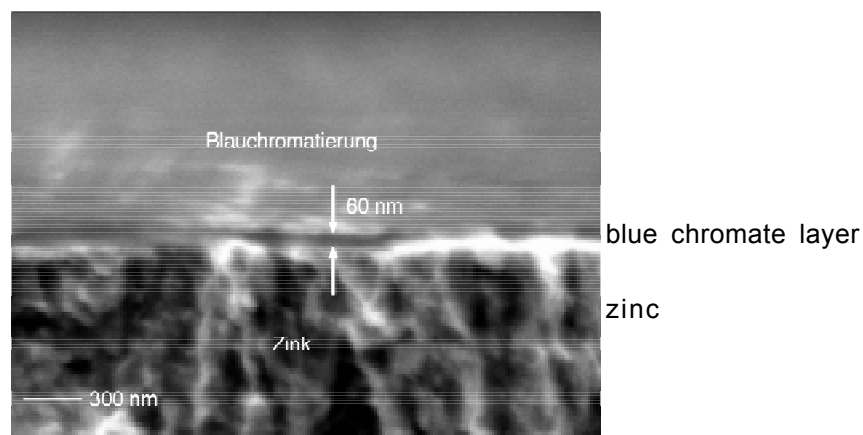


Figure 1. 40,000x magnification of bright zinc plated and trivalent blue chromated steel. Blue chromate layer thickness = 60 nm

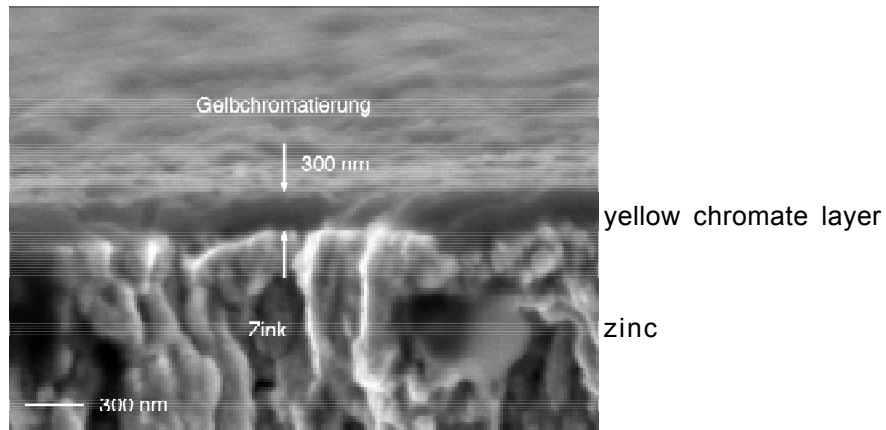


Figure 2. 40,000x magnification of bright zinc plated and hexavalent yellow chromated steel. Yellow chromate layer thickness = 300 nm

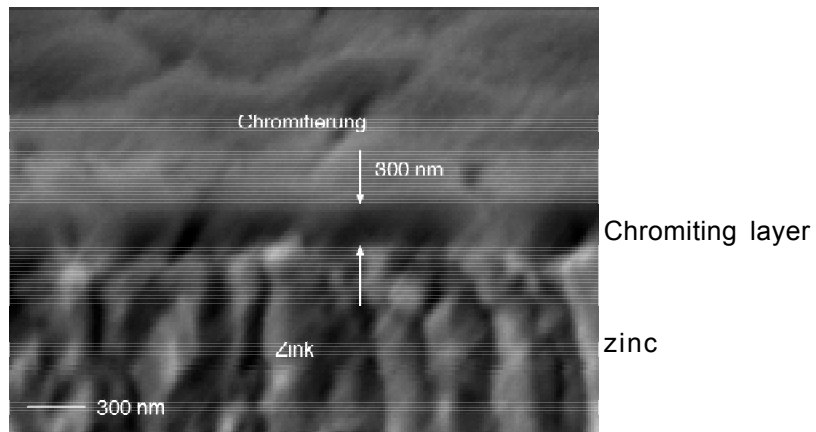


Figure 3. 40,000x magnification of bright zinc plated and trivalent chromited steel. Chromiting layer thickness = 300 nm

Since the chromiting layer contains no chromium(VI), but is considerably thicker than the blue passivator, the finish is green (Fig. 4).



Figure 4. Yellow Chromate Chromiting Blue Chromate

The colour is not a body colour, however, but an interference colour which can be almost totally compensated for by the addition of a transparent (organic) passivating layer (Fig. 5).



Figure 5. Component with Chromiting (left) and with an additional organic protection coating (SurTec 555, right).

The resultant corrosion protection is comparable with yellow chromating (see dia. 1).

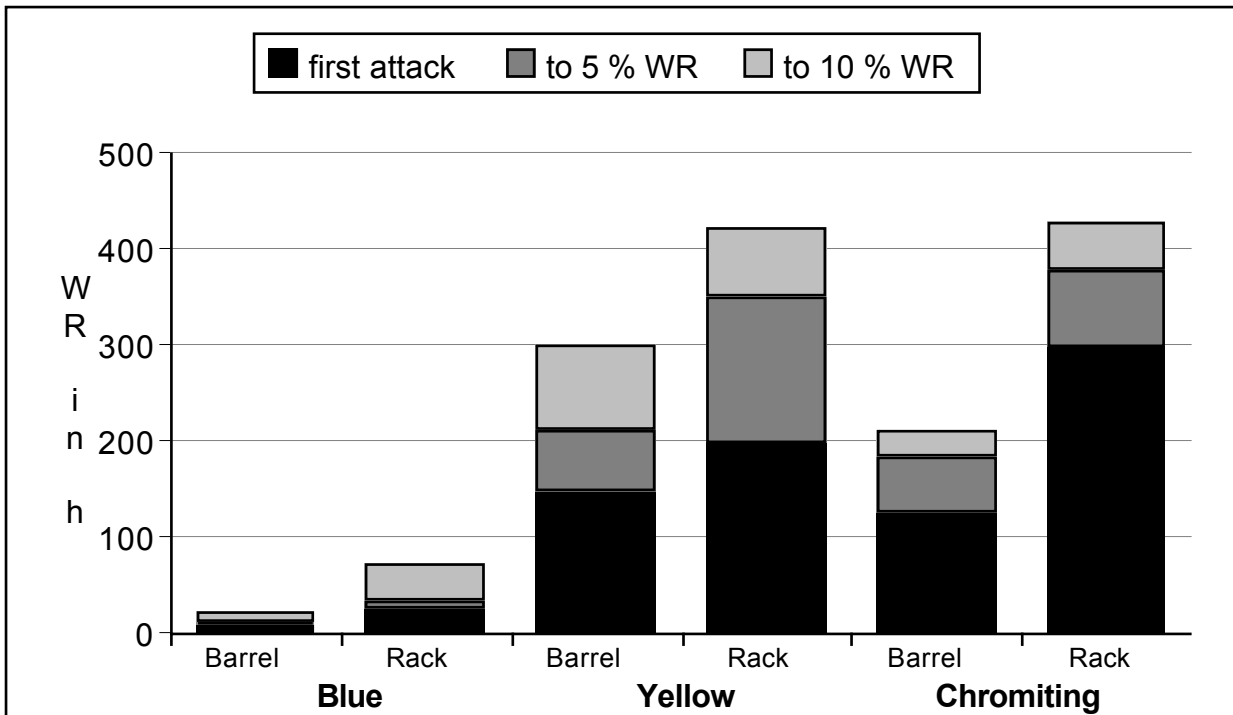


Diagram 1: Corrosion protection of blue and yellow chromate in comparison with Chromiting (neutral salt spray test), WR = white rust

The Chromiting is also suitable without modification (occasional slight alterations in process parameters) as a passivator for Zn/Ni (Ni 6-8 and 11-13 %), Zn/Fe (Fe 0.5 %) and Zn/Co (Co 0.5 %). The corrosion protection is at times better than onto pure zinc (see dia. 2).

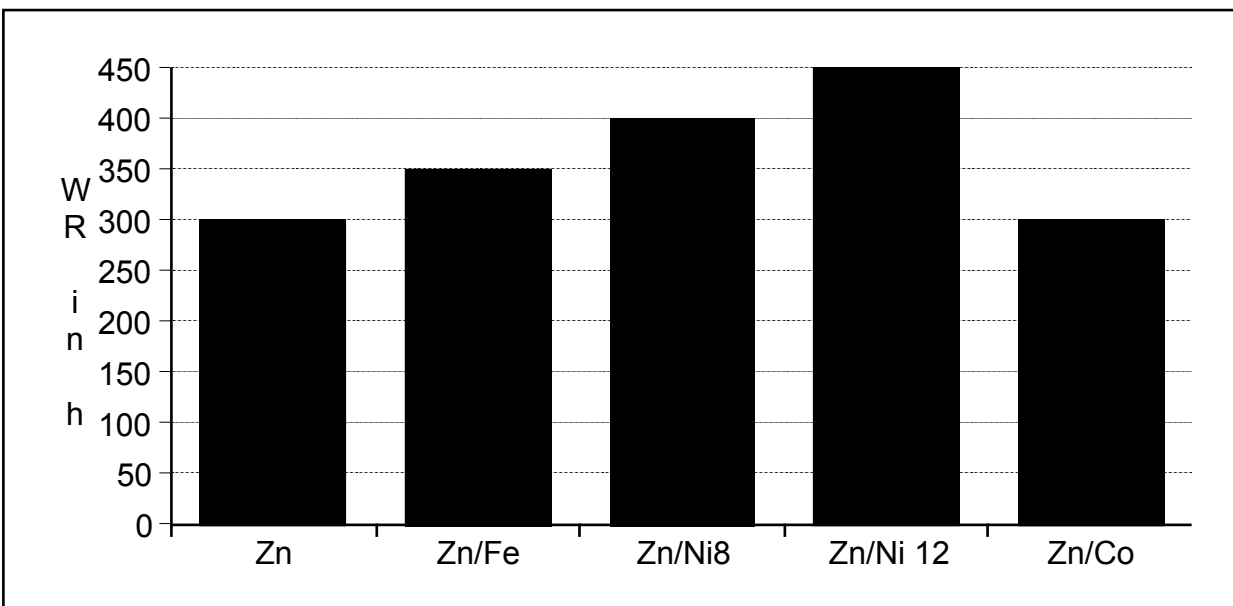


Diagram 2: Corrosion protection of Chromiting onto different alloys, start of white rust

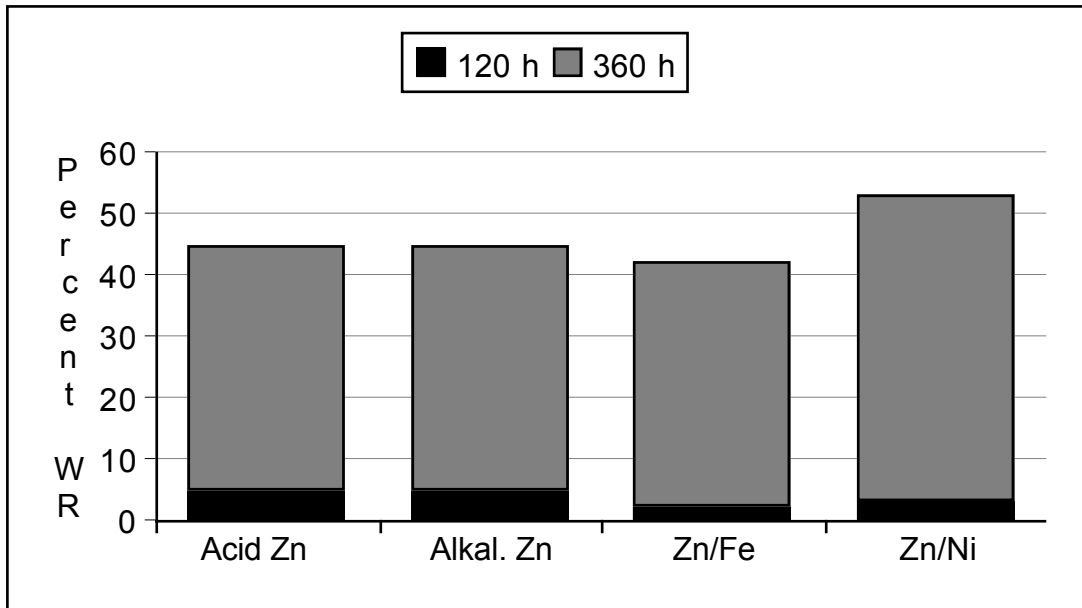
Chromiting is harder and less water-retentive than yellow chromating. When heat treated (prevention of hydrogen embrittlement), significantly smaller and fewer cracks appear than with yellow chromating. This results in only minimal corrosion protection loss after heat treatment in comparison with yellow chromating, whose corrosion protection properties (Table 2) are almost completely destroyed.

	Yellow Chromate		Chromiting	
	% white rust	% red rust	% white rust	% red rust
No heat treatment	5	0	5	0
1 h at 120 °C	15	0	5	0
1 h at 150 °C	50	5	5	0
1 h at 200 °C	100	20	5	0
2 h at 200 °C	100	30	5	0

Table 2. Comparison of white rust and red rust occurrences in yellow chromating and Chromiting after 240 h salt spray test and different heat treatment periods.

3. Chromiting in Combination With Deltacoll Black Coatings

The properties described above (corrosion resistance, zero chromium(VI) content and resistance to heat treatment) make Chromiting an ideal basecoat for Deltacoll. In addition to significantly advanced corrosion protection, this enables the production of black finishes with high corrosion protection which the car manufacturing industry is in constantly demanding (Fig. 3).



Dia. 3. Corrosion protection of Deltacoll 80 (black)-coated zinc and zinc alloys with the use of a lubricant.
Temperature load prior to test: 1 h at 150 °C

The GME 00252 stipulates a white rust formation <10 % after 120 h and no red rust formation after 360 h in the salt spray test. This was achieved in all cases.

Since the colour of the chromiting layer on zinc is too pale for a single coat of Deltacoll black, Zn/Fe alloy coatings (grey finish, Fig. 6) are best suited here.



Figure 6. Zn/Fe chromited screws with and without Deltacoll (black)

4. Outlook

As Chromiting has a different colour finish to that of yellow chromating, it cannot be used without further ado - a usage will be offending current industry specifications.

Some car companies, however, have already altered their specifications to incorporate yellow/green chromium(VI) free passivators while others are well on their way to doing so.

In conjunction with Deltacoll, trials will be carried out in the near future with an electroplating job shop on Chromited Zn/Fe and Deltacoll black (also chromium(VI)-free) coated screws. These will subsequently be tested with a car manufacturer.