Trivalent Black Layers With Cathodic Corrosion Protection

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Subjects

- Why coating? Why black?
- cathodic corrosion protection (and alternatives)
- different coating systems and their application

⇨ Summary

Why coating? Why black?

- most metals but also plastics and partially glass are coated before their technical usage in order to grant to the material at the surface other characteristics, e.g.

  hardness (hard chromium on steel, stainless steel or nickel; chromium on plastic)

  friction properties (chromated galvanised screws, chromium on pressing tools)

  brightness, colour (chromium-plated furniture, matte chromium-plated bath armatures, antique nickel-plated saxophones, blue passivated galvanised screws)

  chemical resistance (electroless nickel, tin plated kitchen tools)

  corrosion protection (phosphates, lacquers, zinc and zinc alloys)

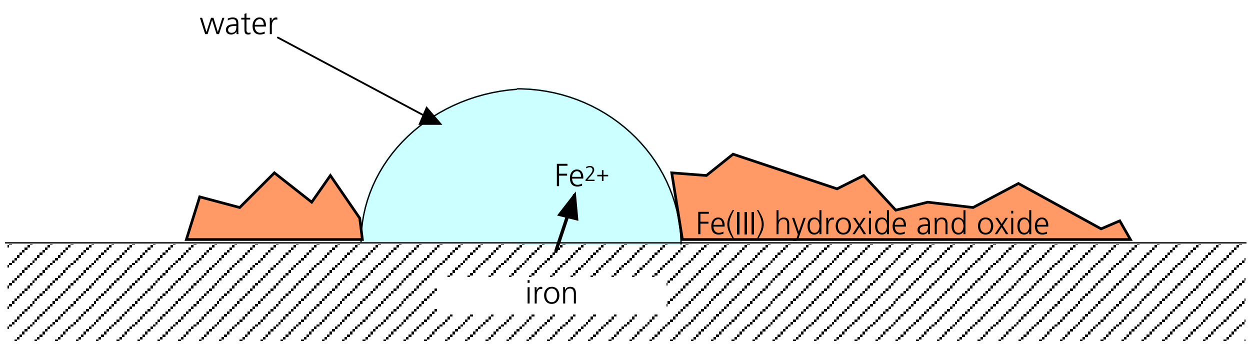
- the base material often *should* have other properties than the surface (harder or softer, tougher, more flexible, lighter, easier to process, cheaper, better recycable)

- often the desired characteristics are obtained only by several coatings one above the other (⇨ layer systems)

- “black is beautiful” (other characteristics are mostly inferior to those of pale layers)

Corrosion and Corrosion Protection

- steel dissolves in (salt and air containing) water under hydrogen formation
- iron oxide layers are not protecting against further corrosion (like e.g. for chromium oxide on chromium or aluminium oxide on aluminium)



- corrosion protection can be made through:

  barrier layers (oil, conversion coatings, lacquer, combination, metallic layers)

  "redox-buffers" (less noble layers, conversion layers with different oxidation levels, organic corrosion protection agents)

  duplex layers (combination of both)

Corrosion Protection by Barrier Layers

- the barrier layer must be mechanically stable for the respective application (or - like oil - replenished constantly)
- it usually must be steady chemically and against UV radiation also (lacquers)
- it must adhere reliably on the base material, also injuries (scratches, particle impact) must not to lead to growing corrosion under the barrier layer (with aluminium there is the special appearance Filiform corrosion, which reproduces itself like worms from an injury)
- since lacquers on bare metal do not adhere well, a conversion layer is usually applied as a basecoat for additional corrosion protection with injuries and for better adhesion
- typical test methods

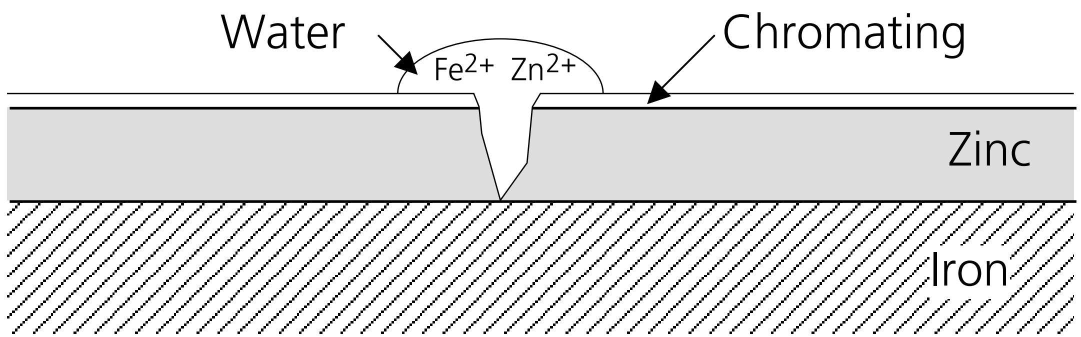
  hot water
  climate chamber
  salt spray
  cyclic alternating conditions (climate, salt spray and dry phases)
  Florida and Camargue test

Cathodic Corrosion Protection by Zinc

This is the typical method for the protection of steel and other ferrous metals because in the electromotive series, iron is located more positively than zinc, and this means:

- zinc is less noble than iron and represents the anode in the galvanic cell whereas iron is representing the cathode
- iron as the more noble metal is consequently protected cathodically until the zinc will be totally corroded

mechanism:



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

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

Influences on the Cathodic Corrosion Protection

- for efficient corrosion protection, the sacrificial layer must be less noble than iron but stable enough to form a protective layer
- only few elements are depositable from aqueous solutions, so the range of possible metals is extremely low
- zinc is the least noble metal which can be deposited in aqueous solution (acid or alkaline)
- most alloying elements are located more positively than iron, so they can only be used in small proportion
- zinc alloys (Co, Fe, Ni, Sn, Cr, Mn) are nobler than pure zinc and thus extending the cathodic corrosion protection
- zinc (alloy) layers are generally chromated, providing a thin barrier layer in addition to the cathodic protection, which improves the corrosion protection again strongly
- the colour is determined by this finish; possible are transparent blue and transparent green (trivalent) as well as yellow, black and olive green (hexavalent)

Black Finishes

- usually for decorative reasons
- in addition, with functional purposes: e.g. as solar collectors
- as an adhesion basecoat, e.g. for thin lacquers

possibilities to achieve black finishes:

- by embedding pigments
- by infiltration of (organic) dyes

In order to infiltrate organic dyes, quite thick chromate or oxide layers are needed.

<u>Examples:</u>

Anodised aluminium (oxide layer around 25 µm) can easily be dyed black by infiltration.

Chromated zinc (chromate layer of 0,05-0,3 µm) cannot be dyed black.

Embedding Black Pigments in Chromate Layers

In hexavalent black passivations, the pigments are received on one hand by evenly embedding finely distributed elementary silver and silver oxide (silver based black chromates for zinc).
Thereby, the corrosion protection becomes worse.

Furthermore, black pigments can be made of alloying metals such as iron, cobalt and nickel by chemical reaction during the passivation process:

iron (Fe) $\longrightarrow$ Fe_3O_4

nickel (Ni) $\longrightarrow$ $NiO(OH)$ / NiO

cobalt (Co) $\longrightarrow$ Co_3O_4

The corrosion protection of the passivation is little influenced by these embedded pigments, it remains almost as good as with a yellow or an olive chromate finishing.

Fig. 2: Black Chromatings: Hexavalent vs. Trivalent

1 For zinc there are only hexavalent black chromatings. The embedded pigment is finely dispersed silver/silver oxide.

2a The hexavalent black chromating on zinc/iron without post dip is frequently blunt. The black pigment which is iron(II)-iron(III)-oxide is not embedded at the surface.

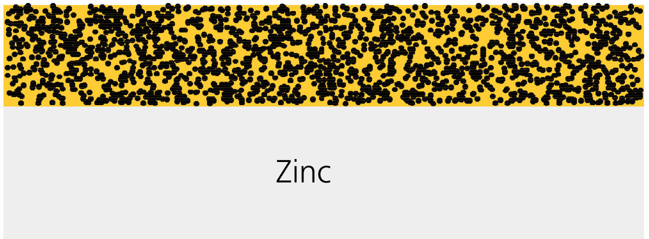
2b Only the chromium(VI) containing post dip fixes the black pigment and grants to the layer a lacquer-like appearance.

3a Also the trivalent Black Chromiting is blunt without post dip. The iron(II)-iron(III)-oxide is not completely embedded at the top of the surface.

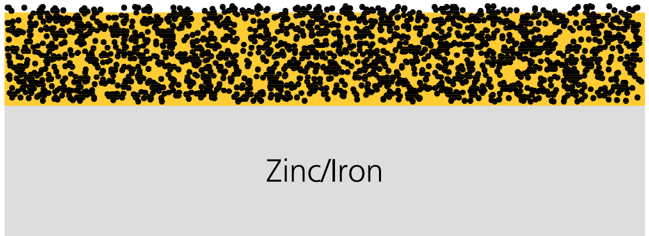
3b By sealing with an aqueous plastic dispersion one receives the lacquer-similar appearance and a good corrosion protection.

4 On zinc/iron a trivalent Chromiting with reduced pigment proportion and therefore improved corrosion protection can be produced. The grey Chromiting provides an ideal adhesion layer for black varnish such as Deltacoll Black (**4a**) or cathodic electrophoretic lacquers (**4b**).

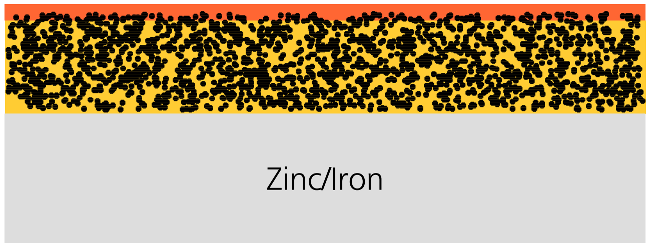
1 hexavalent
black chromating on zinc



2a hexavalent black chromating
on zinc/iron without post dip

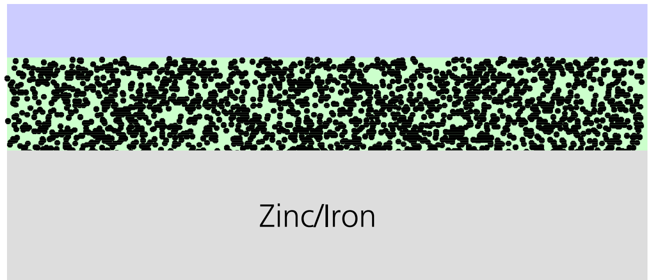


2b hexavalent black chromating
on zinc/iron with hexavalent post dip

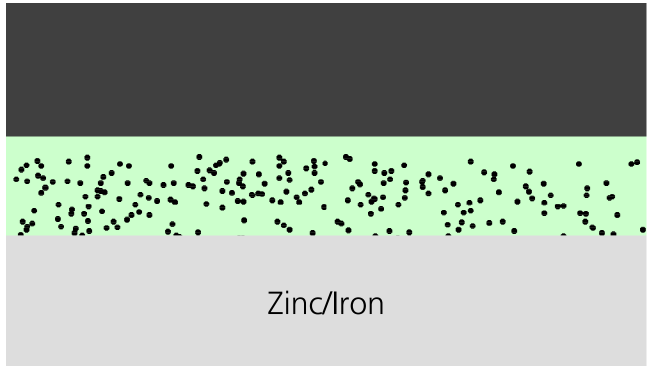


3a trivalent Black Chromiting
without top coat

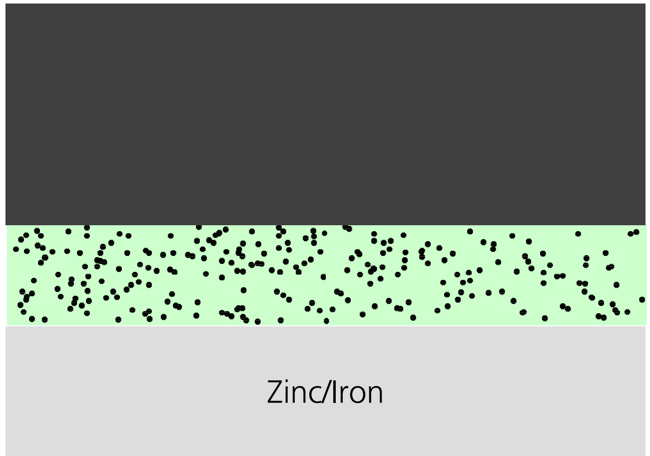
3b trivalent Black Chromiting
coated with a clear organic sealer



4a trivalent grey Chromiting
plus Deltacoll Black



4b trivalent grey Chromiting
plus black cathodic electrophoretic lacquer



Overview on Different Approaches

A. Hexavalent Black Layers

1. Zinc + Black Chromate (silver based) + Fixing (buffer + reduction agent)	*results in lacquer-like glossy layers; problem of colour stability*
2. Zinc/Iron + Black Chromate (silver free) + Post Dip (hexavalent)	*results in semibright layers; problem of soluble chromium(VI)*
3. Zinc/Cobalt + Black Chromate (silver free) + Post Dip (hexavalent)	*results in semibright black layers, "white ear" problem and Cr(VI)*
4. Zinc/Nickel + Black Chromate (silver free) + Post Dip (hexavalent)	*rather matte and blunt layers, tinge of brown, soluble chromium(VI)*
5. newer alloys: Zn/Sn, Zn/Mn, Zn/Cr	*no black finish up to now; imaginable on Zn/Mn, on Zn/Sn only with silver or similar*

Overview on Different Approaches

B. Trivalent Black Layers

1. Zinc
   + Blue Chromate or Chromiting
   + Black Lacquer (2x coated)

Black trivalent conversion layers directly on zinc are not in sight.

2. Zinc/Iron
   + Grey Conversion Coating
   + Black Lacquer (1x coated)

Black trivalent conversion layers on zinc/cobalt are possible, but uneven (pale areas due to different Co contents).

3. Zinc/Iron
   + Black Conversion Coating
   + Transparent Sealing

4. Zinc/Iron
   + Black Conversion Coating
   + Black Sealing

Black trivalent conversion layers on zinc/nickel are producible, but so far without considerable corrosion protection.

5. Zinc/Iron
   + Black Conversion Coating
   + Black Lacquer (1x coated)

Summary

- the meaning and importance of cathodic corrosion protection was shown; for iron and steel it is indispensable
- generally the best and most simply producible cathodic corrosion protection is achieved with zinc and zinc alloys which are depositable in aqueous solutions
- the passivation forms an additional thin barrier layer
- recent developments provide trivalent black layers (Black Chromiting or other trivalent passivations with black lacquers)
- with the suitable topcoats, even highest requirements to the corrosion protection can be fulfilled