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Lanthane 315

High Corrosion Resistance

Thick Film Passivation

for Zinc and Zinc-Iron

Lanthane 315

The product Lanthane 315 does not infringe the patents US 6287704 and EP 0907762

Thereby Coventya can promise, that this process is long-lasting deliverable and can be advanced without any limitations.

The Cr(III)-based salts are produced by our own, that means that there is no dependency on the raw material market.

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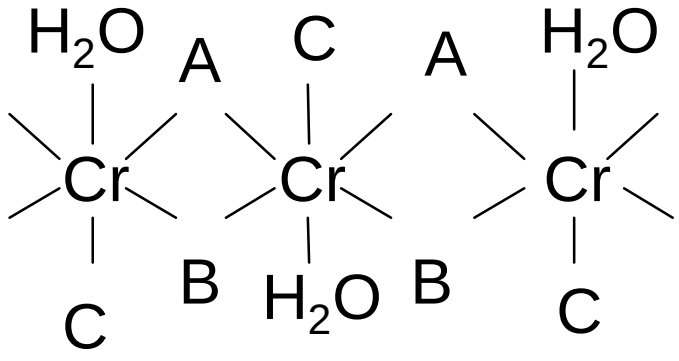
The principle of chromate (Cr VI) creation

- **Oxidation of Zinc in acid environment:**

$$3\,Zn + 2\,CrO_4^{2-} + 10\,H^+ \rightleftharpoons 3\,ZnO + 2\,Cr^{3+} + 5\,H_2O$$

- **Proton consumption:**
  - **increase of pH-value:** precipitation of Zinc and Chromium ⇒ Chromate- Gel
  - **the reaction continues in the adsorbed layer:**

$$-\,Cr_2O_7^{2-} + 8\,H^+ + 6\,e^- \rightleftharpoons Cr_2O_3 + 4\,H_2O$$



mit A = HSO_4^-, $HCrO_4$-
B = OH^-, NO_3^-, Cl^-
C = H_2O, F^-, B or A

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The principle of Cr(III)-Passivation creation

Mechanism of creation:

(in absence of oxidation products: e.g. Nitrates)

Oxidation of Zinc :

$$2\ Zn + 2\ HNO_3 + 4\ H^+ \longrightarrow 2\ Zn^{2+} + 2\ NO_2 + H_2 + 2\ H_2O$$

Precipitation in the passivation- layer :

$$Zn^{2+} + x\ Cr^{III} + y\ H_2O \rightleftharpoons ZnCr_xO_y + 2y\ H^+$$

(Cr VI) chromate vs. Cr(III)-Passivation

Properties of (Cr VI) chromate:

- type of gel film (0,8 – 2 µm)
- curing at approx. 60 °C
- structure: Cr(III) bridge polymer with Cr(VI)-compound
- self healing effect in case of damaging of the layer
- poor heat resistance
- allergic effect; Cr(VI) is toxic

Properties of Cr(III)-Passivation:

- type of gel film (0,1 – 1 µm)
- curing at approx. 60 °C
- structure: Cr(III) bridge polymer; free of Cr(VI)
- no self healing effect
- good heat resistance
- harmless

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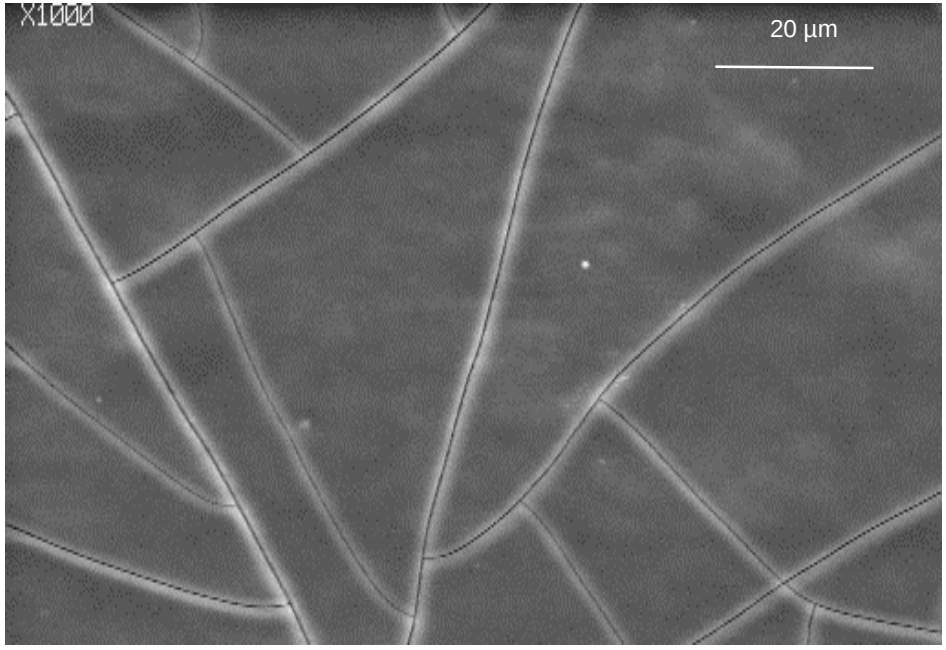
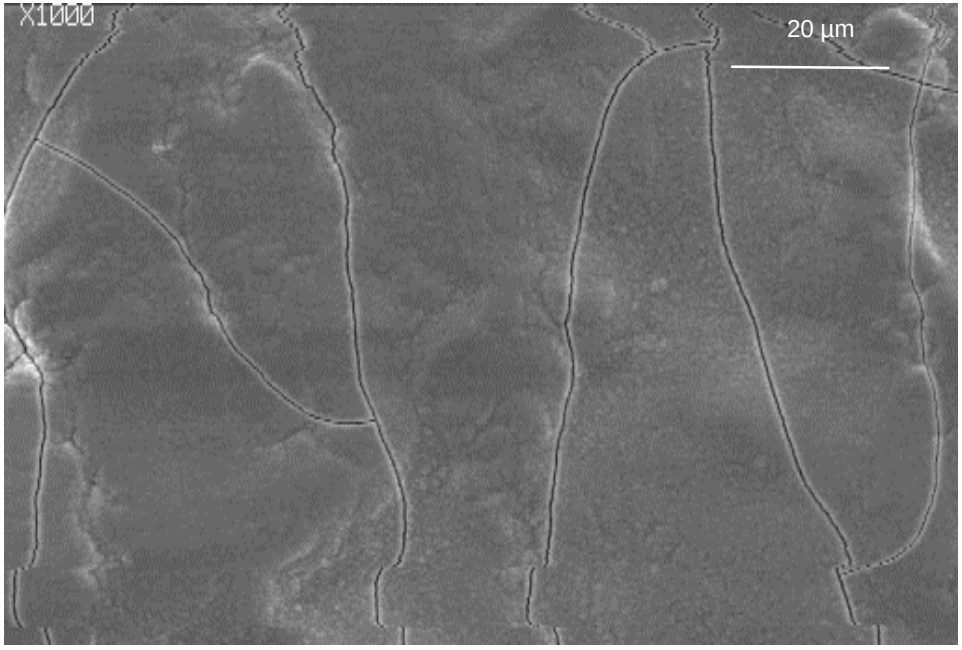
SEM - pictures
Cr^{VI} Chromate / Cr^{III} Passivation



Chromate Cr^{VI}



Passivate Cr^{III}

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Layer system Cr VI- and Cr III

	(Cr VI) chromate	Cr(III)-Passivation
Chromium in total	2 – 6 mg/dm²	0,5 – 2 mg/dm²
Hexavalent chromium (Cr^{VI})	0,5 – 1,5 mg/dm²	-
Trivalent chromium (Cr^{III})	1,5 – 4,5 mg/dm²	0,5 – 2 mg/dm²
Thickness	0,7 – 2 µm	0,3 – 1 µm

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Benefits of Lanthane 315

- chrome(VI)-free system
- small stripping effect
- suitable for zinc as well as for zinc-iron plating
- the corrosion protection of LANTHANE 315 is equal to chrome(VI)- containing chromate layers
- with LANTHANE 315 passivated surfaces are very heat resistance
- suitable for barrel and rack applications

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Benefits of Lanthane 315

- excellent basis for top-coats
- no dependency on patents or the raw material market
- fulfills inter alia the following standards:

➢ VW TL 217 ofl-c342/642 (72 respectively 96 h without WR
168 respectively 240 h without RR)
(without top coat)

➢ VW TL 217 ofl-c343/643 (96 respectively 168 h without WR
168 respectively 360 h without RR)
(with top coat)

➢ Bosch N 67 F (822 01 – 822 06) and others

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aplication / optical characteristics

cyanide free, alkaline zinc **acid zinc**	**OKLANE** **ZETAPLUS**
color without siliceous top coat:	**yellowish-green**
color with siliceous top coat:	**yellowish**

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aplication / optical characteristics

alkaline zinc-iron	**PERFORMA 269** **PERFORMA 260**
color without siliceous top coat:	**yellowish-greenish**
color with siliceous top coat:	**yellowish**

Operating conditions and ranges

parameter	range	optimum
Lanthane 315	180 - 220 ml/l	190 ml/l
pH-value	1,8 - 2,2	2,0
temperature	40 - 70 °C	60 °C
immersion time	50 - 90 seconds	60 seconds

agitation:
- flow by pumping for rack application
- rotation (of barrels or baskets) for barrel application

Temperature

The recommended temperature at the surface of the component is 60 °C (object temperature). Cold and heavy components need higher temperatures of the bath.

For barrel application it is important to realize a good agitation. It is recommended to use higher temperatures of the bath.

When using higher temperatures the immersion time has to be reduced to prevent increasing of aggressiveness of the Lanthane 315.

Concentration

Fluctuations of the concentration have to be avoided.

A clock-pulse-dependent automatically dosing system will increase the process reliability.

To low concentrations have to be avoided.

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pH-value

The optimal pH-value is 2,0.

Above this value the passivating speed will decrease drastically.

In praxis the pH-value can increase to 2,1 and can then be adjusted to a value of 1,9.

Lower pH-values accelerate the increase of zinc and reduces the lifetime of the bath.

Immersion time

The optimal immersion time is 60 s.

For barrel application it make sense to increase the time to 90 s.

Longer immersion times will reduce the corrosion protection behavior.

When using higher temperatures the immersion time needs to be reduced.

Minimum thickness of zinc or zinc alloy plating

Lanthane 315 will remove approx. 1 µm zinc.

If there is a direct electrochemical connection to the substrate, e.g. due to pores at thin zinc thickness (<5µm) or uncovered areas, the corrosion protection can be reduced.

In this case a post treatment with FINIGARD products is recommended.

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Process steps

- cyanide free zinc plating: alkaline zinc, like OKLANE-processes are preferred.
- rinsing in flowing water
- acid dip in nitric acid (0,5 - 1,0%)
- rinsing in flowing water
- passivating: Lanthane 315
- rinsing in flowing water
- drying 60 - 80°C respectively
- FINIGARD
- hot air drying respectively skidding

Plant requirements

Number of rinsing bathes

The use of a cascade with three rinsing bathes is optimal. When circulation water is used a high content of organic compounds should be avoided.

The transfer time from bath to bath should be as short as possible. To long times can cause drying-stains due to the high temperature of the components.

For rack application spray nuzzles reasonable. When using less than three rinsing bathes spray nuzzles are necessary.

Heating

Glass, PTFE and titanium are suitable. Stainless steel and steel are not unsuitable.

Agitation

Due to relatively high concentrated solution a proper agitation has to be realized.

For barrel application it is recommended to lift and abate the barrel once during the immersion time.

Influence of metal contamination

pH-value of starting hydroxide precipitation of different metals:

manganese	**8,7**	**chromium(III)**	**5,8**
nickel	**7,8**	**iron(II)**	**5,5**
zinc	**7,6**	**aluminum**	**4,3**
cobalt	**6,8**	**iron(III)**	**2,9**

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Limit of lifetime

zinc: **12 g/l**
iron: **150 mg/l**
nickel: **no negative influence known**

The maximum concentration of iron depends on the layer system. Pure zinc layers in general are more tolerant.

As an iron-inhibitor EXCC 0203 is available for the application on zinc. It will reduce the accumulation of iron.

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Elimination of contaminants

The increase of zinc is process related.

When loosing components in the bath, they can dissolve and cause a very quickly increase of the iron concentration.

An optimized maintenance is required, e.g. well shutting cap of the barrel, aligned perforation of the barrel, optimized mountings at the racks, rapidly removal of lost components etc.

Dissolved iron and zinc can only be removed by an ion exchanger.

Keeping conditions constantly

A clock-pulse-dependent automatically dosing system for the concentrate, frequent measuring of the pH-value including adjustment as well as keeping constant of the temperature will arise a constantly production.

Corrosion resistance and weight of the layer in dependence on the temperature

Make-up and work-parameter:

concentration	**190 ml/l**
pH-value	**2,0**
immersion time	**60 s**
temperature	**30 – 60 °C**

Rack plated parts, plated with OKLANE STAR, brightened in diluted HNO_3 and passivated at different temperatures.

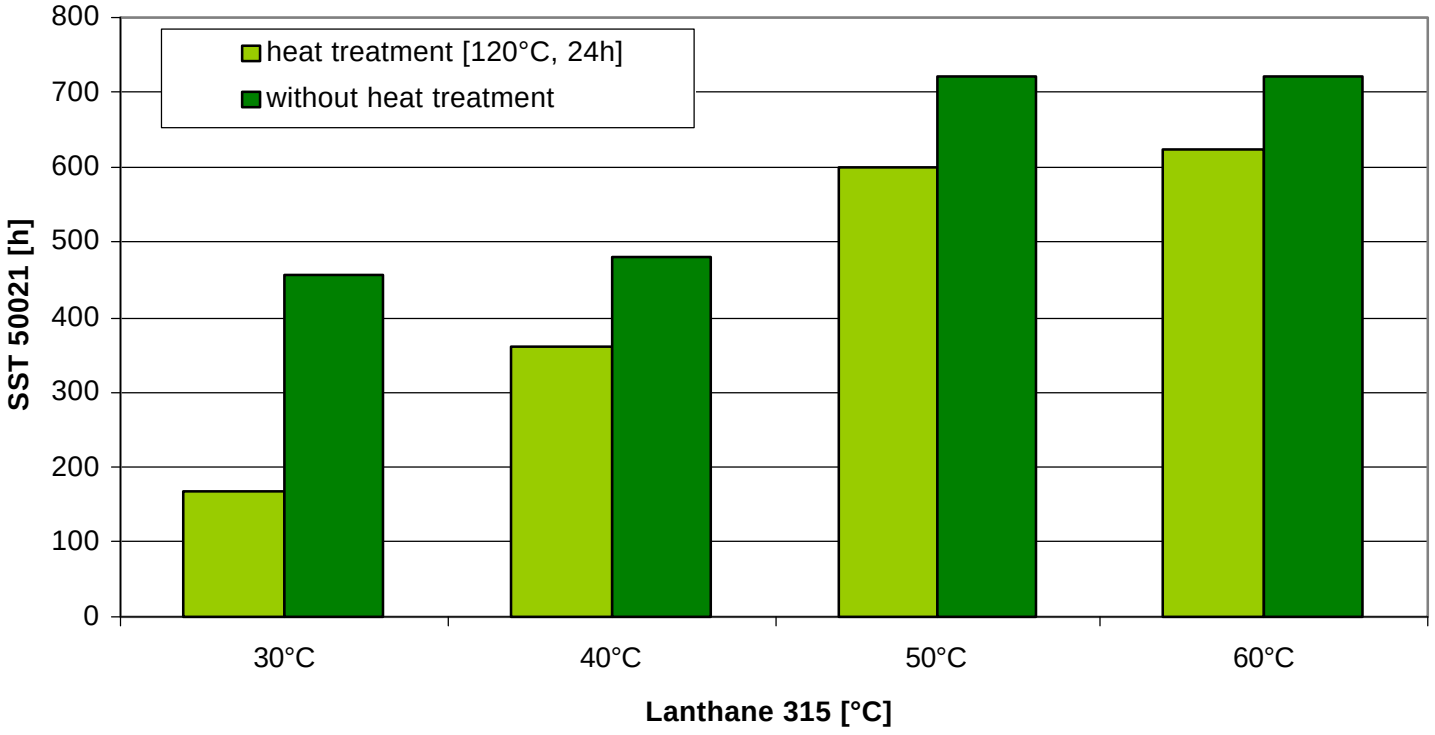
The components were dried for 10 min. in the furnace at 60°C. Afterwards 50 % of the components were heat treated at 120°C for 24 hours.

Weight of layer

40°C	**0,9 - 1,2 mg/dm^2**
60°C	**1,4 - 1,6 mg/dm^2**
70°C	**1,6 - 2,0 mg/dm^2**

Corrosion resistance in dependence on the temperature of the passivation

(Rack plated parts 10 - 12 µm alkaline zinc "Oklane Star")



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Corrosion resistance

Process	Type	Passivation	Without siliceous top coat	With siliceous top coat	Color of passivated surface	corrosion resistance (WB 24 h, 120° C)
Oklane / Zetaplus	Zn	Lanthane 315	X		yellowish-green	barrel > 72 h WR rack > 96 h WR both > 240 h RR
Oklane / Zetaplus	Zn	Lanthane 315		X	yellowish	barrel > 144 h WR rack > 240 h WR both > 360 h RR
Performa 260 / 269	ZnFe	Lanthane 315	X		yellowish-greenish	barrel > 96 h WR rack > 120 h WR both > 300 h RR
Performa 260 / 269	ZnFe	Lanthane 315		X	yellowish	barrel > 192 h WR rack > 360 h WR barrel > 480 h RR rack > 600 h RR

Regeneration by ion exchanger

The regeneration by ion exchanger of Lanthane 315 can be done without loosing properties.

Two different processes are available:

1.) two step process
zinc can be removed by batch treatment only

2.) one step process with addition of H_2O_2
continuously for zinc and iron
upper limit for contamination!

The exact procedure has big influence on the corrosion protection.

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Thank you for your time and attention.