Replacement of Chromium(VI)

in Passivations on Zinc And Zinc Alloys

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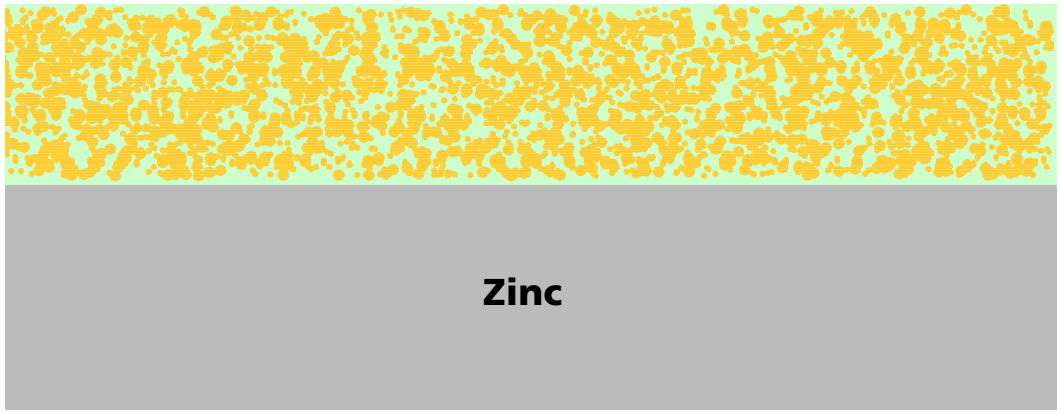
Topics:

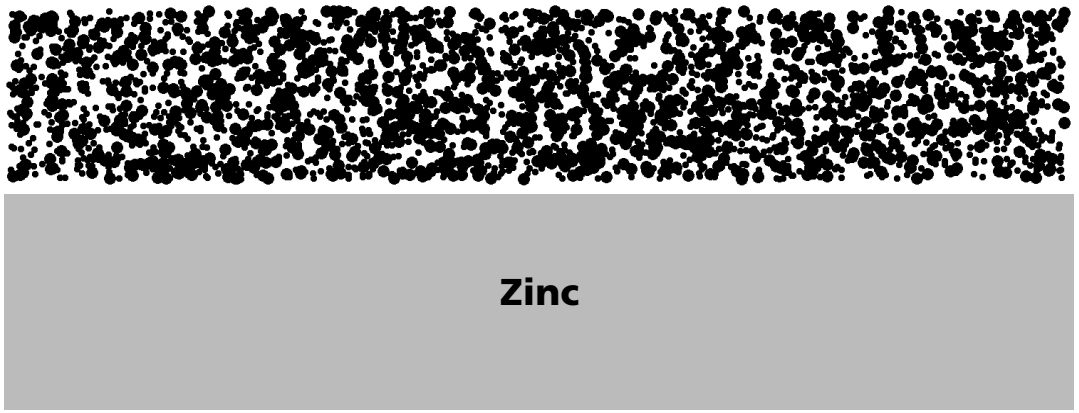
- what are we searching for? – properties of hexavalent passivation films
- criteria for chromium(VI)-free alternatives
- examining the periodic table
- trivalent chromium passivation films
- application

Properties of Hexavalent Passivations

hexavalent yellow chromate

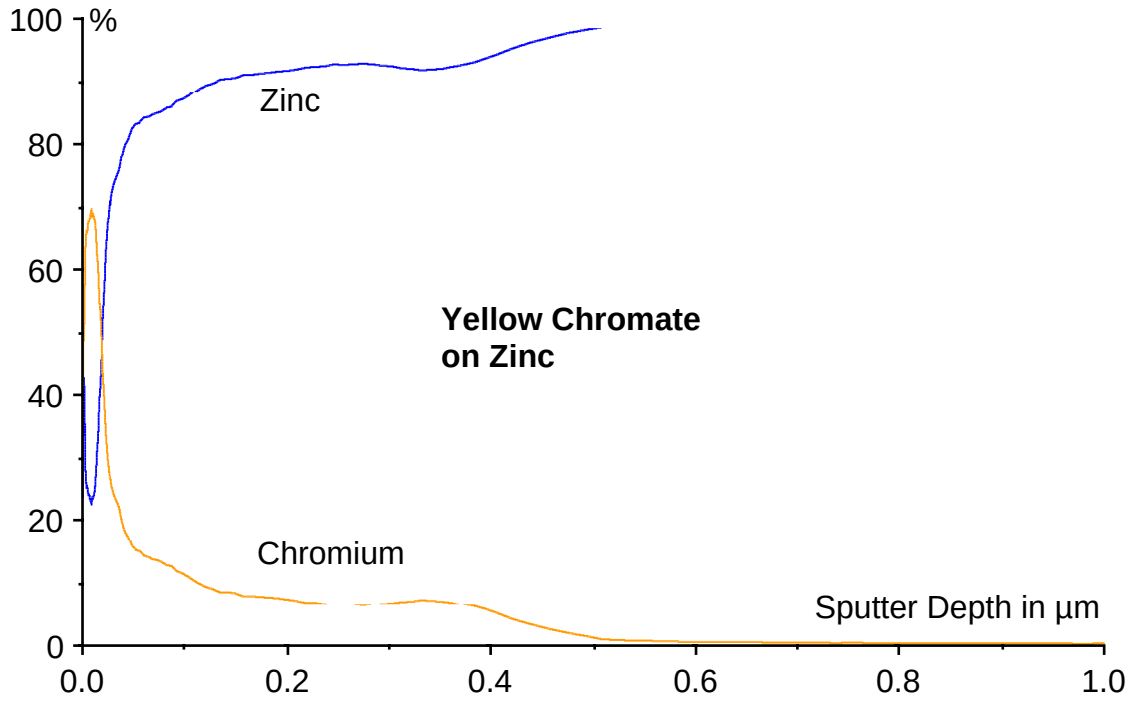


hexavalent black chromate



Type of Passivation	Chromium(VI) in mg/m^2	Layer Thickness in nm	Salt Spray to White Corrosion [hours]
Yellow Chromate	80-220	250-500	200-300
Olive Chromate	300-400	1000-1500	400-500
Black Chromate	80-400	250-1000	150-300
compare:			
Trivalent Blue Chromate	0	25-80	20-40

Properties of Hexavalent Passivations



Criteria for a Chromium(VI)-free Passivation

(how to get the same properties - or better - without hexavalent chromium)

Desirable Chemical Properties

- ▲ component with good water solubility in acidic media
  (a conversion layer typically requires an initial attack on the metal)
- ▲ formation of oxides, which are utmost insoluble in water, in acids and in alkalies

General Requirements

- ▼ adequate availability to support large scale production
- ▼ recyclability (compatability with steel production)
- ▼ economics (consider demand for low raw material costs)
- ▼ known toxicity of all possible oxidation levels

Periodic Table – Infinite Options?

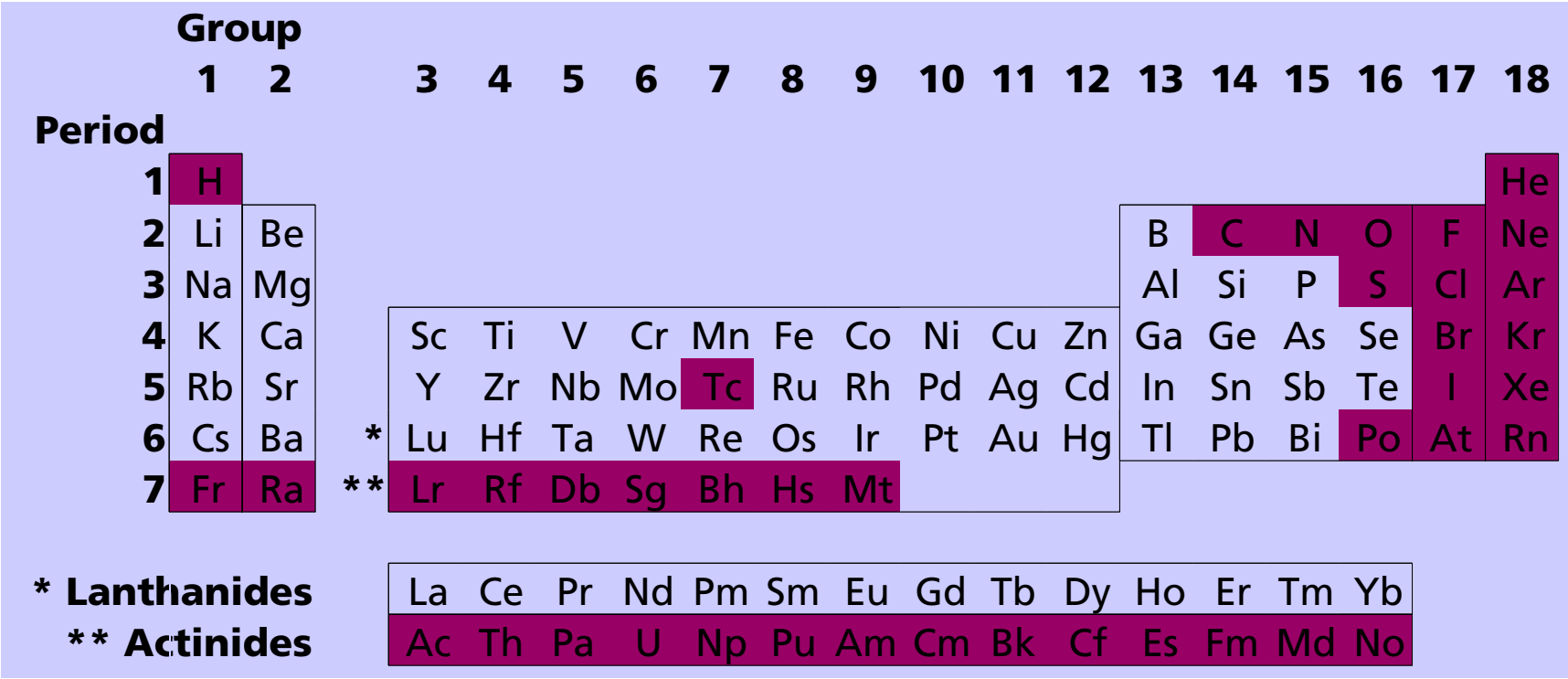
⇨ there are 93 natural elements

Period	Group 1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																		He
2	Li	Be												B	C	N	O	F	Ne
3	Na	Mg												Al	Si	P	S	Cl	Ar
4	K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt									

* Lanthanides	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
** Actinides	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

Periodic Table – Infinite Options?

▼ all gases, radioactive elements as well as halogens drop out of the race



⇨ 70 elements remain

Periodic Table – Infinite Options?

- alkali and earth alkali elements, borium, phosphorus and selenium form only highly soluble oxides; silicium has no well soluble compounds in acids

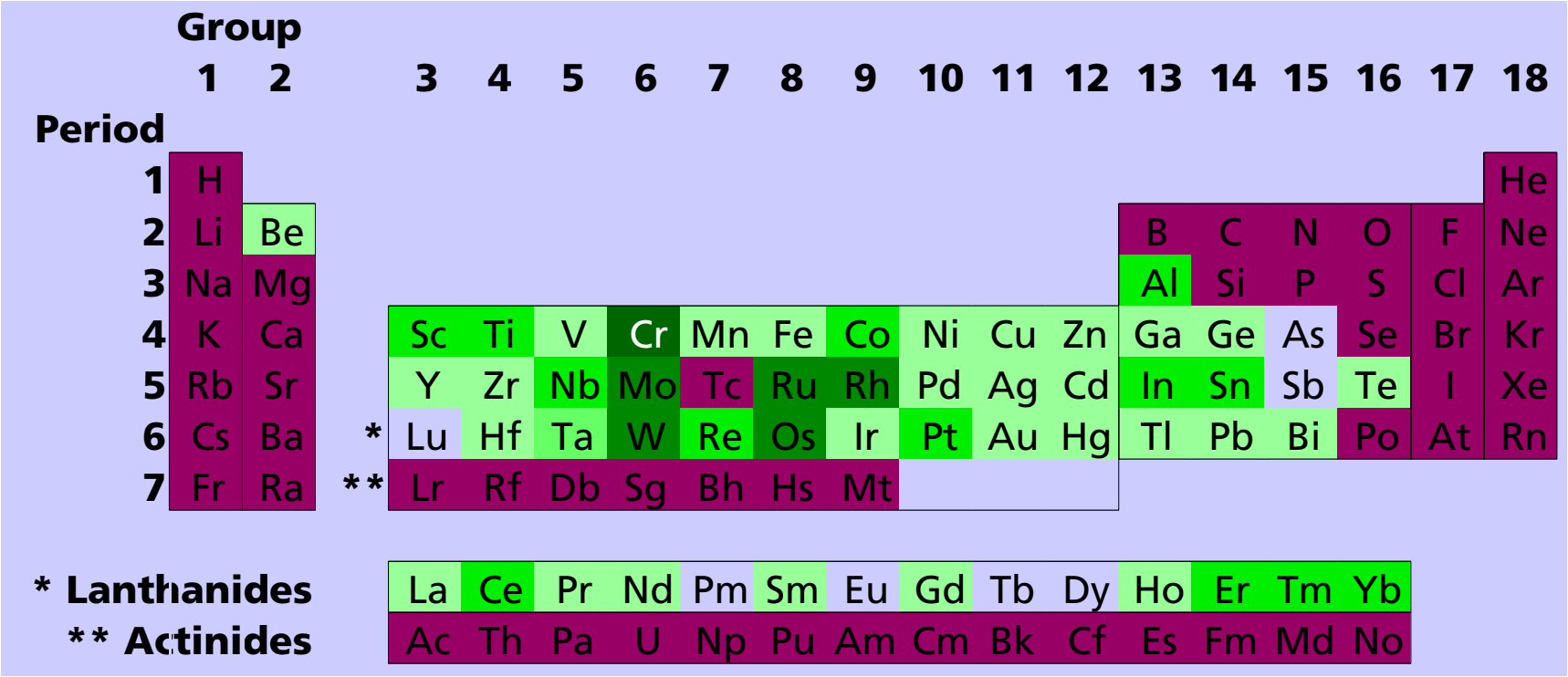
Group / Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	* Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	** Lr	Rf	Db	Sg	Bh	Hs	Mt									

* Lanthanides	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
** Actinides	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

⇨ 55 elements remain

Periodic Table – Infinite Options?

▼ solubilities of oxides: light green (insoluble in water) - green (insoluble in acids or lyes) - dark green (insoluble in acids and lyes)



⇨ 6 element oxides are possible, of those chromium(III) is the least soluble

Layers With Trivalent Chromium

The formation of a conversion layer in solutions of trivalent chromium is described in two reaction equations:

I elemental zinc is dissolved at the surface by the acidic attack:

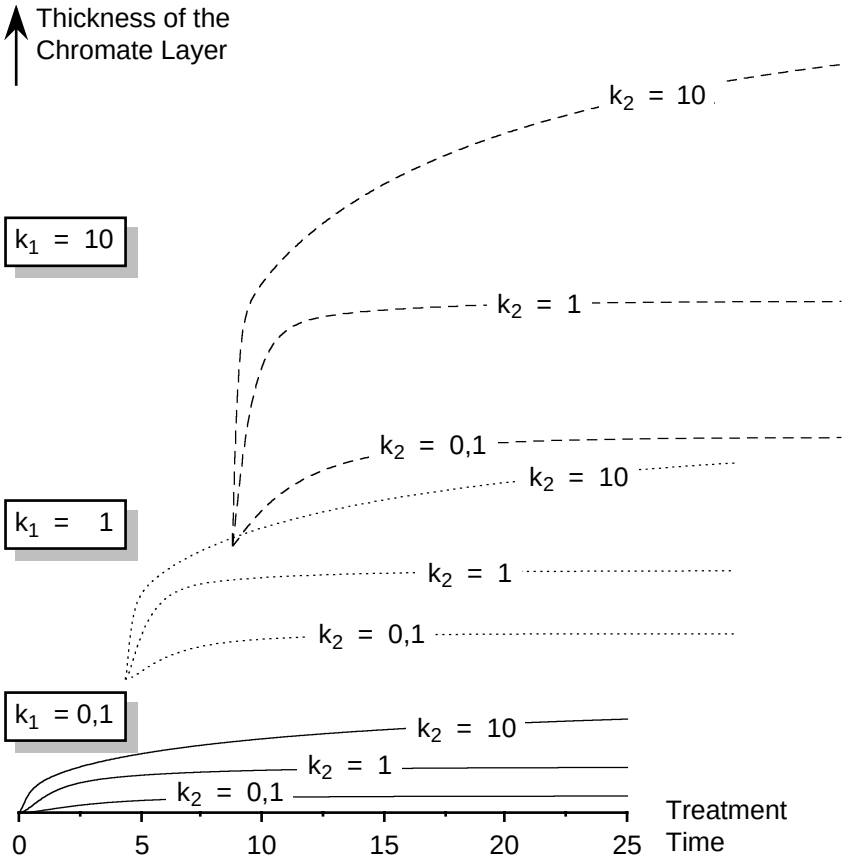
$$Zn + 2\,H^{+} \xrightarrow{k_1} Zn^{2+} + H^{\uparrow}$$

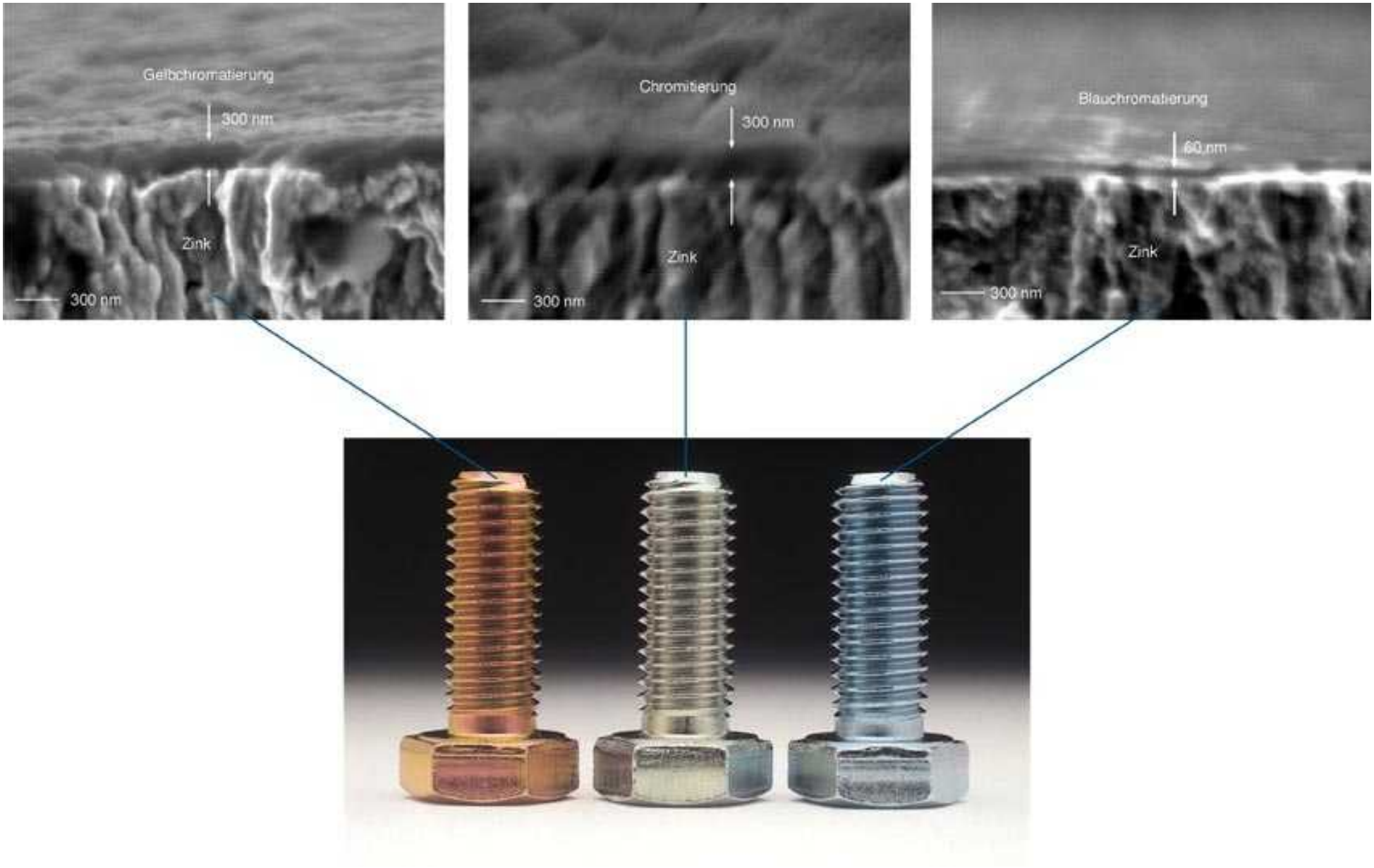
II and precipitates together with chromium(III) as zinc chromium oxide on the zinc surface:

$$Zn^{2+} + x\,Cr(III) + y\,H_2O \underset{k_3}{\overset{k_2}{\rightleftharpoons}} ZnCr_xO_y + 2{\cdot}y\,H^{+}$$

A kinetic model was formed, comprising of differential equations for the concentration development of Zn^{2+}, H^{+}, Cr(III) and for the thickness growth of the ZnCrO layer. The mathematical expressions for the reaction speed take into consideration that reaction **I** is increasingly slowed down by the growing passive layer.
The system of differential equations was numerically solved by a computer, resulting in the development of layer thickness and concentration values as a function of time.

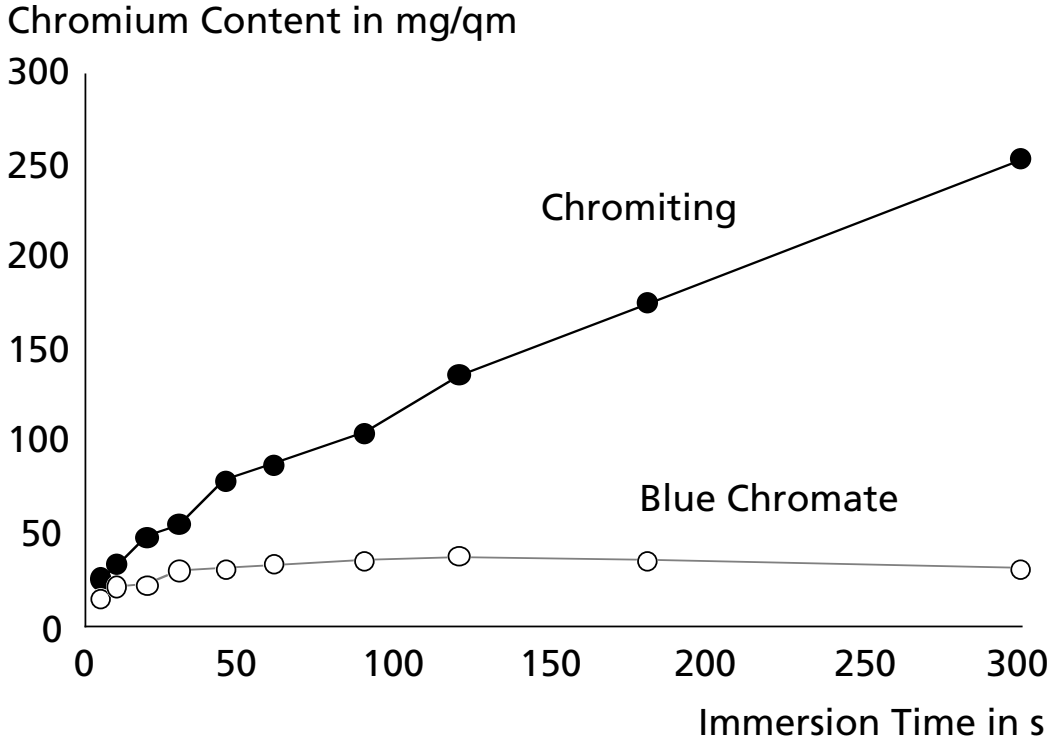
Simulated Development of Layer Thickness



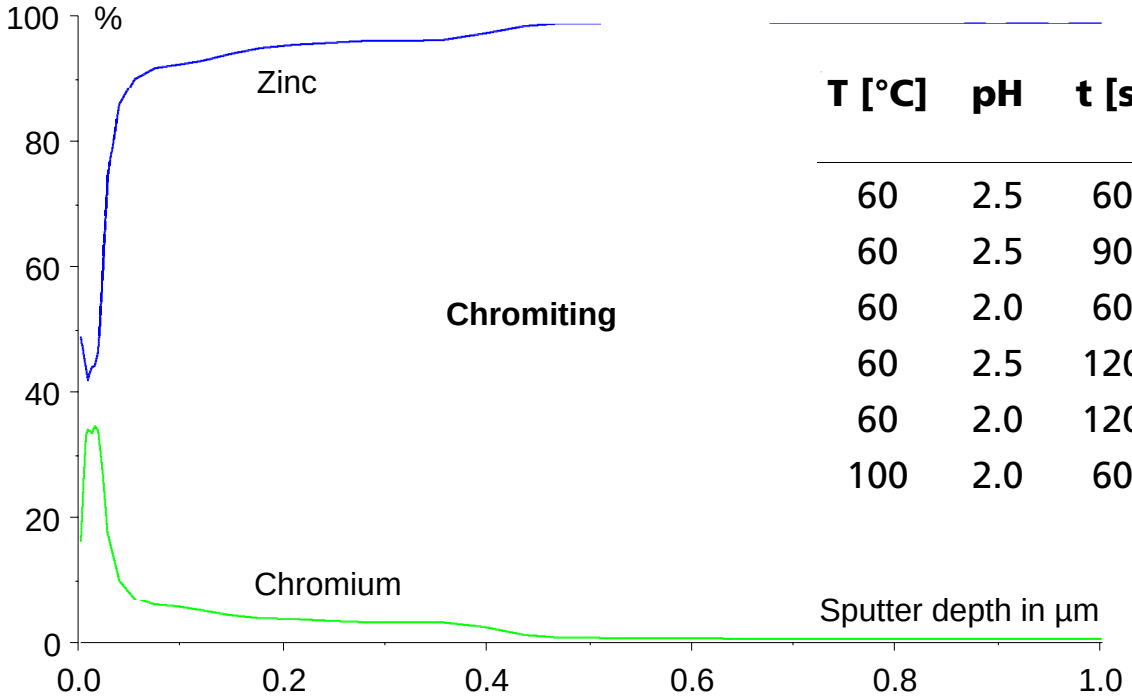

Gelbchromatierung
300 nm
Zink
300 nm
Chromitierung
300 nm
Zink
300 nm
Blauchromatierung
60 nm
Zink
300 nm

Layers With Trivalent Chromium

- the layer thickness is growing with growing immersion time



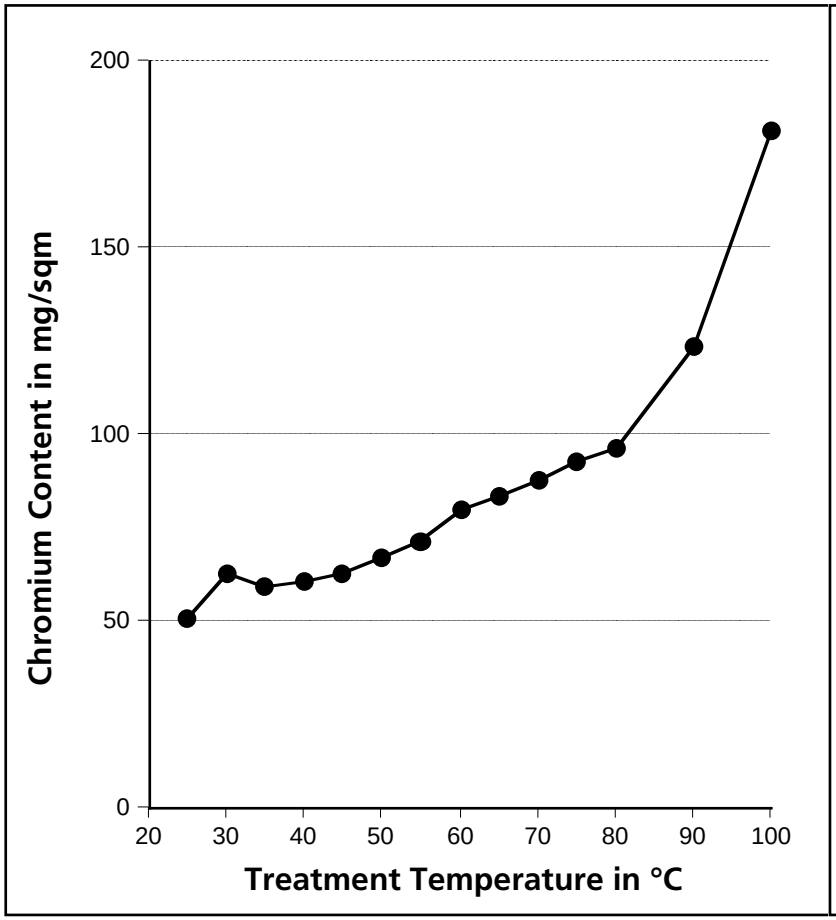
Layers With Trivalent Chromium

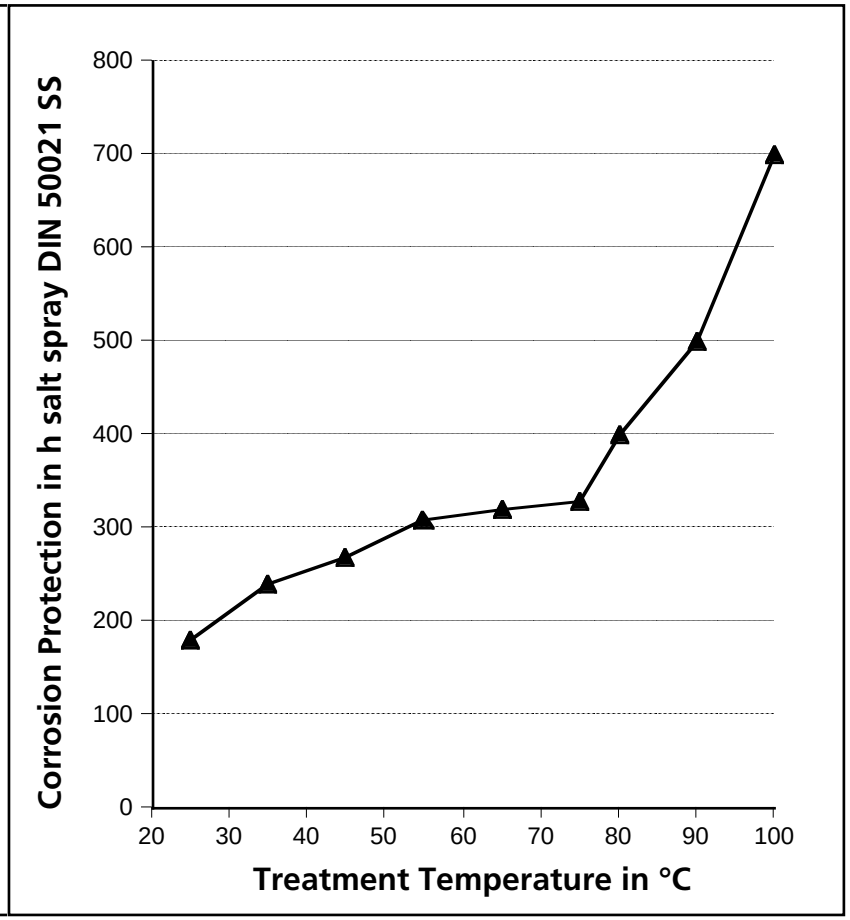


T [°C]	pH	t [s]	SEM	GDOS	Ellipso-metry	Ø
60	2.5	60		195		195
60	2.5	90		295		295
60	2.0	60	300	312	353	322
60	2.5	120	300	435	353	363
60	2.0	120		400	440	420
100	2.0	60		360	580	470

Layers With Trivalent Chromium

▲ layer thickness and relative chromium content are rising with rising temperature





Application Conditions

	trivalent Chromiting	hexavalent yellow chromate
make-up:	12.5 Vol% = 10 g/l Cr(III)	1 Vol% = 2 g/l Cr(VI)
pH-value:	1.7-2.0	1.6-1.8
temperature:	≥ 60 °C	room temperature
contact time:	60 s	20 s
heating:	necessary	in the winter
ventilation:	necessary	recommended
rinsing:	3 steps	2 steps
activation:	recommended	
agitation:	rack agitation/barrel rotation and/or air agitation	
tank material:	(insulated) plastic or steel with plastic inliner	

Qualitätsförderkreis Chromitierung

(German Chromiting quality promotion circle)

- ▲ a qualified group of job platers in and in the vicinity of Germany (currently 7 members)
- ▲ the group applies Chromiting and/or Black Chromiting as well as future developments
- ▲ it exchanges field experience (trouble shooting)
- ▲ commitment to maintain coating parameters at optimum values within a narrow range
- ▲ development of common standards
  (measuring and testing procedures, with guaranteed processability and reproducibility)

⇨ **<u>objective:</u>**
to provide ample plant processing capacity with predictable high quality to meet the (German) car industry's requirements

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"English Version"

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Publications

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Presentations

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"Replacement of Hexavalent Chromium"

and

"Chromiting"